Formation and Characteristics of Carbonaceous Deposits

From Heavy Hydrocarbon Vapours

by

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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF GRADUATE STUDIES

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

May 2006

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Abstract

Coking is an important step in the upgrading of bitumen or other heavy hydrocarbons into lighter products. Deposition of carbonaceous material in the cyclone exit line is a chronic problem for all fluid cokers and is a key process limitation to achieving longer run length. It has been a subject of detailed process studies at UBC. The overall aims of this work were to elucidate the causes of deposit formation via coke characterization with a range of techniques, to examine the evolution of deposit composition and structure over time, to compare the laboratory deposits with industrial samples, and to propose a model of deposit structural evolution during the aging process based on kinetics of the deposit aging process and above characterization results.

Fresh deposits recovered from a laboratory bench-scale cyclone fouling unit and aged laboratory deposits have been compared with samples from the snout region and exit tube of an industrial fluid coker. Extensive characterization studies were conducted using modern analytical techniques, e.g., elemental analysis, X-ray Fluorescence (XRF), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Diffusive Reflection Infrared Spectroscopy (DRIFT), and Solid-state $^{13}$C Nuclear Magnetic Resonance ($^{13}$C NMR). Simulated distillation was also applied to solvent extracts of deposits. Results substantiate that physical condensation rather than chemical reaction is the primary reason for fluid coker cyclone exit line fouling. Entrained liquid droplets also contribute to the deposit formation to a lesser extent. Although the fresh laboratory deposits are much different from the industrial deposits, after days to weeks of aging at elevated temperature, the H/C ratio, TGA characteristics, $^{13}$C NMR, and DRIFTs spectra of the lab deposits become very similar to those of the graphitic industrial deposits. The differences in morphology which remain after aging, are attributed to the difference in hydrodynamic conditions during the deposit laydown. The
various techniques studied yielded a consistent picture of the evolution from the heavy fluid phase components which initially deposit from the vapour to the final massive graphitic coke-like deposit formed in the industrial coker cyclone exit tube.

During aging of fresh lab deposits, a considerable amount of volatile components is released, especially in the initial period. Kinetic models were developed to describe reactions in different aging periods based on thermal behavior of deposits. During the heating period from ambient to final aging temperatures, a first order non-isothermal kinetic model was used to describe the de-volatilization reaction properties of cyclone fouling deposits. A two-stage model is used for the kinetics of the laboratory deposits collected at low temperatures (<500°C), but a single-stage kinetic model can well describe the thermal behavior of the industrial deposits and the laboratory deposits collected at high temperatures. The values of apparent activation energies in the heating period suggest that thermal cracking reactions occur. Isothermal kinetic models were used to characterize the weight loss phenomena with time at different final aging temperatures. A 2\textsuperscript{nd} order exponential decay equation can describe the volatiles decline in the initial stage, and another zero order reaction model can be used to describe the subsequent slow aging reaction period. The aged laboratory deposits and industrial deposit samples have similar but not identical kinetic characteristics. The structural evolution of aging cyclone fouling deposits is proposed following the Marsh-Griffiths model.

Depending on temperature, pressure, and composition, cyclone exit vapours can contain some liquid droplets. Since the cyclone exit tube wall is at a lower temperature than the bulk fluid, physical condensation may occur on the surface, giving rise to the deposits. Alternately adherence of droplets transferred from the bulk fluid may be the cause. A liquid droplet mass transfer model has been developed to describe the deposition in both laboratory and industrial conditions. In the laminar flow range, calculations show that deposition of fine droplets is very
slow; physical condensation on the tube should be the primary reason for the exit tube line fouling under laboratory conditions. In the turbulent flow range, as the droplet size is increased, the deposition mechanism shifts from diffusion to impaction, which would accelerate the droplet deposition rate dramatically and cause much more deposits in the tube entrance region. The droplet mass transfer could cause serious deposition and blockage of tube line in industrial operation conditions, especially for droplets above one micron. Small droplet size and large diameter exit tube will mitigate the deposition problem in industrial fluid coker cyclone operation.
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I wish to express my sincere gratitude to my research supervisor, Dr. A. Paul Watkinson, for the support, encouragement, patience and guidance throughout the course of this work.

I am grateful to Dr. Wenxing Zhang and Mr. Gordon Cheng for their help in running the laboratory fluid coker unit and collecting the samples. Thanks also to Dr. Changchun Yu in the University of Petroleum, China for the discussion and guidance of the DRIFT Spectrometer, to Dr. Dan Bizzotto in the Department of Chemistry, UBC for the discussion about the interpretation of DRIFT spectra. I am indebted to Ms. Celine Schneider and Dr. Colin Fyfe in the Department of Chemistry, UBC for the discussion and performing solid-state $^{13}$C NMR experiment. Mr. Quan Shi in the State Key Laboratory of Heavy Oil Processing Laboratory, China is also greatly appreciated for performing GC simulated distillation, and part of DRIFT experiments. As well, I would like to thank Dr. Kevin Smith and the students in his lab for generous offering the DRIFT instrument.

Research funding from Syncrude Canada, Ltd. and the Natural Sciences and Engineering Research Council of Canada (NSERC) are greatly acknowledged.

I would like to express my thanks to all members of Chemical & Biological Engineering faculty, staff, workshop, stores and graduate students for their assistance in these years.

Special thanks are due to my wife Haiying, family and friends in China for their encouragement, understanding and patience.
Chapter 1 Introduction

1.1 Introduction to The Fluid Coking Process [1, 2]

Fluid coking is a continuous process that uses fluidized solids techniques to convert heavy residue, including vacuum pitches, into more valuable lighter products, such as naphtha and gas oils. In Canada, fluid coking is a key step in upgrading oil sands bitumen into crude oil for refineries. A schematic of the fluid coking process is illustrated in Fig. 1-1 [1]. The overall reactions in the coking process can be expressed as:

\[
\text{Bitumen} \xrightarrow{\text{heat, steam}} \text{Light gases + Butane + Naphtha + Gas oil + Coke}
\]

Fluid coking uses two vessels, a reactor and a burner; coke particles are circulated between these to transfer heat, which is generated by burning a portion of the coke, to the reactor. The residue feed at, for example, 260–370°C, is sprayed into the fluid bed made up of hot, fine coke particles. The particles have a bulk density of 750–880 kg/m\(^3\), with a particle density of 1440 kg/m\(^3\) and a diameter of 100–600 µm. The temperature in the coking vessel range from ca. 480 to 565°C, and the pressure is substantially atmospheric so the incoming feed is partly vaporized and partly deposits on the fluidized coke particles. The material on the particle surface then cracks and vapourizes, leaving a residue that dries to form coke. Steam is introduced at the bottom of the reactor to fluidize the bed and strip off the oil.

The cracked vapour products rise to the top of the reactor, pass through cyclones to remove entrained particles of coke, and then enter the scrubber in the top portion of the vessel. In the scrubber, the vapours are cooled by countercurrent contact with wash oil. At the bottom of the scrubber, the heaviest products are collected in the scrubber pool with the remaining coke dust, which is recycled to the coking reactor. Vapours leaving the upper part of the scrubber tower are separated into gas, naphtha and gas oil.
Coke particles are withdrawn from the bottom of the reactor and conveyed to the burner using steam. The average bed temperature in the burner is 590–650°C, and air is added as needed to maintain the temperature by burning part of product coke. The pressure in the burner may range from 35 to 170 kPa. Flue gases from the burner bed pass through cyclones and discharge to the stack. Hot coke from the bed is returned to the reactor through a second riser assembly.

![Fig. 1-1 Simplified Schematics of Fluid Coking Process [1]](image)

Coke is one of products of the process, and it must be withdrawn from the system to keep the solids inventory from increasing. The net coke produced is removed from the burner bed through a quench elutriator drum, where water is added for cooling and cooled coke is withdrawn and sent to storage.
1.2 Cyclone Fouling Problems in Fluid Coking Process

Unwanted deposition of carbonaceous materials is a general problem during processing of hydrocarbons. In fluid bed cokers, the vapours pass through cyclones in the freeboard of the reactor at temperature of about 550°C. The cyclone exit tube, which is jacketed and insulated, passes through the scrubber pool of agitated liquid which is at a temperature below 400°C. Thus there is a transfer of heat from vapours in the exit tube through the wall to the scrubber pool. Excessive buildups of carbonaceous deposits, which originate in the vapour or gas phase, have been noted to form in cyclones and cyclone exit tubes (see Fig. 1-2).

![Coke deposits](image)

**Fig. 1-2 Fouling Deposit Formation in Cyclones during Fluid Coking Process [3]**

This deposit formation leads to an increased pressure drop through the coker and a reduction in the overall efficiency of the cyclones. This problem worsens with the passage of time until, eventually, the coker must be shut down so that the coke formations can be removed. Cyclone fouling is a chronic problem for all fluid cokers and a key process limitation to
achieving longer run length. Similar problems of deposit formation from the vapour phase also occur in cracking of naphtha or hydrocarbons for olefins production industry, and in the delayed coking process. In order to design equipment rationally, or operate it most efficiently, knowledge of the mechanism by which the deposits are formed is essential.

1.3 Objectives

Previous bench-scale work [5-6] suggests that physical condensation of heavy hydrocarbon species rather than vapour-phase chemical reactions is the primary cause of deposit formation, and entrained droplets also contribute to the deposit. Furthermore, a mathematical model [7] was developed assuming physical condensation on the surface as the mechanism to predict the deposit formation from hydrocarbon vapour products under different operation circumstances. However, it was found that the laboratory deposits which were collected after six hours running from a bench scale continuous bitumen coking reactor are much different than those found in industry. Hence there is some doubt whether the lab scale work is indicative of industrial operation. Therefore, the overall aims of this work are to elucidate the causes of deposit formation via extensive coke characterization with a range of techniques, examine the evolution of deposit composition and structure over time, and to rationalize the differences between the laboratory deposits and industrial samples. As well, a mathematical model based on the deposition of liquid droplets either entrained from the feed or resulting from condensation in the bulk phase will be developed, and predictions compared with those from the surface physical condensation model. The main objectives of this work include the following:

(1) Based on the characterization results of laboratory deposits through chemical compositions, morphology, thermal properties, surface and bulk structures, etc., provide an improved explanation for the mechanisms of cyclone fouling, and identify which classes of molecules take part in fouling.
(2) Explain the differences of deposits from industrial and laboratory units by examining the evolution of deposit structure over time. Characterize industrial samples, fresh lab deposits, and those aged in nitrogen at temperatures of around 550°C.

(3) Propose a model of deposit structural evolution during the aging process, based on kinetics of the deposit aging process and above characterization results.

(4) Develop a liquid droplet mass transfer model to simulate the deposition rate, and compare results with the simulation results of the surface condensation mechanism. Such a model would also have application to other coke deposition situations such as transfer line exchangers.

(5) Interpret the cyclone exit line fouling process based on the results of above objectives in a manner which will assist operators to minimize or eliminate the problem.
Chapter 2 Literature Review

The formation of solid carbonaceous materials from gases or liquids is a complex process. For the hydrocarbon pyrolysis process used in the olefins production industry, the formation of coke is a severe problem, and hence has received attention for many years. Solid deposits occur at two positions in steam crackers for ethylene production: on the wall of the pyrolysis reactor (coil), typically at 750–1000°C, and on the walls of the quench cooler, usually called the transfer line exchanger (TLE), which is a few hundred degrees lower in temperature. Much work [8-24, 33-40, 90-104, 109-115] has been devoted to coil coking, whereas the number of papers [25-33, 105-107] on TLE fouling is small. For the cyclone fouling in fluid-coking process, very little published information [3-7] is available.

2.1 Mechanisms for Deposition of Carbonaceous Materials

It should be noted that olefin production uses very high temperatures (~ 800°C) and light feedstocks (ethane or naphthas), whereas in fluid cokers the temperatures are much lower (~ 530°C) and the feedstocks much heavier (bitumens). Therefore, mechanisms of coke formation may well differ, nevertheless much useful information is available from the literature on pyrolysis. For the coil coking under pyrolysis conditions, there are three mechanisms which appear to contribute to the deposition of a coke layer, as discussed by Froment [8-10], Albright [11] and Trimm [12].

2.1.1 Mechanisms of Coke Formation in Pyrolysis Coil

a. Heterogeneous Catalytic Mechanism [8-24]

Catalytic coke formation is associated with the availability of catalytic sites on equipment surfaces. During the start up of a furnace, the reacting mixture of hydrocarbon vapour and steam is in contact with the bare walls, on which exist significant populations of catalytic sites.
Initially, the coking rate is high, but it gradually decreases with time to reach a constant value: the “asymptotic coking rate”. The high initial coking rate is associated with catalytic carbon formation. However, its importance should not be over-emphasized, because at the operating conditions prevailing in industrial cracking, the period of catalytic coke formation can be negligible with regard to the run length [8-12,90,95,96]. This process, summarized by Froment [10], involves surface reaction, diffusion, and precipitation of carbon [8-10, 12,16,17].

The properties of the metal are very important in this mechanism. For example, the fact that copper is almost inert toward carbon deposition compared to nickel and iron can partly be explained by chemisorption properties different on these metals [8,10,17,23]. Dissolution and diffusion are also crucial steps. Filaments are not formed on metals that show a low solubility for carbon, only encapsulating carbon is formed. Platinum is an example of such a metal. The physical state of the surface, for instance, roughness and grain size [21], pretreatment and history of the surface [8,10,13,14], and even geometry of the reactor [22] also have important influences on this mechanism.

**b. Heterogeneous Noncatalytic Mechanism [8-12]**

This mechanism is the most important one for coke formation in a pyrolysis coil. At the gas/coke interface the polyaromatic layer is not yet completely dehydrogenated. At this surface hydrogen abstraction reactions by free radicals (hydrogen, methyl, and ethyl radicals) from the gas phase can occur. As a consequence, the concentration of the “active sites” at the coke surface becomes a function of the gas phase composition. This explains the experimental observation according to which feedstocks generating a great number of radicals also yield more coke.

At the free radical positions on the coke surface, certain gas phase molecules react via an addition mechanism. All unsaturated molecules from the gas phase are potential coke precursors. In Fig. 2-1, an example of the reaction sequence is shown with 1-hexene as a precursor [9,10].
The long aliphatic side chain of these molecules is subject to decomposition. The remaining part of the molecule reacts in a few steps to a ring structure, in which the dehydrogenation reactions proceed very rapidly. In this way the aromatic structure continues to grow further and the free radical site at the coke surface is regenerated by further hydrogen abstraction.

![Chemical Reaction Diagram]

Fig. 2-1 Growth of Carbon Layer [9, 10]

This mechanism explains the formation of a deposit consisting of graphitic layers containing carbon atoms in sp$^2$ hybridization. The hydrogen content of such a deposit is very low, typically the H/C atomic ratio is 0.35−0.7. Several other reaction sequences, an example of which is shown in Fig. 2-2, yield cross-linked graphitic structures [9,10]. The cross-linking of aromatic layers explains why coke layers are extremely hard.

Since the number of species in the reaction mixture is very large, especially when cracking liquid feedstocks, and the number of possible reaction paths is extremely large, and it is impossible to take into account all those reactions in developing a model for the coke formation.
c. Homogeneous Noncatalytic Mechanism [8-12, 24]

This third mechanism implies the formation of polynuclear aromatics in the gas phase via free radical reactions. These large molecules grow in the gas phase to tar droplets that can be liquid or even solid at the conditions prevailing in a thermal cracking reactor. Some fraction of the droplets impinge on the tube wall. Some rebound into the gas phase, but it is more likely that they adhere to the surface and are incorporated in the coke layer, since the outer surface of the droplets is not completely dehydrogenated. Hence, hydrogen abstraction reactions by gas phase radicals are possible and the coke layer can grow further. This mechanism is considered important only in the cracking of heavy liquid feedstocks, such as atmospheric or vacuum gas oil, or else when the temperature exceeds 900°C.
2.1.2 Mechanisms of Transfer Line Exchanger (TLE) Fouling [25-33]

The properties of carbonaceous deposits, which are formed between about 600°C and 350°C in TLE tubes, differ enormously from those formed at higher temperatures (750~1000°C) in reactor coils. However, only little is known about the details of the formation of these lower temperature deposits, and the events which contribute to TLE fouling are still under controversial debate. The most meaningful work in this area was done by Kopinke et al. [27] and Zou et al. [31].

By means of $^{14}$C-labelled hydrocarbon, Kopinke et al. [27] investigated the contribution of individual components to coke formation on coupons placed in vapours to mimic conditions in a TLE, and the relative rate constants of some selected hydrocarbons for TLE fouling are as those shown in Fig. 2-3. Polycyclic aromatics like acenaphylene, methylanthracene, and chrysene are the most important precursors of deposits. Simple aromatic hydrocarbons such as benzenes or unsubstituted naphthalene are much less important. Of the nonaromatic hydrocarbons, only acetylene and cyclopentadiene have a higher average potential. The lower boiling hydrocarbons, e.g. toluene which represents the group of alklyaromatics and hexyne the unsaturated nonaromatics, contributed no direct fouling via physical condensation in TLE.

![Fig. 2-3 Relative Rate Constants of TLE Fouling of Hydrocarbons [27]](image-url)
With straight run naphtha (50~180°C) as feedstocks, cracking temperature 810°C, Kopinke [27] found that the temperature dependence of the deposition rate on the coupons (Fig. 2-4) favors physical condensation as a key step. With increasing temperature of the coupon the deposition rate decreases. The curve in Fig. 2-4 also gives evidence of a catalytic contribution to the TLE fouling, if the coupon has an active surface. Its activity, however, only becomes significant at temperatures above 400°C. For industrial practice, it is known that a rough inner surface that has been in service for a long time has a higher fouling rate than a new one with a smooth surface. It is an indication of a catalytic route to carbonaceous deposits in TLE. The experimental results [28] of isobutene pyrolysis, in which nitrogen was used as diluent to avoid any suppression of any questionable catalytic route to TLE fouling, confirmed this conclusion. However, in other papers Kopinke et al. [29,30] also suggest vapour phase components reacting on or near the TLE surface could form higher molecular weight species which give rise to deposits.

Fig. 2-4 Temperature Dependence of Deposition Rate (Kopinke et al. [27])
Feed stock: naphtha (50–180°C); Cracking temperature: 810°C; Residence time: 0.4s; Dilution ratio: H₂O/naphtha = 0.7 (wt)
Under the cracking temperature of 740–900°C, gas oil with the boiling point range of 99–368°C as feedstock, the experimental results (Fig. 2-5) of Zou et al. [31] suggested that when the tube wall surface temperature was high (>350°C), mass transfer and physical condensation, whose rate is much lower than that of surface chemical reaction, could be the controlling step for TLE fouling. Whereas, when the wall surface temperature is low (<350°C), surface chemical reaction rate was very slow and hence became rate controlling step for TLE fouling. These results seem to contradict those of Kopinke [27].

![Fig. 2-5 The Relation of TLE Fouling Rate and the Temperature (Zou et al. [31])](image)

Feed stocks: gas oil (99–368°C); Cracking temperature: 840–900°C; Residence time: 0.1–2s; Diluted ratio: H₂O/gas oil = 0.33 (wt) TLE tube length: 6cm; diameter: 1.2 cm

Lohr and Dittman [25] thought that there were three different mechanisms for the TLE fouling: (a) The coke formed in the coil is fractured by the high-velocity gases, and is finally blown from the coil into TLE, depositing especially at the inlet tubesheet. The part of the filamentous coke in the TLE that contains metal particles is believed to form by this mechanism
(b) Nonideal flow distribution in the TLE-inlet chamber and at the hot tubesheet causes turbulent eddies and backmixing, resulting in overcracking and additional fouling (i.e., chemical reactions cause the fouling) (c) Pyrolysis tars can condense on the cool tube wall, because the wall temperature is lower than the dew point. This latter mechanism is most important for gas-oil and heavy-naphtha feedstocks, because they contain much heavier fractions. On the tube wall, the condensed high-boiling hydrocarbons are converted to a coke-like substance.

Kaiser et al. [26] suggested that the determining factor in TLE fouling seemed to be the condensation of high-boiling components and the trapping in a polymeric layer covering the tube walls, thus the potential fouling tendency could be determined by the amount of $C_{10}^+$ formed in cracking coil and the level of unsaturation of $C_{10}^+$ components.

To derive a kinetic model of TLE fouling, Horak et al. [32] considered the following three mechanisms: (1) an irreversible chemical reaction of substances on the surface (2) physical processes are decisive, i.e., condensed material sticks to the surface of the layer (3) a series of reversible exothermic reactions. Aromatic compounds are formed by the Diels-Alder reaction, and then form stable polymers with a network structure on the surface of layer. A subsequent dehydrogenation, finally yields coke. For mechanism (1) and (3), fouling rate increases with temperature. For mechanism (2), it decreases with increasing temperature.

2.1.3 Mechanisms of Fluid Coker Cyclone Fouling

The coke formation mechanisms valid for light gaseous hydrocarbons may not apply in the coking of heavy feedstocks as the deposition phenomena and mechanisms are closely related to feedstock properties and the temperature, both of which usually differ. Despite increasing utilization of heavy hydrocarbons to meet energy demands, there are very few studies on the topic of deposit formation from vapours applicable to the heavy oil coking process.
One mechanism for deposition formation due to chemical reaction fouling, assumes that vapour phase components react on or near the surface to form higher molecular weight liquid species which give rise to deposits, as in the pyrolysis coil. A high surface temperature would promote the reaction, and in this case lead to increasing fouling. A contrasting mechanism of cyclone fouling, as in the TLE, is due to physical condensation. As a multi-component mixture is cooled, liquid is formed at the dew point when one or more of the components condense. The hydrocarbon liquid will either form on the cooled wall with which it is in contact, or if liquid forms in the bulk stream, droplets will be transported to the surface where part or all of the material will adhere, causing fouling. In the fluid bed coker cyclone system, since the fluid temperatures are in excess of 500°C, the liquid which adheres to the surface will age or bake into a coke-like material. Deposition therefore may occur by a physical mechanism, although chemical aging of deposits may follow. To minimize fouling by condensation, the presence of a lower temperature surface is to be avoided, and the tube skin temperature should be kept hot in order to be above the dew point of the heavy hydrocarbons.

Since the physical condensation mechanism, and the chemical reaction mechanism lead to opposite predictions of the effect of increasing the surface or bulk vapour temperatures, the mechanism or root cause of the fouling should be known in order to mitigate deposition.

Mallory et al. [3-4] investigated the role of the vapour phase in fluid coker cyclone fouling by a reactor of thermal cracking pot to simulate fluid coker, and suggested that cyclone fouling is due to chemical reaction mechanism. Within the range of 490 to 560°C the vapour phase derived from thermally cracked bitumen was observed to further react, forming more condensable light hydrocarbons and coke. However, after careful analysis of their experimental data as given in Fig. 2-6, it can be noted that an increase in vapour phase temperature results in a significant increase in vapour phase coke formation only occurring at high residence time. At their lower
residence time, this trend was reversed, which indicated physical condensation mechanism was predominant at lower residence time. Furthermore, it can be noticed that the key experimental conditions used in their study, as summarized in Table 2-1, differ much from the conditions in industry.

![Graph](image)

**Fig. 2-6 Experimental Results of Mallory et al. [3]**

The research work of Watkinson et al. [5-7] appears to substantiate that physical condensation is the primary mechanism for cyclone fouling under their experimental conditions. To obtain information for industrial operators to manipulate conditions with the intent of minimizing deposition at similar conditions, a 7.8 cm diameter continuous bench-scale bitumen fluid coking unit was built. In their typical experiments, the ratio of feed rate of bitumen, atomizing steam and nitrogen was 3:3:2 (wt), and the pressure of the coker reactor was in the range of 7-40 kPag. This resulted in a hydrocarbon-free gas residence time of about 15s in the coker reactor. Test sections for deposition measurement include an external cyclone with a short exit tube and additional longer vertical test tubes of different diameters so that the vapour
residence time in the test section can be varied from 0.05–0.45 s. The effects of different operation variables on deposition, such as coker reactor temperature, steam addition, vapour velocity, and heating or cooling of produced vapour, etc., were investigated to identify the primary deposit formation mechanism.

Simulated distillation of the quenched vapours downstream of the test section showed that there was about 3.6 wt% of species whose boiling point was above 750°C in the vapour phase from the coker. The lower the temperature to which the vapour was cooled the more deposit was found in the cyclone, and for the cyclone exit tube, deposition tends to be lower where the wall was superheated above the vapour temperature. Both of these results suggest the deposition occurs primarily by physical condensation of high molecular mass species. Fig. 2-7 is the experimental results of effect of vapour temperature on deposition rate in cyclone exit tube. These data do not distinguish between wall condensation and bulk condensation followed by deposition of droplets.

![Fig. 2-7 Effect of Vapour Temperature on Deposition Rate in Cyclone Exit tube [6]](image)

(Coker temperature: 535°C)
The conflicting conclusion of cyclone exit tube line fouling mechanism suggested by Watkinson et al. [5-7] and Mallory et al. [3-4] results from the differences in experimental conditions (particularly at residence times), as shown in Table 2-1, together with the complicated coking behaviour of bitumen cracking. In fact, as mentioned above, the experimental data of Mallory et al. [3-4] at lower residence time also suggest that physical condensation can cause deposition. The research work of Watkinson et al. [5-7] provided a better match to the industrial fluid coker vapour residence time, and gave the confidence that the vapours entering the test section are more representative of those in industrial fluid cokers.

Table 2-1 Comparison of Major Conditions
between Laboratory Studies and Industrial Operations

<table>
<thead>
<tr>
<th></th>
<th>Typical industrial</th>
<th>Watkinson et al. [5-7]</th>
<th>Mallory et al [3-4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>fluid coker</td>
<td>bench-scale fluid coker</td>
<td>thermal cracking pot</td>
</tr>
<tr>
<td>τ vapour in reactor</td>
<td>~14s</td>
<td>~15s</td>
<td>~55s</td>
</tr>
<tr>
<td>Steam in vapour mixture</td>
<td>~51 mol%</td>
<td>~65 mol%</td>
<td>0 mol%</td>
</tr>
<tr>
<td>τ vapour in test tube</td>
<td>~0.14 s</td>
<td>~0.05-0.45s</td>
<td>~0.4-4.4s</td>
</tr>
<tr>
<td>Surface material</td>
<td>stainless steel</td>
<td>stainless steel</td>
<td>quartz</td>
</tr>
</tbody>
</table>

Vapours produced by bitumen fluid coking contain a very wide spectrum of species, which include water vapour from addition of the steam, gases such as nitrogen carrier gas, hydrogen, low-molecule hydrocarbons, and condensable vapours from C₅ up to heavy gas oil species. Unconverted or partially converted feed materials with normal boiling points in excess of 750°C are also present as liquid droplets. Jankovic [116] gave an estimate of boiling point distribution of cyclone vapours calculated by HYSIS as in Fig. 2-8a. It can be observed that there is about 3.5 vol % species whose boiling point are above 700°C. From the estimated molecular weight distribution of those species (Fig. 2-8b), there are about 3 vol % is above 1000.
2.2 Types and Morphology of Coke Deposits

At least three types of coke [34,35] are formed during pyrolysis-type operations: these families are generally designated as amorphous, filamentous, and graphitic cokes, but various subtypes have been proposed.

Globular (or spherical) coke is considered as a subtype of amorphous coke. Amorphous coke forms readily, especially at higher temperatures (e.g., 700 to 900°C) on all types of surfaces including stainless steels, aluminized (or alonized) stainless steel, and Vycor glass. It has a low or essentially zero metal content. On stainless steels, the amorphous coke is sometimes mixed with filamentous coke, with the result that some metal particles such as iron or nickel are
detected in the coke. Filamentous coke can be divided into at least several subtypes, for example, constant diameter and braided (or ropelike) filaments, tree-stump coke, ribbon-like filament, column and arrowhead cokes. Filamentous coke is formed by surface-catalyzed reaction at relatively low temperature (e.g. 500 to 600°C), and at higher temperature (e.g. 800 to 900°C), mainly by gas-phase reactions. Graphitic-type coke with a high density and relatively high thermal conductivity is formed mainly at higher temperatures (≥900°C). Fig. 2-9 is a summary of major routes by which coke are formed.

![Fig. 2-9 Mechanism for Production of Filamentous and Amorphous Cokes](image)

Albright et al. [34-37] examined the coke formed on solid surfaces during the pyrolysis of light hydrocarbons by scanning electron microscope (SEM) and energy dispersive X-ray analyzer (EDAX). Seven types of coke have been identified: braided filament, uniform diameter filament, needle or spike, ribbon, fluffy or cotton-like fibers, knobby, and amorphous. The first four types were always magnetic, containing metal, which were primarily iron and nickel.
However, the last three types contain little or no metal particles. The magnetic cokes formed on stainless steel or alloy surfaces, but never on Vycor glass or aluminized metal surfaces. Fluffy coke is characterized as gas phase coke. The fact that more than one type of coke was noted in some surfaces strongly supports the postulate that more than one coking mechanism is occurring. Through the morphology of the coke, Cozzani [38] found that the coke during polyethylene cracking was formed not only by catalytic wall effects but also by a gas-phase coke formation mechanism.

Bennett et al. [39] examined the coke formed by naphtha cracking at the temperature of around 850°C, and found that the coke consisted of two layers. The inner most layer was formed by heterogeneous reaction catalyzed by iron and nickel. The outer deposit layer was fairly uniform in thickness, had a columnar radial and axial layered structure, which together with the absence of any inorganic contaminants suggested it was formed by a gas-phase mechanism.

Borsa et al. [40] found the coke during 1,2-dichloroethane pyrolysis process was formed by gas-phase mechanism. The coke material is first formed as a liquid and subsequently becomes solid. The coke is initially deposited as a highly viscous fluid material and is shaped to large rounded features by the flowing gas above it before it solidifies.

Very little research work has been published on the morphology of cyclone fouling deposits. Watkinson et al. [6] found that the deposits collected on the coker reactor exit filter showed clusters of hollow spheres. The deposits formed on the cyclones and exit tubes generally have the same morphology, in which small spherical or near-spherical particles were observed, an evidence of physical condensation mechanism.

2.3 Studies of Chemical Composition and Structure of Carbonaceous Species

The formation of carbonaceous residues is of considerable technological and economic importance to the petrochemical industry. Knowledge of their chemical composition and
structure is essential in order to clarify their deposition mechanism, and prevent or alleviate their formation. As a result, a great deal of work has been carried out to study the nature and formation of these residues in recent years, especially for the coke formed as an unwanted byproduct in catalytic processes.

The chemical identity of the coke components can be determined by various spectroscopic techniques: infrared (IR), ultraviolet and visible spectroscopy (UV–Vis), electron spin resonance (ESR), $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) generally with high resolution techniques (magic angle spinning or MAS, cross polarization or CP, high field decoupling), etc. As these techniques cause generally no change in coke composition, several of them can be successively used. However, none of above techniques are adequate to identify individual components in the coke mixture. A solvent extraction technique proposed by M. Guisnet and co-workers [41-45] has been particularly successful in the study of individual components in part of the coke mixture. In the first step, the carbonaceous compounds are liberated from the zeolite by dissolution of the aluminosilicate matrix in a hydrofluoric acid solution (40%) at room temperature. In the second step, the soluble components are extracted by chloroform as a solvent and the non-soluble components are recovered. Blank tests with samples of an inert solid (SiO$_2$) impregnated with very reactive compounds show that the treatment with the acid solution causes no chemical changes of the carbonaceous compounds. The chemical identity of the components soluble in chloroform can be determined using IR, UV–VIS, H and $^{13}$C NMR, etc. while their developed formula can be deduced from GC, MS, and GC/MS experiments. The characterization of unsoluble coke can then proceed via aforementioned various physical techniques.

2.3.1 Solvent Extraction and Soluble Coke Composition

Chloroform [41,44-50] was a commonly used solvent in the extraction process, however, hexane [46], CH$_2$Cl$_2$[47], CCl$_4$[47,48], cyclohexane [49], toluene [46,49,50], iso-octane [50], N-
methyl-2-pyrrolidone [47,48], pyridine [51,52] etc. are also have been reported to be used as solvent(s) in this extraction process, in which CCl₄ [47,48] could be used to remove externally accessible coke, because the molecule of CCl₄ is too large to enter the pore of zeolite. A Soxhlet apparatus [45,46] may be employed for extraction. Supercritical Fluid Extraction (SFE) [53] was also reported as a method to extract the soluble portion of the coke from the coked FCC catalysts. The extracts (soluble coke) were further analyzed by GC-MS for individual, and the structure of unsoluble coke could be further analyzed by elemental analysis and various physical techniques, such as SEM, TGA, DRIFT, ¹³C NMR, etc.

Table 2-2 Soluble Coke Structures Formed by Propene on Zeolites at 450°C [44]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Structure</th>
<th>General Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylcyclopentapyrenes</td>
<td></td>
<td>CₙH₂ₙ₋₂₆</td>
</tr>
<tr>
<td>Alkylbenzofluoranthenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylbenzoperylenes</td>
<td></td>
<td>CₙH₂ₙ₋₃₂</td>
</tr>
<tr>
<td>Alkyldienopyrenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylcoronenes</td>
<td></td>
<td>CₙH₂ₙ₋₃₆</td>
</tr>
<tr>
<td>Alkylbenzoidenopyrenes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using GC/MS, Guisnet et al. [41] determined that the major constituents of soluble carbonaceous deposits (chloroform as solvent) formed during n-heptane cracking on Zeolite USY are polyaromatic (3-7 aromatic rings) compounds having small alky groups. Moljord et al. [44] found that the distribution of chloroform-soluble coke components (3-7 aromatic rings),
formed by propene on HY zeolites at 450°C, could be classified into three main families as in Table 2-2, whose general formula are \(C_nH_{2n-26}\), \(C_nH_{2n-32}\) and \(C_nH_{2n-36}\), respectively.

In order to determine the chemical nature of coke deposited on a Pt-Sn catalyst after the reaction of conversion of n-alkanes \((C_{10}-C_{19})\) to mono-olefins under industrial conditions, Afonso et al. [46] submitted the deactivated catalyst to a sequential extraction of soluble coke in a Soxhlet apparatus with n-hexane, chloroform, and toluene (in this order); and the time of extraction was 24 h per solvent. In a separate experiment, another mass of deactivated catalyst was extracted with toluene only for 24 hours. In case of sequential extraction, the results in Table 2-3 indicate that the amount of each extract decreases in the sequence n-hexane-chloroform-toluene. The sequential extraction procedure removed approximately 1/5 of the coke present in the deactivated catalyst. Data of one step toluene extraction indicates that the amount of extractable coke was not influenced by extraction procedure.

<table>
<thead>
<tr>
<th>Extract</th>
<th>% wt/wt of coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential extraction</td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>10.3</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.5</td>
</tr>
<tr>
<td>Non-extractable coke (insoluble coke)</td>
<td>82.0</td>
</tr>
<tr>
<td>Single-step extraction</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>16.6</td>
</tr>
<tr>
<td>Non-extractable coke (insoluble coke)</td>
<td>83.4</td>
</tr>
</tbody>
</table>

The composition of each extract in the sequential extraction of Afonso et al. [46] from the coke deposition on a Pt-Sn catalyst after the reaction of conversion of n-alkanes \((C_{10}-C_{19})\) to mono-olefins is listed in Table 2-4 [46].
Table 2-4 Approximate Compositions of the Extracts for the Coke on Pt-Sn Catalyst [46]

<table>
<thead>
<tr>
<th>Extracts</th>
<th>n-Alkanes (C_{10}-C_{19})</th>
<th>n-Alkanes (C_{20}-C_{37})</th>
<th>Mono and Di-olefins</th>
<th>Aromatic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>83</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>41</td>
<td>8</td>
<td>3</td>
<td>48</td>
</tr>
<tr>
<td>Toluene</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>87</td>
</tr>
<tr>
<td>Toluene (single step)</td>
<td>45</td>
<td>5</td>
<td>3</td>
<td>47</td>
</tr>
</tbody>
</table>

One can recognize that the composition of the extract obtained after single-step toluene extraction corresponds to the sum of composition of partial extracts (see Table 2-3 and 2-4). Therefore, it appears that the extraction procedure (sequential versus single) does not affect the amount of extractable coke (chemical composition and quantity). Data also confirm the increasing aromatic character in the extracts as the solvents were changed from n-hexane-CHCl₃-toluene. For aromatic compounds, the alkyl/alkenybenzenes are more concentrated in n-hexane extract, those of 2-3 rings in the chloroform extract and those 3 or more rings in the toluene extract.

Kozhevnikov et al. [49] used toluene, cyclohexane and dichloromethane to extract coke on the catalyst of propene oligomerisation over silica-supported heteropoly acid catalyst, respectively, and found that dichloromethane showed the better result. During the study on the coke composition on HZSM-5 catalyst used in the cracking of hexadecane, Holmes et al. [48] found N-methyl-2-pyrroldione could dissolve the insoluble coke. After treatment with N-methyl-2-pyrroldione, no insoluble coke could be found using standard extraction techniques. Benito et al [51] and Magnoux et al [52] used pyridine as a solvent to distinguish light coke (soluble in pyridine) and heavy coke (nonsoluble).
Qian et al [53] used Supercritical Fluid Extraction (SFE) to remove and concentrate leachable coke molecules from the coke deposits on FCC (Fluid Catalytic Cracking) catalyst. The coked catalyst was first extracted by supercritical fluid CO₂ using 25% of toluene as a modifier for 10 min. The pressure and temperature of the extraction vessel were controlled at 450 atm and 373K, respectively. The samples were then extracted for additional 40 min using 5% of methanol as a modifier. The SFE extracts were further analyzed by using mass spectrometer.

Mass spectrometric analyses of SFE extracts of the coked FCC catalysts [53] suggest that a large percentage of extractable coke is composed of N-containing molecules. Figure 2-10 gives the mass spectrum of an SFE extract. Nitrogen molecules clearly predominate the spectrum as indicated by the strong intensity of odd mass peaks. The relatively low molecular weights (m/z < 400) observed suggest that leachable coke molecules are mostly 3-5 ring nitrogen and hydrocarbon aromatics with short alkyl substitutions. In Figure 2-10, there are two predominant nitrogen homologues (labeled by • and Δ); each contains at least two different core structures. The major compound type is alkylcarbazoles. Pyridinic type molecules (basic nitrogen) and aromatic amides also present abundant levels. This enrichment implies that basic nitrogen and amides have a higher tendency to be converted into coke on the catalyst acid sites.

Fig. 2-10 Mass Spectrum of Extractable FCC Coke Molecules [53]
2.3.2 Physical Techniques for Studies of the Structure of Carbonaceous Materials

Various physical techniques, for example, DRIFT, $^{13}$C NMR, ESR, Raman spectroscopy, thermal analysis, SEM, etc. can be used to elucidate the composition and structure of the carbonaceous solids. Table 2-5 (page 36) lists the physical techniques and the corresponding properties they can identify.

(1) Diffuse-reflectance Infrared Fourier Transform (DRIFT) spectrometer [54-64]

Infrared spectra (IR) are obtained by excitation of molecular vibration through absorption of infrared energy. IR spectroscopy provides detailed information on the characteristics of the samples, and it has been used for over 60 years in studying surface species. However, IR investigation of intractable carbonaceous materials such as carbon black, coal chars, activated carbons and graphite, is very different, and needs special sample preparation and instrument techniques [54]. In recent years, Fourier Transform Infrared (FT-IR) spectroscopy has been reported in the literature [55-61] as a very valuable technique to characterize carbonaceous materials deposited by very different materials on different processes. Samples can be analyzed by transmission or by reflection. The Diffuse-reflectance Infrared Fourier Transform (DRIFT) spectrometer uses a set of flat and elliptical mirrors, and this device can measure a sufficient amount of light diffused by a sample dispersed in KBr (or KCl) powder. By comparing the diffused reflection obtained with neat KBr (or KCl), a result resembling the transmission spectrum is obtained. Kubelka-Munk’s correction can be used to improve the spectrum. DRIFT [62-64] is a very valuable technique to characterize highly absorbing powered solids (e.g., carbon, catalyst, etc.).

Based on the shift of wave-number and the change of intensity, the characteristics of the deposit can be derived. As an example, DRIFT spectra of the coked Al-MCM-41 samples [64] are presented in Fig. 2-11. Two main frequency regions in which the detected bands occur
(2800-3000 and 1300-1500 cm\(^{-1}\)) and an intense broad band (at ca. 1600 cm\(^{-1}\)) can be distinguished. The two regions contain paraffinic and/or olefinic bands, and the 1600 cm\(^{-1}\) band is known as the coke band. Single bands at ca. 3070, 1700, 1670, and 1510 cm\(^{-1}\) are observed in the presented spectra as well.

Fig. 2-11 DRIFT Spectra of the Coked Al-MCM-41 Samples [64]

In the range of the C-H stretching vibrations in alkanes (2800-3000 cm\(^{-1}\)), the bands occurring at 2870, 2926, and 2955 cm\(^{-1}\) are assigned to the symmetric vibrations of CH\(_2\) and CH\(_3\), the asymmetric vibration of CH\(_2\), and the asymmetric vibration of CH\(_3\), respectively. The 3070 cm\(^{-1}\) band is probably due to the stretching vibration of C-H in polyalkenes or in aromatics. The band at 1670 cm\(^{-1}\) is attributed to the stretching vibration of C=C in alkenes. The band at 1700 cm\(^{-1}\) presumably originates from vibrations of tetra-substituted C=C in olefinic compounds (traces of C=O might also be present). The 1510 cm\(^{-1}\) band might correspond to vibrations of aromatic rings as the bands between 1500 and 1525 cm\(^{-1}\) usually arise when simple aromatics are converted to a mixture of more complex aromatics, perhaps para-substituted ones.
(2) $^{13}$C Solid-State Nuclear Magnetic Resonance ($^{13}$C NMR) [64-76]

$^{13}$C NMR is frequently used to study the nature of carbonaceous deposits. The development of sophisticated techniques such as magic-angle-spinning (MAS), cross-polarisation (CP) as well as availability of high field magnets makes $^{13}$C NMR a promising technique to obtain high-resolution spectra of carbonaceous compounds in solid-state.

$^{13}$C solid-state NMR spectra of coked samples show resonances in two regions of the chemical shift corresponding to aromatics and olefins (115-150 ppm) and to paraffins (5-60 ppm). The nature and the state of the carbonaceous residues can be inferred from the chemical shift, linewidth, and relaxation times data. In general [70,72], mobile species normally exhibit narrow, well-resolved $^{13}$C resonance lines while more condensed carbonaceous compounds normally yield a broad, featureless line. For the former, a major contribution may arise from volatile and/or physically adsorbed (soft) cokes, coke precursors, and retained reactants or products. In most cases, these mobile species can be removed by simple sample evacuation treatment. For the latter, the broad resonance is normally ascribed to the bulky, polyaromatic (hard) coke which cannot be removed easily.

As an example, $^{13}$C solid-state NMR spectra of coked Al-MCM-41 samples (see Fig. 2-12) [64] show resonance in two regions of the chemical shift corresponding to aromatics and olefins (115-150 ppm) and to paraffins (5-60 ppm). The main downfield peak, centered at ca. 127 ppm, originates from aromatic CH groups, and the shoulder at ca. 140 ppm (spectrum a) can be assigned to substituted aromatic carbons, olefinic CH groups, or olefinic carbocations. The occurrence of several single peaks in the paraffinic region (14, 19, 21, 27, 34, 40, and 44 ppm) suggests that the CH$_3$, CH$_2$, and CH groups in the sample are in a number of distinctly different surroundings. The peak at 14 ppm can be assigned to the methyl groups in paraffins. The 19 ppm peak is probably associated with the methyl groups attached to polyaromatics. The peak at 21
ppm is presumably due to the methyl groups connected to olefinic carbons. The 27 ppm peak can be assigned to the α-methylene groups in paraffins and in alkyl substituents of olefins, and that at 34 ppm to the internal methylene groups in paraffins and olefins. The peaks at 40 and 44 ppm probably originate from tertiary paraffinic carbons present in different surroundings.

Fig. 2-12 Solid $^{13}$C Solid-state NMR Spectra of Coked Al-MCM-41 Samples [64]

To elucidate coke structure, several earlier studies [73,74] have been carried out by $^{13}$C NMR using the CP-MAS technique, but unfortunately, quantitative data can be obtained only under specific conditions and the analysis is rather tedious. The method of proton gated decoupling pulse sequence has been used by A. Fonseca, etc. [66-68] for quantitative analysis of coke model compounds and coke deposits in catalyst, and they also proposed a model molecular structure to the catalyst cokes based on the quantitative $^{13}$C NMR spectra. A calibration curve for quantitative $^{13}$C NMR analysis of coke samples was first established by model compounds, in which pyrene was chosen to represent polyaromatic carbons and cholestane represented aliphatic carbons, respectively. It was found that the weight percentage of cholestane, pyrene carbon and
their corresponding spectra integrals has a good linear relationship. Moreover, the linearization of the integrals of the aromatic or aliphatic carbons of the model-compound spectra gives the same slope, which means all the carbons of the model compounds contribute equally to the intensity of $^{13}$C NMR spectra.

Paramagnetic species interact with the nuclei around them (e.g., $^{13}$C) by spin-spin interaction, causing a dramatic decrease in their transverse relaxation time. This results in extreme broadening of corresponding resonance lines, making them invisible to NMR. A simple paramagnetic compound, containing magnetic $^{13}$C, which may be present in the cokes is graphite. In Fonseca’s work [66-68], an attempt was made to observe pure graphite by $^{13}$C NMR under the same experimental conditions with other samples, and absolutely no signal was detected. Therefore, it can then be assumed that all the invisible carbons of the cokes are graphitic-like. The proportion of aromatic and aliphatic carbons in the cokes observed by NMR can then be calculated by the integrals of different coke spectra and calibration line.

(3) Temperature Programmed Techniques [43,46,77-85]

Coke properties, such as amount, type, and location in matrix, are affected by feed type, substrate type, and reaction conditions. Temperature programmed techniques, such as temperature-programmed oxidation (TPO) combined with either evolved-gas or thermogravimetric analysis (TG) is often employed to investigate these coke properties [43,46,77-85]. The characteristics of coke can be inferred from the area under TPO profiles and the position of TPO or TG, DTG (Differential thermogravimetric analysis), and DTA (Differential Thermal Analyzer) peaks. Additional factors, which can affect the shape of these profiles, could also be derived from the profiles.

The thermal analysis of LTC (low temperature coked) and HTC (high temperature coked) catalysts in propane aromatization, pretreated under non-oxidative atmosphere (pure helium, free
from any traces of O₂) at 600°C for 1 h, was carried out under static air at a linear heating rate of 10°C min⁻¹ [43]. The TG, DTG and DTA curves for the pretreated LTC and HTC catalysts are shown in Fig. 2-13.

Fig. 2-13 TG, DTG and DTA of LTC and HTC catalyst under static air (10°C/min) [43]

The LTC catalyst shows a very small weight loss, with a single DTG peak (at 90°C), which is mostly due to the presence of adsorbed water. However, this catalyst shows two endothermic DTA peaks: a first one at about 100°C (which is due to desorption of the adsorbed water vapours) and a second one at 275°C (which is due to desorption of strongly adsorbed species). By contrast, the HTC catalyst shows an appreciable weight loss only at higher temperatures (above 550°C) and a very small weight loss at lower temperatures (50–150°C). The corresponding DTG peaks are observed at 85 and 610°C. This catalyst, however, shows two DTA peaks. The first peak (which is endothermic) at 90°C is due to the desorption of adsorbed water vapours and the
second peak at 600°C (which is exothermic) is due to oxidation of coke on the catalyst. It is interesting to note that no exothermic DTA peak is observed for the LTC catalyst, indicating the absence of coke on the catalyst. Thus, the results clearly show that the high temperature coke is non-volatile but the low temperature coke is volatile; it is removed almost completely by desorption during the non-oxidative pretreatment of the LTC zeolite.

The coked samples of Pt-Sn catalyst studied by Afonso [46] were employed for temperature-programmed-oxidation (TPO): 50mg in power form were oxidized using a low mixture of \( \text{O}_2/\text{He} \) (1%, 30ml/min), raising the temperature in the range of 25-600°C (10°C/min); the effluent gas was analyzed by a quadrupole-mass spectrometer (monitoring of \( \text{O}_2 \), \( \text{CO}_2 \), and \( \text{H}_2\text{O} \)). Fig. 2-14 presents the profile of \( \text{O}_2 \) consumption, appearance of water and \( \text{CO}_2 \) for the deactivated catalyst before and after extraction of soluble coke.

The profiles of \( \text{O}_2 \) and \( \text{CO}_2 \) correlate very well. In the case of sample before extraction one can realize the existence of two oxidation zones: the first one, of limited contribution, at low temperature (ca. 260°C) and the second zone at high temperature (350~520°C) with two maximum peaks, around 410°C and 460°C in both \( \text{O}_2 \) and \( \text{CO}_2 \) profiles. After extraction of soluble coke, the low temperature oxidation zone disappeared and the initial high temperature oxidation zone region diminished (ca. 350°C). However, the two maximum peaks at high temperature were not modified. The absence of the low temperature oxidation zone (260°C, corresponds to a small portion of the coke, <10%) and of the initial high temperature oxidation zone (ca. 350°C) seems these regions correspond to the soluble coke. The presence of two maximum at high temperature oxidation zone (350~520°C) could be due to coke formation with different degree of graphitization. Concerning the water profile, one can observe the presence of two regions: the first one corresponds to water physically adsorbed (maximum at 170°C) and the second region corresponds to water formed during oxidation of coke (350-520°C).
Zeolites in the absence of coke deposition show no ESR signal [43,60,72,75], indicating the absence of any paramagnetic species on them. The ESR spectra for the zeolite coked at higher temperatures (hard coke) show a strong ESR signal, whereas those of zeolite coked at lower temperatures (soft coke) show weak ESR signals. g-value is often used in ESR, which is a dimensionless constant for an electron in a particular environment. The observed g-values for the zeolite coked at different reaction conditions are quite close to each other (average g-value=1.97±0.01G). The g-values are quite close to that observed for the sp$^2$ hybridized aromatic carbon (g=2.0023). The observed weak ESR signal for soft coke indicates the presence of the paramagnetic carbon species at low concentration, whereas the strong ESR signal for the hard coke indicates a high concentration of paramagnetic carbon species. ESR spectra for the HTC
and LTC catalysts [43], obtained at room temperature and liquid N$_2$ temperature, are shown in Fig. 2-15.

Fig. 2-15 ESR Spectra of HTC and LTC at Room Temperature and Liquid N$_2$ Temperature [43]

(5) UV-Raman [54, 86, 87]

Raman spectroscopy is potentially an ideal technique for studying the chemical structure of coke species. However, some carbonaceous contaminants induce extremely strong fluorescence from the surface, make it difficult for study by conventional Raman spectroscopy using visible wavelength excitation. UV Raman spectroscopy was developed with an intent of avoiding fluorescence and enhancing the Raman intensity by resonance effects. According to the UV Raman spectra the coke species can be categorized into the following groups (as in Fig. 2-16), absorbed olefinic and polyolefinic species (1390, ~1635, ~2980cm$^{-1}$), aromatic species (~1385, 1610cm$^{-1}$), polyaromatic species (1365-1385, 1595cm$^{-1}$) and pregraphites (1365, 1585cm$^{-1}$).
(6) Ultraviolet and Visible (UV-Vis) Spectrum [64]

UV-Vis spectrum is also reported to be used in characterization of coke formed in catalysts, however, it is not as commonly used as other techniques. As reported by Rozwadowski et al. [64], in the range of 200-270 nm, two distinct bands are observed for coked catalyst in the UV-Vis spectrum. That at ca. 230 nm most probably indicates the presence of olefins, and that at 270 nm is associated with phenyl groups. The latter band can also be ascribed to cyclic dienes with two double bonds in a ring. Weak bands in the range of 360-385 nm are assigned to polyenyllic carbocations. A weak band at ca. 430 nm is attributed to condensed aromatic rings typical of carbonaceous deposits.

(7) Other Techniques

Besides the above techniques, SEM [33-39,88,89] is frequently used to show the morphology of the coke. Further more, EDAX [33-37] can provide information on the type and contents of metal species in the coke surface. Elemental analysis of C, H, N, O and S is used
frequently to characterize the coke bulk, especially for H/C ratio. For example, H/C atomic ratio between 0.35–0.70 is believed to be the characteristic of polyaromatic compound [42].

**Table 2-5 Physical Techniques and Their Identified Corresponding Properties**

<table>
<thead>
<tr>
<th>Method</th>
<th>Properties of Deposit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IR</td>
<td>Polyaromatic structures, coke band, and aliphatic structures, etc.</td>
<td>1600cm&lt;sup&gt;1&lt;/sup&gt; band is known as coke band. Two main frequency regions in which the detected bands occur (2800–3000cm&lt;sup&gt;1&lt;/sup&gt; and 1300-1500cm&lt;sup&gt;1&lt;/sup&gt;) and an intense broad band (1600cm&lt;sup&gt;1&lt;/sup&gt;) can be distinguished.</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>The groups have conjunction effect structures.</td>
<td>230nm (olefins), 270nm (phenyl groups), 360-385nm (polyenylic carbocations), 430nm (condensed aromatic rings)</td>
</tr>
<tr>
<td>&lt;sup&gt;13&lt;/sup&gt;C MAS-CP NMR</td>
<td>Differentiating the aromatic, olefinic and paraffinic structures.</td>
<td>Two regions of the chemical shift: 115-150ppm (aromatic and olefins), 5-60ppm (paraffins).</td>
</tr>
<tr>
<td>UV-Raman</td>
<td>Distinguishing paraffinic, olefinic, aromatic, polyaromatic and graphitic structures.</td>
<td>Absorbed olefinic and poly-olefinic species (1390, ~1635, ~2890 cm&lt;sup&gt;-1&lt;/sup&gt;), aromatic species (~1385, 1610 cm&lt;sup&gt;-1&lt;/sup&gt;), polyaromatic species (1365–1385, 1595cm&lt;sup&gt;-1&lt;/sup&gt;), pregraphite (1365, 1585cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>ESR</td>
<td>Polyaromatic characteristics</td>
<td>g-value = 1.97, strong ESR signal indicates a high concentration of paramagnetic carbon species.</td>
</tr>
<tr>
<td>TPO</td>
<td>The conversion of deposit to H&lt;sub&gt;2&lt;/sub&gt;O, CO, CO&lt;sub&gt;2&lt;/sub&gt; in case of consumption of O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>The relative quantity of soluble coke and insoluble coke.</td>
</tr>
<tr>
<td>Thermal Analysis (TG, DTG, DTA)</td>
<td>The volatile properties of the deposit</td>
<td>The relative quantity of soluble coke and insoluble coke.</td>
</tr>
<tr>
<td>Elemental Analysis</td>
<td>H, C, S, N, etc.</td>
<td>H/C ratio between 0.35–0.70 is the characteristic of polyaromatic compounds</td>
</tr>
<tr>
<td>EDAX</td>
<td>Local surface composition</td>
<td>Detecting the elements with atomic number from 4 to 98</td>
</tr>
<tr>
<td>SEM</td>
<td>Surface morphology</td>
<td>Filament, amorphous, graphitic structure, etc.</td>
</tr>
</tbody>
</table>
2.4 Studies on Kinetics and Modeling of Carbonaceous Species Formation

2.4.1 Methodology for Modeling of Deposit Formation in Different Processes

After the root cause of deposition is clearly understood, the deposit formation rate equations can be modeled. Then, the simulation of deposit formation in different industrial processes, e.g., in thermal cracker, TEL, or coker cyclones, is possible by coupling the deposit formation equation with the continuity equation, pressure drop equation, energy and momentum equation in different processing equipments or piping lines.

2.4.2 Deposition Equations Due to Different Formation Mechanisms

a. Kinetics of Deposition Due to Chemical Reaction Mechanism

For the light hydrocarbon pyrolysis process in olefins industry, it is clear that the coke formation in the coil reactor is due to chemical reaction mechanism as described in section 2.1.1. The coking rate is very high in the beginning, but rapidly decreases to an asymptotic value. Since the initial period is very short when compared to total run length, the asymptotic coking rate is the coking rate of most interest and is most readily obtained experimentally.

Even for the pyrolysis of a simple hydrocarbon as ethane, the detailed chemical reactions for coke formation are highly complicated due to the large number of radical reactions. For the modeling of coke formation, the number of reactions can be decreased by restricting the number of coke precursors, which permits only overall and simplified coking mechanisms to be established. The coking rate and various precursor concentrations could be experimentally measured. Therefore the estimated model parameters, e.g., frequency factor, activation energy and reaction order, can be determined. Among several competing models, those which have non-significant parameters, e.g., negative activated energy or reaction order, etc. are discarded. Then, the most preferred kinetic model of coke formation and the parameters can be found by a statistical analysis.
Table 2-6 shows the simplified coking mechanisms and coke precursors proposed by Sundaram and Froment [90] for thermal cracking of propane. This provides an example for more complex feedstocks. Assuming that the reaction order of coke formation is the first order, and expansion factor $\varepsilon$ is 2, thus for the parallel mechanism of Model I, the coking rate may be written:

$$r_c = k_2 C_{C_3H_8} = k_2 \left[ \frac{1 - x}{1 + \delta + x RT} \right]$$

(2-1)

For the series mechanism of Model II, the rate expression for the coking reaction is:

$$r_c = k_3 C_{C_3H_6} = k_3 \left[ \frac{x \cdot y_{C_3H_6} \cdot P_l}{1 + \delta + x RT} \right]$$

(2-2)

<table>
<thead>
<tr>
<th>Table 2-6 Coking Mechanisms in Propane Cracking [90]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parallel mechanism</strong></td>
</tr>
<tr>
<td><strong>Model I</strong></td>
</tr>
<tr>
<td>1 $C_3H_8 \rightarrow$ products $k_1$</td>
</tr>
<tr>
<td>2 $C_3H_8 \rightarrow$ coke $k_2$</td>
</tr>
<tr>
<td><strong>Consecutive mechanisms</strong></td>
</tr>
<tr>
<td><strong>Model II</strong></td>
</tr>
<tr>
<td>1 $C_3H_8 \rightarrow$ products $k_1$</td>
</tr>
<tr>
<td>3 $C_3H_6 \rightarrow$ coke $k_3$</td>
</tr>
<tr>
<td><strong>Model III</strong></td>
</tr>
<tr>
<td>1 $C_3H_8 \rightarrow$ products $k_1$</td>
</tr>
<tr>
<td>4 $C_2H_4 \rightarrow$ coke $k_4$</td>
</tr>
<tr>
<td><strong>Model IV</strong></td>
</tr>
<tr>
<td>1 $C_3H_8 \rightarrow$ products $k_1$</td>
</tr>
<tr>
<td>5 $C_3H_6 \rightarrow$ coke $k_5$</td>
</tr>
<tr>
<td>6 $C_2H_4 \rightarrow$ coke $k_6$</td>
</tr>
</tbody>
</table>

Measuring the rate of coking and the outlet concentration of propylene in a mixed flow reactor, allows $k$ to be determined from the equation. Similar series mechanisms with ethylene as intermediate (Model III) and both propylene and ethylene as intermediates (Model IV) were also
tested. Model IV was discarded due to non significantly determined parameters. Since the activation energy for coking reaction is very high for the parallel reaction, Model I is not plausible. Both Model II and Model III are positive, however, a preference to Model II was given since the residual sum of squares of reaction rates was smaller for Model II than Model III. The experimental results also substantiated that the Model II is superior to Model III. Therefore, for the coke formation rate in propane cracking, equation (2-2) is the deposit formation equation, with the frequency factor \( 1.08 \times 10^{15} \) g coke/(mol/L-m\(^2\)-s), and the activation energy 314 kJ/mol.

Zou et al. [91,92] suggest that the key coke precursors for propane pyrolysis are ethylene and propylene. Twenty-one possible coke formation models were proposed, including single reaction models, two parallel reactions models, and three parallel reactions models. The coke formation model suggested by them is:

\[
\begin{align*}
C_2H_4 \rightarrow \text{coke} & \quad k_{01} = 5.89 \times 10^{10} \quad E_{a1} = 230 \text{ kJ/mol} \quad (2-3a) \\
1/3C_3H_6 \rightarrow \text{coke} & \quad k_{02} = 2.21 \times 10^8 \quad E_{a2} = 165 \text{ kJ/mol} \quad (2-3b)
\end{align*}
\]

A similar procedure can be used for ethane pyrolysis [95,96]. For kinetics of ethane cracking, \( C_4^+ \) (the major components in \( C_4^+ \) fractions are butadiene and benzene) is used as the immediate coking precursor, the order was found to be one, the activation energy 225.8 kJ/mol and frequency factor \( 2.51 \times 10^{11} \) s\(^{-1}\).

P. Kumar and D. Kunzru [97-99] used the same procedures as mentioned above to investigate the kinetics of coke formation in naphtha pyrolysis in the temperature range of 760~820°C. The proposed models were that coke could be formed either from reactant, aromatics, \( C_6^+ \), 1,3-butadiene, ethylene, propylene or from both \( C_6^+ \) and aromatics. The results indicated that the preferred deposition equation was

\[
\text{Aromatics} \rightarrow \text{Coke}
\]
and 

\[ r_c = k_0 \exp\left(-\frac{E_a}{RT}\right)C_{Ar}^n \]  \hspace{1cm} (2-4)

For the steam which contained 50 ppm CS\(_2\), frequency factor is \(2.07 \times 10^{15} \text{ kg coke/}(\text{m}^2\cdot\text{hr} \cdot \text{kmol/m})\), activation energy 212 kJ/mol, reaction order 1.97 in aromatic content. However, for no sulfur in steam, the frequency factor is \(1.53 \times 10^{14} \text{ [kg coke/} m^2 \cdot \text{hr} \cdot \text{kmol/m}^3]\), activation energy 245 kJ/mol, reaction order 1.32.

Unsaturates (especially C\(_4\) compounds) and aromatics were supposed as important coke precursors by Reyniers and Froment et al. [9] for naphtha cracking over the temperature range of 740~850°C. However, they didn’t give any further quantitative equations.

Recently, Wauters et al. [100, 101] described a methodology for developing a detailed network for the coke formation during thermal cracking of hydrocarbons based on elementary reaction steps, and a kinetic model for coke formation based on elementary reactions between gas-phase components and coke surface is proposed. However, this model is too complex, and it is impractical to be employed in the industrial process.

b. Deposition Equation Due to Mass Transfer-Chemical Reaction Mechanism

In the pyrolysis process for converting gas oil into olefins, Z. Wang et al. [102,103] proposed a mass transfer-chemical reaction mechanism for the coke formation. In this model, the coke precursors can be either aromatics in the feed or the produced unsaturated hydrocarbons. The coke precursors first transport to the tube wall through mass transfer, and then form deposits through chemical reactions on tube wall surface. There is no coke formation taking place in the bulk fluid vapour phase. The suggested coke formation model can be expressed as the following steps:

I. The formation of coke precursors from feed or cracked unsaturated products:

\[ F \xrightarrow{k_1} P \xrightarrow{k_2} C^* \]

\[ A \xrightarrow{k_3} C^* \]  \hspace{1cm} (2-5)
where F and A represent non-aromatics and aromatics in the feedstocks, respectively. P is the cracked unsaturated gas products, and C* is the coke precursors.

II. The mass transfer of coke precursors from bulk gas fluid to the tube wall:

\[ C^* \xrightarrow{k_m} C_w^* \quad (2-6) \]

III. The formation of coke on the tube wall through chemical reactions, assuming it is a first order reaction:

\[ C_w^* \xrightarrow{k_c} \text{Coke} \quad (2-7) \]

The mass transfer rate in step II can be expressed by:

\[ r_m = k_m (C^* - C_w^*) \quad (2-8) \]

where \( k_m \) is the mass transfer coefficient of coke precursors in the bulk fluid, and can be determined from theoretical or empirical equations. The chemical reaction rate in step III can be expressed by:

\[ r_w = k_c C_w^* \quad (2-9) \]

At any location at the tube wall: \( r_m = r_w \), and eliminating the unknown \( C_w^* \), then

\[ r_c = \frac{k_c C^*}{1 + k_c / k_m} \quad (2-10) \]

From the material balance based on the concentration of coke precursors in any element of volume of the reactor:

\[ \frac{v}{S} \frac{dC^*}{dZ} + C \cdot \frac{d(v/S)}{dZ} + \frac{r_c D_z}{S} - r_c^* = 0 \quad (2-11) \]

Based on the step I, the formation rate of coke precursors can be expressed by:

\[ r_c^* = k_2 C_A + k_3 C_P \quad (2-12) \]

where \( S \) is the cross section area of the tube, \( v \) is the volumetric flowrate of the fluid, and \( D_z \) the circumference length at the location \( Z; \ k_I, k_2, k_3 \) and \( k_c \) are the specific reaction rate coefficient at the temperature \( T \), which can changes with the position in the tube and will be supplemental with
a energy balance. The frequency factors and activation energies of above reaction constants can be determined by experimental or empirical methods. Combining equation (2-10) to (2-12), the distribution of deposition rate along the tube length can be determined.

In a commercial pyrolysis coil, the temperature at the tube wall is considerably higher than the bulk temperature of gas [104]. At these high temperatures, evidences have indicated that the reaction rate constant, \( k_c \), is much higher than the mass transfer coefficient, \( k_m \). In this case, the coking is a mass transfer controlled process, and equation (2-10) can be approximately written as:

\[
\frac{r_c}{k_m} = C' \quad (2-13)
\]

The mass transfer equation at a given point in a pyrolysis coil can be expressed as:

\[
\frac{2}{S_e} k_m = \frac{0.023m^{0.8} \mu^{0.2}}{D^{1.8} (\pi / 4)^{0.8}} \quad (2-14)
\]

The coking rate then can be simplified as the following equation when considering transport phenomena in the coil reactor by Fernandez-Baujin, et al. [104].

\[
r_c = \frac{K^* m^{0.8}}{(D - 2\delta_c)^{1.8}} \quad (2-15)
\]

in which

- \( m \) = total mass flow rate in the pyrolysis tube
- \( D \) = inside diameter of pyrolysis tube
- \( \delta_c \) = coke thickness
- \( \mu \) = viscosity
- \( S_e \) = Schmidt number
- \( K^* \) = function of feedstock, cracking selectivity, dilution steam ratio, cracking severity and other system properties.

This means that at a given mass transfer, temperature and composition, the rate of coke formation is higher for a small diameter tube to the same extent that the rate of heat transfer is
greater for a small tube. Also the rate of coke formation in the small tube increases more rapidly
during the length of a run because coke build-up in a small tube increases the mass transfer
coefficient more rapidly than in a large tube as indicated by the term \((D-2\delta)^{1.8}\). This coil coking
model has been tested in a number of plants. The agreement between the predicted and the actual
run length was very good, and confirmed the assumption in the development of the model.

c. Deposition Equation Due to Condensation Mechanism

Experimental study of deposition from hydrocarbon vapours in a tubular test section
downstream of a bitumen coking reactor indicated that physical condensation is the dominant
deposit formation mechanism as mentioned in the section 2.1.3. Among the fouling mechanism
in TLE, physical condensation is also considered a primary contribution when cracking heavier
hydrocarbons, such as gas oils. However, very few papers address the deposition due to
condensation.

Horak and Beranek [32] discussed the coke formation in coolers for the products of
pyrolysis, and they include physical condensation as one of the possible mechanisms. However,
the physical condensation rate was not modeled. Instead they assumed the decisive step was the
sticking of the fouling material to the surface. This sticking process was considered as a coke
layer growth rate with negative activation energy, such that higher surface temperatures yielded
lower coke deposition rates. Thus, the transport of coke precursor was not taken into account and
the handling of the physical condensation step is questionable. Recently, Manafzadeh et al. [105]
postulated that, in the first half of TLE, the deposit formation rate was determined by a chemical
reaction mechanism, and in the down stream half of the tubes, the deposition was mainly because
of physical condensation of polycyclic hydrocarbons, as a result of lower temperatures
\((T<500^\circ C)\). Based on the work of Kopinke et al. [27], they ascribed that the main condensation
components to be acenaphene, anthracene, and chrysene, and assume the condensation rate is
Chapter 2 Literature Review

equal to their formation rate in the gas stream. A mathematical model which incorporates the physical condensation mechanism for a TLE in industrial plant was developed based on the method of Huntrods et al. [106, 107]. However, it is not clear how the authors determined the condensation temperature of individual components.

Assuming physical condensation as the mechanism, Zhang and Watkinson [6,7] developed a two-dimensional mathematical model to predict the deposit formation from hydrocarbon vapour products in straight tube with either constant and uniform wall heat flux or constant and uniform outside wall temperature. A single condensable pseudo-component is modeled to transport, condense, and form the deposit layer on the wall. Properties and concentration of the pseudo-component remain as parameters in the model. Two cases corresponding to different physical situations were simulated. The model was first used to simulate deposition results in a long tube downstream of a laboratory bitumen coking reactor. Experimental trends of the effects of vapor temperature, addition of secondary steam, and vapor residence time or vapor velocity on deposition compared favorably with model calculations. The agreement between modeling and experimental trends supported the assumption of dominant role of the physical condensation mechanism in this system. The second case modeled a single transfer line exchanger tube, which is characterized by highly turbulent flow. The temperature profiles of quenched vapour and tube skin, vapor pressure drop, and the thickness of the deposit layer are predicted.

In their model, a multiple component gas mixture with one condensable species (denoted as B) which flows in a smooth circular tube are considered. The condensable species B, usually at a very low concentration in the vapour phase at practice, coming into contact with the tube wall will condense and form as a layer of deposit on the wall, if the tube wall temperature is lower than its dew point at a given partial pressure. It is assumed that the concentration of species B is
low, and all condensed material is incorporated into the deposit, and no reentrainment of the deposit into the bulk stream is considered.

The condensation rate of species \( B \) is equal to the mass transfer rate of \( B \) from the bulk fluid to the wall, thus

\[
 r_c = N_B = k_m \left( \frac{P_B,\text{bulk}}{RT_{\text{bulk}}} - \frac{P_{B,w}^*}{RT_w} \right)
\]

(2-16)

where the mass transfer coefficient, \( k_m \), can be obtained from relevant empirical correlations or theoretical equations for conventional mass transfer in the literature. For a pure condensable species, \( P_{B,w}^* \) can be calculated through equation (2-17)

\[
 \log P_{B,w}^* = A + \frac{B}{T_w} + C \log T_w + D T_w + E T_w^2
\]

(2-17)

where \( A, B, C, D \) and \( E \) can be obtained from the literature for a specified component. In the case of unknown species, an alternative method, as shown in eqs (2-18) and (2-19), could be applied to determine the relationship between \( P_{B,w}^* \) and \( T_w \), provided the boiling point of the pseudo-condensable species \( T_B \) is specified.

The relationship between the vaporization enthalpy \( \Delta H_{vB} \) and \( T_B \) is written as [108]:

\[
 \frac{\Delta H_{vB}}{T_B} = K_F (8.75 + R \ln T_B)
\]

(2-18)

where \( K_F \) is a coefficient, which is determined by the carbon number and molecular structure. In the present case, a value of unity is taken for \( K_F \) and \( R = 1.92 \) cal mol\(^{-1} \) K\(^{-1} \). The Clausius-Clapeyron equation is then applied to determine the saturation pressure of \( B \) \( (P_{B,w}^*) \) at the particular inner wall temperature:

\[
 \ln \left( \frac{P_{B,w}^*}{P_1} \right) = -\frac{\Delta H_{vB}}{R} \left( \frac{1}{T_w} - \frac{1}{T_B} \right)
\]

(2-19)

where \( P_1 \) is the absolute atmosphere pressure.
d. Deposition Due to Other Mechanisms

Based on the fouling mechanisms in TLE, mass transfer-condensation is considered as controlling step at high temperature, and surface chemical reactions as controlling step at low temperature by Zou et al. [31]. The fouling mode for TLE proposed by Zou et al. [31] is given as follows, however, the author didn’t justify it in the paper.

\[
\begin{align*}
    r_c &= r_{c1} - r_{c2} \\
    r_{c1} &= x_1 T_g^{(1.5-0.47x_6)} G^{0.8} d_i^{-0.2} f(p_s) \left( \frac{p_g^*}{T_g} - \frac{p_w^*}{T_w} \right) \\
    r_{c2} &= x_{11} \exp(-x_{12}/T_w) \\
    f(p_s) &= 1 + x_8 p_s + x_9 p_s^{10} \\
    p_g^* &= x_3 + x_4 p_s + x_5 p_s^2 \\
    p_w^* &= \exp(x_1 - x_2/T_w)
\end{align*}
\]

where \(r_{c1}\) is the coking rate of mass transfer and condensation step, and \(r_{c2}\) is the coking rate of surface chemical reaction step, and \(x_i\) is coefficient.

2.4.3 Simulation of Deposition Profiles in Different Chemical Processes

a. Deposition Profiles in Industrial Coil Reactor

The simulation of an industrial reactor requires the integration of the continuity equations for each species, the energy equation and the pressure drop equation as described in a series of papers by Froment and co-workers [8,9,95,96, 109-115]:

\[
\begin{align*}
    \text{Continuity equation} & \quad \frac{dF_j}{dz} = -\left(\sum s_i r_i\right) \frac{na_i^2}{4} \\
    \text{Energy equation} & \quad \frac{dT}{dz} = \frac{1}{\sum F_j C_{pj}} \left[ q(z) na_i + \frac{na_i^2}{4} r_i (-\Delta H_i) \right] \\
    \text{Pressure drop equation} & \quad \frac{dp_i}{dz} = \frac{1}{M_m P_i} \left( \frac{1}{M_m} \frac{dT}{dz} + Fr \right) - \frac{1}{\alpha G^2 RT}
\end{align*}
\]
Here the friction factor, $Fr$, incorporates the effects of tube bends. For propane and other paraffins cracking, molecular reaction schemes have been proposed by Sundaram and Froment [93,94] based on the observed product distribution, radical mechanisms, and thermodynamic principles. The complex reaction scheme involved ten molecular reactions and gaseous species whose steady-state axial concentration profiles are given by equations (2-26) to (2-28). Under the clean tube conditions, a continuous heat flux profile along the reactor is used. Then, the simulated gas temperature, conversion and pressure profiles under clean tube condition can be obtained.

However, the coke deposition alters both the inner tube diameter and the heat transfer. To account for this, a suitable coking rate equation has to be coupled with continuity, energy and pressure drop equations. For example, a single reaction is taken to produce the coke for propane cracking: $C_3H_6 \rightarrow$ Coke. Since the rate of coke deposition is low, quasi steady state conditions were assumed. The increase in coke thickness $\Delta \delta_c$ in the time interval $\Delta t$ in the reactor between $z$ and $z+\Delta z$, e.g., for the heterogeneous case is given by

$$\Delta \delta_c = \frac{k_0 \exp(-E_a / RT) \bar{C} \Delta t}{\rho \times 10^6}$$  \hspace{1cm} (2-29)

The tube diameter $d_t$ was updated periodically. The updated local diameter becomes:

$$d_{t,\text{new}} = d_{t,\text{old}} - 2 \Delta \delta_c$$  \hspace{1cm} (2-30)

A step by step application of the above formula yields the coke thickness along the reactor at any given instant. The profile for the maximum tube skin temperature, outgas temperature, conversion and inlet pressure as a function of run length, and evolution of tube skin temperature as a function of time can also be derived from above equations.

Z. Wang et al. [102, 103] used a similar method to the above to simulate the coke profile in the coil coker based on the mass transfer-chemical reaction deposition mechanism.
b. Deposition Profiles in TLE Fouling During Pyrolysis of Hydrocarbon

Huntrods et al. [106,107] presented a procedure also based on the approach of Froment for modeling of coke formation in TLE of ethane and propane cracking furnaces. The model incorporated existing molecular kinetic data for predicting coke formation rates, and a semi-empirical coke deposition model for the thermal and hydrodynamic behavior of the TLE, following equations (2-26) and (2-27) with \( q(z) = U(T - T_w) \). Equation (2-28) was simplified to:

\[
\frac{dP}{dz} = \frac{-2FrG^2}{d_i \rho} \quad (2-31)
\]

and the coke thickness \( \delta_c = \delta_c(z, t) \) \( (2-32) \)

The ethane and propane pyrolysis molecular reaction scheme of Sundaram and Froment [93] was chosen as the kinetic model. The following equation, a re-statement of equation (2-29), gives the change in coke thickness, \( \delta_c \), over a time step, \( \Delta t \).

\[
\Delta \delta_c = \frac{\alpha M_c r_c}{\rho_c} \Delta t \quad (2-33)
\]

where \( r_c \) is the rate of coke formation and \( r_c = kC_i^+ \); \( \alpha \) is a coke “lay-down factor” defined as the fraction of coke formed that deposits on the tube wall. The best value for describing industrial TLE was taken as 0.17<\( \alpha <0.23 \).

For the molecular kinetic scheme, the model described by above equations is actually an initial value problem involving over 10 simultaneous coupled ordinary differential equations. In addition, coke formation as a function of operating time was incorporated through equation (2-32) by repeating the solution of mass, energy and momentum equations at every time interval.

The overall heat transfer coefficient, \( U \), is defined based on the outside tube area as:

\[
\frac{1}{U} = \frac{D_0 f_i}{D_i} + \frac{D_0}{h_i D} + \frac{\delta_c D_0}{k_c D_c} + \frac{x_w D_0}{k_w D} + \frac{1}{h_0} + f_f \quad (2-34)
\]
where the subscript \( i \) and \( o \) indicate inside and outside tube, respectively. The coke thermal conductivity, \( k_c \), varies from 0.55 W/m-K for the amorphous coke to 76 W/m-K for the condensed coke. The tube wall conductivity, \( k_w \), is given by

\[
k_w = 24.4 + 0.0041(T - 977.6)
\] (2-35)

The inside convective heat transfer coefficient was calculated using the Dittus-Boelter equation:

\[
Nu = 0.023Re^{0.8}Pr^{0.33}
\] (2-36)

The Fanning friction was calculated using the following expression for smooth pipes:

\[
Fr = 0.046Re^{-0.2}
\] (2-37)

Manafzadeh et al. [105] used almost the same method to describe the fouling of heavy hydrocarbon cracking in TEL based on the mechanism that deposition is caused by chemical reaction mechanism in the first half of TEL, and physical condensation as the mechanism in the down stream half of the tube.

c. Deposition Profiles of Cyclone Exit Tubes in Fluid Coking Process

Incorporating the continuity equation, energy equation and pressure drop equation with the deposition equation derived from physical condensation mechanisms as mentioned in section 2.4.2, the deposition profiles of cyclone exit tube in fluid coking process can be simulated. A two-dimensional physical condensation model is developed based on this method by Zhang and Watkinson [6,7]. In cylindrical coordinates, the pressure drop is the same with the equation (2-31), and continuity equation of condensable B is:

\[
\frac{1}{r} \frac{\partial}{\partial r} (r N_{Br}) + \frac{\partial}{\partial z} N_{Bz} = 0
\] (2-38)

The energy equation in the system is:

\[
\rho C_p V_z \frac{\partial T}{\partial Z} = -\frac{1}{r} \frac{\partial}{\partial r} (rq_r)
\] (2-39)

where \( r \) is the radial distance cylindrical coordinate. Solving the two differential equations, the radial and axial distribution of temperature and deposition rate can be found. Together with the specified operation conditions and the gas mixture properties, similarly with the
aforementioned method, the deposition profile in the cyclone exit tube can be simulated. The simulation and the experimental trends agreed with each other very well and supported the condensation mechanism as the primary reason for the laboratory study of fluid coker cyclone fouling.

2.5 Research Content in This Study

Based on the aforementioned work, this thesis will focus on the following aspects:

(1) Characterization of Deposit Collected in Fluid Coking Process

Collect deposit samples in the cyclone exit tube and long vertical test section from experiments in the UBC coker (see Chapter 3 for apparatus) using different feedstocks and different operation variables characteristic of cooling and heating condition in the test section. Deposits from industrial and laboratory units will be characterized by different techniques to demonstrate similarities and differences.

The following techniques will be employed. SEM will be used to examine the morphology of the deposits. Elemental analysis will yield hydrogen, carbon, sulfur, nitrogen contents and H/C atomic ratio in the deposits. X-ray fluorescence (XRF) spectroscopy will be conducted to analyze the metal content in the deposits. By TGA, the volatile properties of the deposits and relative quantity of volatile species and more condensed carbonaceous compounds can be found. Furthermore, it will be attempted to employ DRIFT and $^{13}$C NMR to identify detailed structural information in different deposits, although the complex nature of these deposits is expected to make interpretation a challenge.

Different solvents, e.g., chloroform, toluene, pyridine and N-methyl-2-pyrrolidone, will be used to extract soluble materials from the deposits. By comparison of the amounts of soluble deposit, the best solvent(s) for extraction will be determined. GC/MS and simulated distillation will be used to identify the detailed composition in the soluble deposits.
All the aforementioned experimental results will provide a much more comprehensive and detailed characterization of the deposits than has been undertaken to date. This is expected to lead to an improved explanation of the mechanisms of deposit formation under different conditions, and identify which classes of molecules take part in fouling.

(2) Aging Study of Deposits Collected in Laboratory Experimental Unit

In order to compare the differences of deposits between industrial and laboratory units, and to examine the evolution of deposit structure over time, an aging study of fresh deposits from laboratory units will be conducted. Fresh deposits under nitrogen are placed in a muffle oven at about 550°C for different specific aging times, and then characterized by the techniques mentioned above, e.g., elemental analysis, SEM, XRF, TGA, DRIFTs, \(^{13}\)C NMR and solvent extraction.

After a comprehensive analysis of the above experimental results, a structural evolution model of the deposit during the aging process will be proposed to explain the differences between laboratory and industrial deposits.

(3) Kinetic Study of Cyclone Fouling Deposit Aging

During the deposit aging process, the composition and structure of deposits change with time. The release of volatile components involve complex chemical reactions, such as thermal cracking, dehydrogenation, cyclization, skeleton rearrangement, etc., and finally leads to more condensed structures. This process is quite complex, and almost no mechanism and kinetics has been proposed in the literature. In this work, the deposit aging kinetics will be studied through thermogravimetric analysis, based on different non-isothermal kinetic pyrolysis models.

(4) Modeling Study of Droplet Mass Transfer Deposition

Mathematical modeling of deposition will assist in interpreting experimental results, and also provide guidance on the effects of process variables on fouling. Liquid droplets can be
present from heavy feed components or because of bulk condensation. The major objective of this work is to simulate the deposition rate from liquid droplet mass transfer, and to compare with those predicted by physical condensation on the exit tube wall. Incorporating the above aging kinetics will permit the calculation of deposit composition and amount with time.

All the proposed work is aimed at identifying unequivocally what is the root cause of cyclone fouling deposition in fluid coking processes, and getting a comprehensive knowledge of the physical and chemical nature of deposits. This work will help elucidate the mechanisms of fouling and interpret the reasons for the differences of deposits between industrial and laboratory units, permit industrial users to mitigate fouling by manipulation of process variables, and eventually raise efficiency and reduce energy in production of crude oil from oil sands.
Chapter 3 Experimental Materials, Apparatus and Methods

In this chapter, the experimental materials used in the bench-scale fluid coker cyclone fouling equipment are presented, and the main operating parameters of the unit are discussed. As well, the collected laboratory deposits and their corresponding operating conditions are given. The different techniques which are employed to characterize the structure and composition of deposits are also described. Furthermore, the experimental procedures for deposit aging are given.

3.1 Experimental Materials of Bench-Scale Fluid Coking Equipment

The feedstock, atmospheric topped bitumen (ATB), normally used for laboratory fluid coker cyclone fouling tests was provided by Syncrude Canada, Ltd. The whole oilsands bitumen usually contains about 13.5 vol % light gas oil (LGO) and 86.5 vol % atmospheric topped bitumen (ATB) [117]. ATB will undergo further upgrading such as coking, hydrocracking, etc., for lighter oil products. Two different ATB samples (denoted as ATB-A and ATB-B) from Syncrude Canada, Ltd. were used during this investigation. The comparison of typical properties for different Syncrude ATBs and the feedstocks (ATB-A and ATB-B) are listed in Table 3-1.

From the Table 3-1, it can be observed that all the ATB used in different studies have similar properties. The feedstock, ATB, for the fluid coker is a kind of very heavy oil. Its density is about 1.01–1.04 g/cm$^3$, heavier than water; its H/C atomic ratio is around 1.5; microcarbon residue (MCR) is between 12–20 wt%; over 50 vol % distillates whose boiling point is above 525°C and even 17 vol % distillates is above 750°C. All of these properties are characteristics of heavy oils. It also contains some metals, such as Ni, V, Fe, Ca, Na, etc., and a considerable amount of fine particles. For its chemical compositions, over 30 wt% are resins and asphaltene,
### Table 3-1 Typical Properties of Atmospheric Topped Bitumen (ATB) *

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, g/cm³</td>
<td>1.024</td>
<td>1.016</td>
<td>1.02-1.04</td>
<td>1.010</td>
</tr>
<tr>
<td>Carbon, wt%</td>
<td>82.48</td>
<td>82.82</td>
<td>83.1</td>
<td>84.0</td>
</tr>
<tr>
<td>Hydrogen, wt%</td>
<td>10.20</td>
<td>10.32</td>
<td>10.24</td>
<td>10.70</td>
</tr>
<tr>
<td>H/C atomic ratio</td>
<td>1.50</td>
<td>1.49</td>
<td>1.47</td>
<td>1.53</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>0.61</td>
<td>0.45</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>4.78</td>
<td>5.10</td>
<td>4.97</td>
<td>4.45</td>
</tr>
<tr>
<td>Microcarbon residue (MCR), wt%</td>
<td>15</td>
<td>/</td>
<td>19.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Ni, ppm (wt)</td>
<td>85</td>
<td>102</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>V, ppm (wt)</td>
<td>200</td>
<td>245</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Fe, ppm (wt)</td>
<td>200</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Ca, ppm (wt)</td>
<td>/</td>
<td>10.9</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Na, ppm (wt)</td>
<td>/</td>
<td>9.2</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Solids at 0.7 μm ppm (wt)</td>
<td>5000</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Viscosity at 80°C, cp</td>
<td>/</td>
<td>2182.9</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Saturates, wt%</td>
<td>/</td>
<td>20.68</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Aromatics, wt%</td>
<td>/</td>
<td>44.3</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Resins, wt%</td>
<td>/</td>
<td>19.3</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Asphaltenes, wt%</td>
<td>/</td>
<td>13.1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Aromatic carbon fraction, wt%</td>
<td>/</td>
<td>33.8</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Gas Oil, vol %</td>
<td>/</td>
<td>/</td>
<td>43</td>
<td>46.7</td>
</tr>
<tr>
<td>&gt;525 °C, vol %</td>
<td>/</td>
<td>/</td>
<td>57</td>
<td>53.3</td>
</tr>
<tr>
<td>&gt;750 °C, vol %</td>
<td>/</td>
<td>/</td>
<td>17</td>
<td>/</td>
</tr>
</tbody>
</table>

* / means that items are not determined.
which are very difficult to upgrade; saturates in ATB are quite low, only 20 wt%, and over 40 wt % are aromatics. For the feed used in this investigation, from Table 3-1, ATB-A has much more heavy fractions, more microcarbon residue (MCR) and lower H/C atomic ratio, and exhibits a more heavy oil characteristic than that of feed ATB-B.

3.2 Experimental Apparatus of Bench-scale Fluid Coking Unit

The bench-scale fluid coking unit was modified from that in the research of Watkinson et al. [5]. The whole unit was enclosed in a rigid frame with plexi-glass doors to reduce emissions while permitting access from three sides as shown in Fig. 3-1, and the flowsheet of this fluid coker cyclone fouling unit is given in Fig. 3-2.
Fig. 3-2 Flowsheet of Fluid Coker Cyclone Fouling Unit
The coker unit consists of a 7.79 cm diameter × 0.70 m length reactor equipped with an atomization system, and a 15.2 cm diameter × 20 cm high freeboard section with internal filters to remove coke particles and droplets from the product vapour. The detailed sketch of the fluid coker is given in Fig. 3-3. Previous experimental results [5] indicated that there is no difference in the deposition yield whether there is a bed of coke particles or not. Hence, the coke reactor was kept empty in all the work on the effects of other variables on fouling. Auxiliary equipment consists of a bitumen storage tank and feed pump, and primary and secondary steam generators. Test sections for deposition measurement include an external cyclone with a short exit tube (17 cm), and an additional 90 cm long Type 304 drawn stainless-steel vertical tube test section, which was added for this study. The design sketch of the cyclone is shown in Fig. 3-4. The downstream of the test sections are a condenser and liquid accumulator tank, a scrubber, and an afterburner system.

![Detailed Sketch of Fluid Coker](image_url)

Fig. 3-3 Detailed Sketch of Fluid Coker
During the experiments, the equipment is preheated to a desired temperature in a nitrogen flow. The heated bitumen (at ca. 150°C), together with atomizing nitrogen, is introduced into the reactor through an atomizing nozzle at the bottom. Water and a small stream of nitrogen (acting as a means to monitor the blockage of the steam feeding line) are fed to a steam generator to produce feeding steam. The mass flow rates of bitumen, primary steam, and nitrogen (including primary and atomizing nitrogen) are about 0.3 kg/h, 0.3 kg/h, and 0.2 kg/h, respectively. The average vapor residence time in the empty reactor is 15 s. To prevent the liquid droplets or carbonaceous particles from being entrained into the test section, the cracked gas stream is forced to flow through two parallel filters, which are mounted in the freeboard section. Filter materials of differing pore size were used to investigate effects on the deposition rate; however, for most of experiments, one layer of 3M ceramic fiber with a filter rating of 10 μm was used as
the filtration medium. This was wrapped tightly around the perforated metal tubes as shown in Fig. 3-5. With the 10 μm filter in place, deposition is assumed to arise from the vapor phase, rather than from coke particles. A system for injection of secondary steam or nitrogen was added upstream of the cyclone for use in selected experiments to investigate dilution effects. The vapors passed through the cyclone system and its short exit tube, and then into the new 90 cm long test section, where the experimental conditions could be independently controlled. After cooling, the condensable products in the hot stream - namely, hydrocarbon and water - were collected in the accumulator vessel and the off-gas passed through a NaOH scrubber and then an afterburner before being exhausted.

Fig. 3-5 Sketch of Filter Tube
All the temperatures were recorded each minute by a data logging system. The feed rate of water to the steam system is monitored through the weight change in the water tank, and that of the bitumen is confirmed by measuring the bitumen level in the feed tank every 10 min. During the course of most runs, the reactor pressure slowly increased from 0 psig to 10~20 psig over the 6 hours experiment, because of the accumulation of carbonaceous materials on the filters. To keep the nitrogen flow rate steady, the nitrogen tank outlet pressure was regulated constantly, to maintain the pressure drop across the flow meters and, thus, a steady flow rate.

After 6 hours of operation, power to all of the furnaces and heating tapes will be shut off. After shutting off the bitumen feed, Varsol is pumped through the bitumen feed line for about 3 minutes to wash out residues and avoid blockage. A small flow of nitrogen is maintained through the system until the equipment is completely cooled. The entire system was then dismantled for cleaning and collecting deposits. The deposits in the cyclone and exit tube system, and in the long tubular section, were carefully collected using a plastic brush, and the weight difference before and after cleaning is taken as the deposit weight in each section. Although deposits are heavier toward the cooler end of the long test section, local deposition rates are not determined. Results are expressed as a deposition yield, in terms of grams of deposit per kilogram of bitumen feed (g deposit/ kg bitumen feed), or a rate, because the bitumen feed rate is constant at 0.3 kg/h. The cyclone and exit tube, and the long test section, are all reused after cleaning without any additional surface preparation. The main experimental conditions are summarized in Table 3-2.
## Table 3-2 Summary of the Main Experimental Conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value/Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feeding flow rate</strong></td>
<td></td>
</tr>
<tr>
<td>Bitumen (kg/h)</td>
<td>0.3</td>
</tr>
<tr>
<td>Primary steam (kg/h)</td>
<td>0.3</td>
</tr>
<tr>
<td>Secondary steam (kg/h)</td>
<td>0–0.55</td>
</tr>
<tr>
<td>Total nitrogen* (kg/h)</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Coking reactor conditions</strong></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>500–570°C (535°C for most runs)</td>
</tr>
<tr>
<td>Residence time (s)</td>
<td>15 s</td>
</tr>
<tr>
<td>Coke particles</td>
<td>Absent from reactor (empty reactor)</td>
</tr>
<tr>
<td><strong>90 cm long test tube</strong></td>
<td></td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td>5.8–15.7 (9.0mm for most runs)</td>
</tr>
<tr>
<td>Linear velocity (m/s)</td>
<td>2.2–16.5 (usual value is 6.9 m/s)</td>
</tr>
<tr>
<td>Residence time (ms)</td>
<td>50–415 (usual value is 130 ms)</td>
</tr>
<tr>
<td>Tube material</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Run time (h)</td>
<td>6</td>
</tr>
</tbody>
</table>

* Atomizing and primary

As shown in Fig. 3-2, there are two test sections for deposition measurement, an external cyclone with a short exit tube and 90 cm length vertical tube. A 38 cm length furnace (1.7 KW) is used to enclose the cyclone and the short exit tube. Thermocouples are used to measure the vapour or tube wall temperatures in different locations, i.e., T6 is for the vapour temperature in the connecting tube between coker and cyclone, T7 for the vapour temperature in cyclone, T9 vapour temperature in the exit tube, and T8 and T10 are for the temperatures of the bottom and
top of exit tube, respectively. BHT4 is the block heater for the cyclone and short exit tube. To obtain a good data reproducibility, it is important to ensure the consistency of thermocouple positions in different runs. Generally, the controlled thermocouple temperature of furnace, T9, is set at 550°C in all experimental runs to keep downstream conditions constant and generate reproducible experimental data. T6, the vapour temperature between coker and cyclone is kept constant at 535°C by regulating the voltage of heating tapes wrapped on the tube. Other measuring thermocouples, i.e., T7, T8, T10 and BHT4 normally varied in the range of ±10°C for most runs.

For the 90cm length vertical tube test section, it is enclosed by three independently controlled furnaces, each 30.5 cm in length. The temperature of the three furnaces can be set to heat or cool the vapour phase in the tube, in order to compare temperature effects on the deposition. Four thermocouples, i.e., T11, T12, T13 and T14, are used to measure the temperatures at different locations. Vapour temperature (T11) in the connecting tube between the cyclone and the long test tube is controlled at 535°C through regulating the voltage of the heating tapes. Thermocouples, T12, T13 and T14 measure the vapour temperature within the long tube test sections as shown in Fig. 3-2. BHT5, BHT6 and BHT7 are controlled thermocouples for the three furnaces, which were tightly clipped on the outside tube wall at specified positions to obtain reproducible experimental data.

3.3 Deposit Samples and Their Corresponding Operation Conditions

The effects of different operation conditions, e.g., coker temperature, steam addition, vapour velocity, and the heating or cooling of produced vapour, on deposition were investigated in the study, and the deposits were collected from cyclones, cyclone exit tubes and long vertical test sections in every run for further characteristic analysis. Forty-one experiments were run, and the samples and the corresponding temperatures in reactor, cyclone and test sections are listed in
Table 3-3. For the reason of simplicity, the T4 (temperature of lower coker) is designated as the coker reactor temperature, T7 (vapour temperature in cyclone) as the cyclone temperature, T13 the vapour temperature in the long test tube, and BHT6 the wall temperature of the long test tube. For the detailed temperatures of each test position in each individual run, see the Appendix 1. The deposition rate, liquid collection efficiency, steam addition and other specified operation conditions of each run are given in Appendix 2.

Table 3-3 Deposit Samples and Temperatures in The Reactor and Test Sections

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reactor (°C)</th>
<th>Cyclone (°C)</th>
<th>Vapour in long tube (°C)</th>
<th>Long tube wall (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>535</td>
<td>535</td>
<td>519</td>
<td>530</td>
<td>10 μm filter</td>
</tr>
<tr>
<td>B2</td>
<td>535</td>
<td>536</td>
<td>524</td>
<td>530</td>
<td>Without filter</td>
</tr>
<tr>
<td>B3</td>
<td>535</td>
<td>513</td>
<td>521</td>
<td>530</td>
<td>10 μm filter</td>
</tr>
<tr>
<td>B4</td>
<td>535</td>
<td>515</td>
<td>526</td>
<td>530</td>
<td>Without filter</td>
</tr>
<tr>
<td>B5</td>
<td>535</td>
<td>496</td>
<td>535</td>
<td>530</td>
<td>150 μm filter</td>
</tr>
<tr>
<td>B6</td>
<td>535</td>
<td>521</td>
<td>539</td>
<td>530</td>
<td>Without filter</td>
</tr>
<tr>
<td>B7</td>
<td>535</td>
<td>509</td>
<td>525</td>
<td>507</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B8</td>
<td>535</td>
<td>517</td>
<td>540</td>
<td>558</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B9</td>
<td>535</td>
<td>521</td>
<td>506</td>
<td>460</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B10</td>
<td>535</td>
<td>516</td>
<td>584</td>
<td>604</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B11</td>
<td>535</td>
<td>524</td>
<td>619</td>
<td>618</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B12</td>
<td>535</td>
<td>531</td>
<td>600</td>
<td>608</td>
<td>Heating vapour</td>
</tr>
<tr>
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<td>535</td>
<td>517</td>
<td>NA</td>
<td>608</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B16</td>
<td>535</td>
<td>518</td>
<td>579</td>
<td>603</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B17</td>
<td>535</td>
<td>522</td>
<td>645</td>
<td>633</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B18</td>
<td>535</td>
<td>511</td>
<td>680</td>
<td>658</td>
<td>Heating vapour</td>
</tr>
<tr>
<td>B19</td>
<td>535</td>
<td>519</td>
<td>448</td>
<td>428</td>
<td>Cooling vapour</td>
</tr>
</tbody>
</table>
### Table 3-3 Deposit Samples and Temperatures in The Reactor and Test Sections (continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reactor (°C)</th>
<th>Cyclone (°C)</th>
<th>Vapour in long tube (°C)</th>
<th>Long tube wall (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20</td>
<td>535</td>
<td>517</td>
<td>473</td>
<td>443</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B21</td>
<td>535</td>
<td>515</td>
<td>498</td>
<td>500</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B22</td>
<td>535</td>
<td>519</td>
<td>524</td>
<td>500</td>
<td>With 2nd steam addition</td>
</tr>
<tr>
<td>B23</td>
<td>535</td>
<td>517</td>
<td>505</td>
<td>500</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B24</td>
<td>535</td>
<td>524</td>
<td>506</td>
<td>500</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B25</td>
<td>535</td>
<td>515</td>
<td>512</td>
<td>500</td>
<td>More 2nd steam added</td>
</tr>
<tr>
<td>B26</td>
<td>570</td>
<td>520</td>
<td>514</td>
<td>500</td>
<td>Coker temperature 570°C</td>
</tr>
<tr>
<td>B27</td>
<td>500</td>
<td>510</td>
<td>521</td>
<td>500</td>
<td>Coker temperature 500°C</td>
</tr>
<tr>
<td>B28</td>
<td>535</td>
<td>535</td>
<td>507</td>
<td>500</td>
<td>With 2nd nitrogen</td>
</tr>
<tr>
<td>B29</td>
<td>535</td>
<td>531</td>
<td>522</td>
<td>500</td>
<td>3/4&quot; dia. long test tube</td>
</tr>
<tr>
<td>B30</td>
<td>535</td>
<td>523</td>
<td>520</td>
<td>500</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B31</td>
<td>535</td>
<td>530</td>
<td>532</td>
<td>500</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B32</td>
<td>535</td>
<td>528</td>
<td>525</td>
<td>500</td>
<td>3/4&quot; dia. long test tube</td>
</tr>
<tr>
<td>B33</td>
<td>535</td>
<td>523</td>
<td>538</td>
<td>535</td>
<td>No steam feeding in coker</td>
</tr>
<tr>
<td>B34</td>
<td>535</td>
<td>NA</td>
<td>525</td>
<td>500</td>
<td>1/4&quot; dia. long test tube</td>
</tr>
<tr>
<td>B35</td>
<td>535</td>
<td>532</td>
<td>525</td>
<td>500</td>
<td>1/4&quot; dia. long test tube</td>
</tr>
<tr>
<td>B36</td>
<td>535</td>
<td>510</td>
<td>495</td>
<td>443</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B37</td>
<td>535</td>
<td>530</td>
<td>505</td>
<td>443</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B38</td>
<td>535</td>
<td>NA</td>
<td>NA</td>
<td>425</td>
<td>Not in normal</td>
</tr>
<tr>
<td>B39</td>
<td>535</td>
<td>528</td>
<td>510</td>
<td>428</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B40</td>
<td>535</td>
<td>520</td>
<td>458</td>
<td>425</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B41</td>
<td>535</td>
<td>537</td>
<td>487</td>
<td>425</td>
<td>Cooling vapour</td>
</tr>
</tbody>
</table>
Because of the complexity of safely operating a pilot scale unit such as this, experiments were carried out by a team: Dr. W. Zhang, Mr. G. Cheng and, for most runs, the author. From Table 3-3, it can be noted that the laboratory deposits were collected in all kinds of experimental conditions, e.g., heating or cooling vapour, different pore size filter, with or without filter, steam/nitrogen addition, etc. Furthermore, deposits were also collected under different coker temperatures. A sub-set of typical deposits were selected by the author for further chemical composition and structure analysis by means of different chemical and physical analytical techniques. Runs were selected to represent both heating and cooling conditions, and high versus low temperatures, for conditions where sufficient amount deposit was available.

Two deposit samples from an industrial fluid coker unit were provided by Syncrude Canada, Ltd. Sample B was collected from cyclone snout outlet, and sample D was from gas outlet tube. The main difference between the deposits collected from laboratory bench-scale unit and those of industrial fluid coker unit is that the industrial deposits had been in place aging at the temperature around 500°C for months even over one year, whereas the fresh laboratory deposits were collected after 6 hours running.

3.4 Apparatus and Instruments for Characterization of Deposits

Different apparatus and instruments will be employed to study the structure and composition of different deposits. A Soxhlet extraction apparatus is used to extract the solvent soluble fractions in the deposits, and the soluble fractions further analysed by GC/MS or simulated distillation to identify their individual components or boiling point distribution. Elemental analysis will be used to study the elemental chemical composition of the deposits, and different physical techniques, e.g., SEM, TGA, DRIFT, $^{13}$C NMR, etc. will give valuable detailed information of the deposits. Attempts were made to use XRD on deposit samples, however, only a broad peak was found.
3.4.1 Soxhlet Extraction [119]

Soxhlet extraction is widely used for the extraction of a soluble fraction from a solid material. Typically, deposits are placed inside a thimble made from glass or filter paper (See Fig. 3-6), which is loaded into the Soxhlet extractor. The extractor is attached to a flask containing a solvent and a condensor. The solvent is heated, causing it to evaporate. The hot solvent vapour travels up to the condenser, where it cools and drips down onto the test material. The chamber containing the test material slowly fills with warm solvent until, when it is almost full, it is emptied by siphon action, back down to the flask. This cycle repeats many times. During each cycle, a portion of the solid material dissolves in the solvent. However, once the soluble fraction reaches the solvent heating flask, it stays there. It does not participate in the extraction cycle any further. This is the key advantage of this type of extraction; only clean warm solvent is used to extract the solid in the thimble. This increases the efficiency of the extraction when compared with simply heating up the solid in a flask with the solvent. At the end of an extraction, the excess solvent may be removed using a rotary evaporator or by natural evaporation, leaving behind only the extracted solid materials.

Fig 3-6 A Schematic of Soxhlet Extraction Apparatus
Chloroform, toluene, pyridine and 1-methyl-2-pyrolidone (MPD) were selected as extraction solvents based on the literature, and a 125ml Soxhlet apparatus is employed for the extraction process. The procedure is to weigh about 0.0500g of deposit collected from long tube test section or 0.1000g from filter, and then add 100~120ml solvent to the flask. The deposit sample is then extracted in the Soxhlet apparatus for 24 hours. After extraction, the deposit residue within the thimble is dried in the fume hood. The deposits are weighed together with the thimble before and after extraction respectively in order to get the weight loss during extraction. The extracted solutions are evaporated in the fume hood with a low heat to concentrate them up to ~2 ml and kept for further GS-MS or simulated distillation analysis.

The industrial deposit samples were first ground into fine particles using a mortar and pestle, and then 10g deposits are used for Soxhlet extraction.

3.4.2 Gas Chromatograph-Mass Spectroscopy (GC-MS)

The soluble deposit components extracted from different solvents were analyzed by gas chromatography (Varian 3600, couple with Star working station). A 30 meters DB-5ht capillary column (ID 0.25mm, 0.10um) was used with the following conditions:

Carrier gas: He; injector temperature: 300°C; detector: FID, 300°C; column head pressure: 20psi; heating temperature: 10°C/min from 40~80°C, and then at 3°C/min ramped to 335°C. The volume injected was 0.8ul with splitless injection mode. The splitless injection mode is used for analysis of trace components in the sample. The splitter solenoid valve is activated just prior to injection, and deactivated after 0.7min, venting the remaining sample. The remainder of the analysis is performed with the solenoid deactivated.

Experimental results indicated that there are almost no soluble component effluents in the GC chromatography for both laboratory and industrial samples (See Fig. 3-7 and 3-8, as examples) except the solvent and its impurities. However, it is found that the column end in the
injector section was always contaminated, which means that there are must be much heavier components in the extracts which cannot be evaporated under the temperature of the injector. Thus, the method of high temperature GC simulated distillation is tried to identify the boiling point distribution in the extracts.

Fig. 3-7 GC Spectrum of Extracts from Laboratory Fresh Deposits (Run B9)

Fig. 3-8 GC Spectrum of Extracts from Industrial Deposits (Sample B)
3.4.3 Simulated Distillation [120]

Simulated Distillation is a gas chromatographic method designed, through hardware and software technology, to simulate the actual physical distillation of petroleum raw materials and products. Samples are analyzed on a non polar chromatographic column that separates the hydrocarbons in order of their boiling points. These are correlated with the retention times, through a calibration curve obtained by running under the same conditions a known mixture of hydrocarbons, usually n-alkanes, covering the boiling range expected in the sample. Results are reported as a correlation between the boiling points and the percentages of the sample eluted from the column. In this experiment, an AC/Agilent SIMDIS Analyzer is used for simulated distillation analysis according to ASTM-D6352, which can determine the boiling point data up to 750°C. A 5 m DB-HT Sim Dis column was used (0.53mm, 0.15µm) with the temperature from 30–430°C at 10°C/min, and then holding for 5 mins at 430°C. FID was used as the Detector at the temperature of 450°C. The injector is ramped from 55 to 450°C at 2°C/min. This experiment was performed at the State Key Laboratory of Heavy Oil Processing, Beijing, China.

3.4.4 Scanning Electron Microscope (SEM) [121]

SEM is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. It also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas.

In this study, SEM (HITACHI S-3000N, Japan) is used for the morphological examination of different deposits, which is coupled with X-ray Microanalysis (EDAX) for elemental
composition in the deposits. EDAX is a surface analysis method which measures local surface composition at a point or a small area to a depth of 1~2 μm. This unit reportedly can detect the elements with atomic number from 4 to 98. However, for the elements whose concentration is low, the analytical precision is quite low (e.g., concentration is from 10~1%, the precision decreases from 5~50%). EDAX values for surface carbon, oxygen and sulfur should therefore be compared with elemental chemical analysis which represents bulk composition.

3.4.5 Thermogravimetric Analysis (TGA) [122]

The thermogravimetric analysis (TGA) provides a graph of mass loss vs. temperature over the range of 25 to 1200°C. This analytical technique is widely used to measure the loss of volatile components or thermal stability of a sample in the milligram range. The experiments are usually run with a temperature ramp of ca.10~50°C /min and can be carried out in inert atmospheres, such as nitrogen, to study thermal stability or volatility, or in oxidizing atmospheres to study oxidative decomposition. The mass losses can be characteristic of a material and, where the losses are in discrete steps, the TGA experiment can offer quantitative data on the course of a decomposition. The TGA also can be run in an isothermal mode, where the rate of weight loss at a fixed temperature is measured. This type of experiment can be used to predict loss rates of volatiles or decomposition rates for materials.

In this investigation, experiments are carried out with a TGA-50 thermogravimetric analyzer (Shimadzu, Japan) on 5~15 mg samples under nitrogen with a flow rate 50 ml/min. Industrial deposits were first ground to a fine powder with mortar and pestle, whereas the powdered lab deposits needed no grinding. The temperature is first ramped to a specified temperature from ambient at a heating rate of 10°C/min then either stopping the experiments at the final temperature or maintaining at this final temperature for a specified time period. The weight changes of the sample with the temperature and time are recorded on line by running a
Chapter 3 Experimental Materials, Apparatus and Methods

TA-60WS Collection Monitor software. The experimental data are further processed by a TA60 software. Most samples were run in duplicates.

3.4.6 Diffuse-reflectance Infrared Fourier Transform (DRIFT) Spectrometer [62]

Diffuse reflectance is widely used for examining rough surface materials, samples abraded on substrates, powder and reactions on powder. A set of flat and elliptical mirrors is used in the DRIFT spectrometer, and this device can measure a sufficient amount of light diffused by a sample dispersed in KBr (or KCl) powder [62]. By comparing the diffused reflection obtained with neat KBr (or KCl), a result resembling the transmission spectrum is obtained.

Kubelka-Munk’s correction can be used to improve the spectrum. The diffuse reflectance spectrum of a diluted sample of “infinitely thick” layer (i.e., at least 3mm) is usually calculated with reference to the diffuse reflectance of the pure diluent to yield the reflectance, R. The Kubelka-Munk’s equation is written as:

\[ f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} \]  

where \( k \) is the absorption coefficient, and \( s \) is the scattering coefficient. The Kubelka-Munk theory predicts a linear relationship between the molar absorption coefficient, \( k \), and the peak values of \( f(R) \) for each band, provided \( s \) remains constant. Since \( s \) is dependent on particle size and range, these parameters should be made as consistent as possible if quantitative data are needed. It has been shown [62] that for dilute samples in low absorbing or non-absorbing matrices:

\[ k = 2.303\alpha c \]  

where \( \alpha \) is the molar absorptivity and \( c \) is the molar concentration.

In this investigation, DRIFT spectra are recorded with a Bio-Rad FTS 175 spectrometer running Bio-Rad’s Win IR version 4.14 software, Harrick DRIFT accessories, liquid-nitrogen-cooled MCT (Mercury Cadmium Telluride) photoconductive detector within the range of
700~4000 cm\(^{-1}\) at resolution 4 cm\(^{-1}\) after 256 scans. All the samples were ground to a fine power, and were diluted to 1~5% in KBr or KCl. The spectra were plotted assuming the model of Kubelka and Munk for the diffuse reflectance, with the Kubelka-Munk function being analogous to absorbance. To show comparison spectra, several samples are shown in one plot by adding a constant to the Kubelka and Munk function. The detailed experimental procedures are as follows:

1. Fill MCT detector’s dewar with liquid nitrogen. Wait about 20min until the dewar comes to thermal equilibrium. Then, turn on the main power of FTS 175 spectrometer, power on indicator light will be on (green).

2. Add sufficient fine KBr (KCl) powder to the sample supporter. If the test sample is to be running under a certain temperature, cooling water should be supplied. If a carrier gas/reaction gas is required, the gas should be supplied according to the experiment. If the DRIFT sample requires pretreatment, evacuate the sample using the vacuum system after the sample treatment.

3. Turn on the computer, and start Win-IR software. Click menu item “Collect -> Align->auto align” to align the FTS 175 system. The bigger the absolute signal value, the better it is (usually bigger than 0.3 is fine).

4. After alignment, adjust DRIFT module (up/down) to get the best signal (the bigger absolute magnitude value the better) under the align mode. Then, click menu item “Collect -> Rapid scan”, inputting proper scan parameters, file storage path and file name.

5. Start a background scan under the scan number of 256. Then, start normal IR spectrum scan to check the scan is proper or not, the flat spectrum (no peak) indicate a good background scan. (The absorbance of CO\(_2\), H\(_2\)O should be less than 1\(\times\)10\(^{-3}\)).

6. Put the sample which was diluted to 1~5 wt% in KBr above the KBr powder layer in the sample supporter. Then start normal IR spectrum scan under the scan number of 256, and with Kubelka-Munk function being analogous to absorbance. Save the scan results to the computer.
DRIFT measurements were made by the author; some samples were repeated in Microanalytical Service Center, China.

3.4.7 $^{13}$C Solid-State Nuclear Magnetic Resonance ($^{13}$C NMR) [66-68]

High resolution nuclear magnetic resonance was originally limited to solutions, however, techniques have more recently developed which make it possible to obtain well resolved $^{13}$C NMR also from solids. This form of $^{13}$C NMR spectroscopy is especially important for investigating polymers, biopolymers, coal and surface chemistry [131]. As described in the Chapter 2, $^{13}$C NMR experimental results [66-68] indicated that all the carbons except graphite in the test sample contribute equally to the intensity of $^{13}$C NMR spectra. Paramagnetic species, e.g., graphitic-like carbon, are invisible to NMR. Therefore, the proportion of aromatic and aliphatic carbons in the deposits observed by NMR can then be calculated by the integrals of different coke spectra and calibration line. The fraction of graphitic carbons, $f_G$, in the coke can be calculated by the equation [66-68]:

$$f_G = 1 - \frac{C_{NMR} \%}{C_{real} \%} \quad (3-3)$$

where the $C_{NMR} \%$ is the carbon contents visible to $^{13}$C NMR, which is results calculated from 13C NMR spectra integrals. $C_{real} \%$ is the carbon contents analyzed by elemental methods. The fraction of aromatic carbons in the coke can be expressed by the equation as follows,

$$f_a = f_G + f_a^* (1 - f_G) \quad (3-4)$$

Therefore, the aliphatic carbon can be calculated by the following expression:

$$f_p = f_p^* (1 - f_G) \quad (3-5)$$

where $f_a^*$ and $f_p^*$ are the fraction of the aromatic and aliphatic carbons considering only those detected by quantitative $^{13}$C NMR, respectively.
In this study, $^{13}$C solid state NMR spectra are collected using a 9.4 T Bruker spectrometer in the Department of Chemistry, UBC, operating at the frequency of 100.57 MHz for $^{13}$C. In order to obtain the quantitative data, single pulse excitement (SPE) were used with a pulse length $p_1 = 4.5$ s, a delay time $d_1 = 50$ s. The sample was spun in a 4 mm zircon rotor at 15 kHz and 1200 scans are collected for each spectrum. Adamantane was used as external reference for the chemical shift. These experiments were run by Celine Schneider in the Department of Chemistry, UBC.

3.4.8 Other Techniques

X-Ray Fluorescence Spectroscopy (XRF) was done at Syncrude Canada Research Lab for semi-quantitative analysis of metal contents in the deposits. The elemental composition and H/C atomic ratio of deposits are analysed by Canadian Microanalytical Service Ltd.

3.5 Aging Study of Laboratory Fresh Deposits

The procedure is to weigh the sample together with a glass tube (O. D. 10 mm), and then insert the sample and the tube into a stainless steel tube (7.8 cm long, 12.7 mm O. D.) with Swagelok caps at the two ends. The tube was purged with nitrogen under a very low flow rate for about 2 minutes to keep the sample in an inert atmosphere. Ceramic wool was used to plug the open end of the glass tube, in order to reduce nitrogen escape while the top-end-cap was tightened to seal the samples in the N$_2$ atmosphere. A number of samples were placed in the muffle oven at 550°C for different specific aging times of the order of days.

Each sample was taken out and cooled after a different aging time, and the sample together with glass tube were weighed to calculate the weight loss during the aging period. Elemental analysis, SEM, TGA, DRIFT, $^{13}$C solid-state NMR, and solvent extraction were used to characterize the composition and structure of the fresh and aged deposits.
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Carbonaceous deposits, which originate from the vapour phase, form in cyclones and cyclone exit tubes in the bitumen fluid coking process leading to operating problems. Knowledge of the deposit formation mechanism and structure is considered essential to mitigate deposition. In this chapter, deposits collected from a laboratory fluid coker cyclone fouling unit are compared with industrial samples. Deposits are characterized using elemental analysis, scanning electronic microscopy with energy dispersive X-ray (SEM-EDAX), thermogravimetric analyses (TGA), X-ray fluorescence spectroscopy (XRF), Diffuse-reflectance Fourier Transform (DRIFT) spectrometer, and $^{13}$C solid-state Nuclear Magnetic Resonance ($^{13}$C NMR). Solvent extraction is also employed to investigate extraction of soluble deposit fractions, and the soluble portions are analyzed by GC simulated distillation.

4.1 The Elemental Analysis of Different Deposits

The fresh laboratory deposit samples were collected from different test positions in the bench fluid coker cyclone unit after running six hours in some representative experiments, whose operating conditions are given in Table 3-3. Industrial Samples B and D were provided by Syncrude Ltd., Canada. Sample B is collected from cyclone snout outlet, and Sample D from the gas outlet tube. Table 4-1 gives the elemental composition and H/C atomic ratio (analysed by Canadian Microanalytical Service Ltd.) of different laboratory deposits and industrial samples.

From Table 4-1, it can be seen that H/C ratio of the deposits in the reactor bottom are much higher than those in the upper reactor wall, and close to the H/C ratio of bitumen feed (H/C atomic ratio ~1.50). This is because perhaps there is some unreacted bitumen in the reactor bottom mixed with the coke formed after thermal reaction in the coker. The H/C ratio of the filter deposits from the reactor freeboard is much lower than those collected in the downstream long
### Table 4-1 Elemental Compositions and H/C Atomic Ratio of Different Deposits

<table>
<thead>
<tr>
<th>Deposits</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>S (wt%)</th>
<th>N (wt%)</th>
<th>C+H (wt%)</th>
<th>H/C atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor bottom Run B20</td>
<td>81.63</td>
<td>7.13</td>
<td>N/A</td>
<td>1.29</td>
<td>88.76</td>
<td>1.05</td>
</tr>
<tr>
<td>Reactor upper wall Run B15</td>
<td>89.24</td>
<td>1.56</td>
<td>N/A</td>
<td>2.19</td>
<td>90.80</td>
<td>0.21</td>
</tr>
<tr>
<td>Filter Run B18</td>
<td>83.88</td>
<td>2.73</td>
<td>N/A</td>
<td>1.74</td>
<td>86.61</td>
<td>0.38</td>
</tr>
<tr>
<td>Exit Tube Run B1</td>
<td>83.91</td>
<td>3.61</td>
<td>N/A</td>
<td>1.56</td>
<td>87.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Exit Tube Run B19</td>
<td>85.42</td>
<td>4.24</td>
<td>N/A</td>
<td>1.69</td>
<td>89.66</td>
<td>0.59</td>
</tr>
<tr>
<td>Exit Tube Run B20</td>
<td>85.54</td>
<td>4.05</td>
<td>6.44</td>
<td>N/A</td>
<td>89.59</td>
<td>0.57</td>
</tr>
<tr>
<td>Exit Tube Run B30</td>
<td>84.92</td>
<td>4.10</td>
<td>6.27</td>
<td>N/A</td>
<td>89.02</td>
<td>0.58</td>
</tr>
<tr>
<td>Exit Tube Run B40</td>
<td>84.89</td>
<td>3.80</td>
<td>N/A</td>
<td>N/A</td>
<td>88.69</td>
<td>0.54</td>
</tr>
<tr>
<td>Syncrude B</td>
<td>88.75</td>
<td>1.57</td>
<td>N/A</td>
<td>4.49</td>
<td>90.32</td>
<td>0.21</td>
</tr>
<tr>
<td>Syncrude D</td>
<td>87.85</td>
<td>1.18</td>
<td>N/A</td>
<td>1.34</td>
<td>89.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* N/A means the item was not analyzed.

test tube, and indicates more coke-like characteristics than in exit tube deposits. All four fresh laboratory exit tube deposits collected under cooling conditions have similar elemental composition: about 85% carbon, 4% hydrogen, 6% sulfur, and less than 2% nitrogen. The total contents of hydrogen and carbon are about 88–90%; and the H/C atomic ratio is about 0.54–0.58. An H/C atomic ratio between 0.35–0.70 is the typical of polyaromatic compounds [42], thus the elemental analysis of fresh exit tube deposits indicates a polyaromatic structure. However, the exit tube deposits of Run B1, which were collected under heating conditions ($T_w = 530^\circ C$), have a little lower H/C (~0.52) ratio than the others which were collected under cooling conditions. The industrial deposits have lower hydrogen and higher carbon contents compared with those from the laboratory unit, and a much lower H/C atomic ratio (0.16–0.21). This indicates different characteristics from laboratory exit tube deposits. Moreover, Sample B,
collected from the cyclone snout outlet, has a little higher H/C atomic ratio than that of Sample D from the gas outlet tube.

4.2 X-Ray Fluorescence Spectroscopy (XRF) Analysis of Deposit Samples

Table 4-2 is the semi-quantitative XRF analysis results of several laboratory deposits and industrial samples measured at Syncrude Research. All the deposits contain considerable amounts of sulfur, silicon and different metals, e.g., Ni, V, Al, Ti, Ca, etc., in which K, Zn, Pb, Mn, Mo, Cr, Cu, Zr are in trace amounts. Aluminum and silicon are possibly carried from the clays in the bitumen feed, and other metals perhaps come from the droplets in the vapour phase which were carried over from the bitumen feed, and then condensed on the tube wall to form the deposits. Evidence from previous experimental results [6] also indicated that the entrainment of fine droplets could contribute to deposit formation, although it was not the primary cause of deposits. Nickel and vanadium are present in the feed (Table 3-1) at a ratio of about 1:2.3, which compares with an average of 1:2.1 for the lab deposits. However, Table 4-2 shows that laboratory deposits have much higher Ni and V contents than the industrial samples. Iron contents in the industrial samples are high, possibly due to the material of construction of the coker unit.

4.3 The Morphology and the EDAX Analysis of the Deposits

The deposits collected in the long-tube test section and filter under different operation conditions were subject to SEM-EDAX analysis. The deposits from the long tube were carefully collected from the tube inner surface with a nylon brush. The EDAX analysis results are compared with those of bulk elemental analysis. Through the morphology and elemental composition of the deposits, the possible formation mechanisms could be inferred. The main operating conditions for the selected deposits are summarized in Table 4-3.
### Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

#### Table 4-2 Semi-quantitative X-Ray Fluorescence Spectroscopy (XRF) Analysis of Deposit Samples*

<table>
<thead>
<tr>
<th>Sample</th>
<th>S</th>
<th>Ni</th>
<th>V</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ti</th>
<th>Ca</th>
<th>K</th>
<th>Zn</th>
<th>Pb</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run B3</td>
<td>226000</td>
<td>2750</td>
<td>6490</td>
<td>4730</td>
<td>2410</td>
<td>6290</td>
<td>1800</td>
<td>2460</td>
<td>810</td>
<td>710</td>
<td>780</td>
<td>/</td>
<td>/</td>
<td>47</td>
<td>/</td>
<td>430</td>
</tr>
<tr>
<td>Run B19</td>
<td>231000</td>
<td>3570</td>
<td>7590</td>
<td>1000</td>
<td>850</td>
<td>2050</td>
<td>360</td>
<td>690</td>
<td>/</td>
<td>310</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Run B21</td>
<td>202000</td>
<td>3140</td>
<td>5660</td>
<td>1350</td>
<td>1920</td>
<td>4030</td>
<td>1010</td>
<td>1150</td>
<td>/</td>
<td>560</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Run B36</td>
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<td>3150</td>
<td>7680</td>
<td>420</td>
<td>170</td>
<td>1380</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>570</td>
<td>800</td>
<td>/</td>
<td>/</td>
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<tr>
<td>Run B41</td>
<td>235000</td>
<td>4420</td>
<td>8360</td>
<td>2640</td>
<td>1520</td>
<td>5130</td>
<td>490</td>
<td>1120</td>
<td>630</td>
<td>830</td>
<td>730</td>
<td>/</td>
<td>/</td>
<td>58</td>
<td>220</td>
<td>/</td>
</tr>
<tr>
<td>Sample B</td>
<td>221000</td>
<td>1650</td>
<td>3390</td>
<td>3330</td>
<td>1440</td>
<td>17200</td>
<td>1070</td>
<td>340</td>
<td>590</td>
<td>/</td>
<td>1250</td>
<td>420</td>
<td>/</td>
<td>140</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Sample D</td>
<td>213000</td>
<td>2940</td>
<td>4970</td>
<td>4330</td>
<td>2090</td>
<td>61200</td>
<td>3140</td>
<td>1650</td>
<td>630</td>
<td>/</td>
<td>/</td>
<td>1190</td>
<td>1060</td>
<td>160</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

* Provided by Syncrude Research

** / means that the element was not detected.
Table 4-3 The Main Operation Conditions of the Deposits Collected for SEM-EDAX

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reactor (°C)</th>
<th>Cyclone (°C)</th>
<th>$T_v$ (°C)</th>
<th>$T_w$ (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B9</td>
<td>535</td>
<td>521</td>
<td>506</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td>B19</td>
<td>535</td>
<td>519</td>
<td>448</td>
<td>428</td>
<td></td>
</tr>
<tr>
<td>B20</td>
<td>535</td>
<td>517</td>
<td>473</td>
<td>443</td>
<td>$T_w&lt;500°C$</td>
</tr>
<tr>
<td>B40</td>
<td>535</td>
<td>520</td>
<td>458</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>B25</td>
<td>535</td>
<td>515</td>
<td>512</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>B30</td>
<td>535</td>
<td>523</td>
<td>520</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>B11</td>
<td>535</td>
<td>524</td>
<td>619</td>
<td>618</td>
<td>$T_w&gt;500°C$</td>
</tr>
<tr>
<td>B12</td>
<td>535</td>
<td>531</td>
<td>600</td>
<td>608</td>
<td></td>
</tr>
<tr>
<td>B16</td>
<td>535</td>
<td>518</td>
<td>579</td>
<td>603</td>
<td></td>
</tr>
<tr>
<td>B17</td>
<td>535</td>
<td>522</td>
<td>645</td>
<td>633</td>
<td></td>
</tr>
</tbody>
</table>

*T_v* is the vapour temperature in long tube; *$T_w$* is the temperature of long tube wall

4.3.1 Deposit Formed in the Long Tube at Lower Temperature Conditions

Fig. 4-1 ~ 4-4 show scanning electron micrographs (SEM) of the deposits (Run B9, B19, B20 and B40) collected from the long test tube under lower temperature conditions (*$T_w<500°C$*). All deposits of Fig. 4-1 ~ 4-4 consist of the mixtures of amorphous portions and platelet portions of sizes mostly about 1mm to 50 μm, although much smaller platelets are also visible in some cases. However, the amorphous structure appears predominant in all the four deposit samples, especially for Run B19, B20 and B40, which were collected at much lower tube wall temperatures (<450°C).
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-1 SEM of the Deposits in Exit Tube (Run B9, $T_{\text{wall}} = 460^\circ\text{C}$)

Fig. 4-2 SEM of the Deposits in Exit Tube (Run B19, $T_{\text{wall}} = 428^\circ\text{C}$)
Fig. 4-3 SEM of the Deposits in Exit Tube (Run B20, T_{wall} = 443°C)

Fig. 4-4 SEM of the Deposits in Exit Tube (Run B40, T_{wall} = 425°C)
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-5 and 4-6 are enlarged micrographs of the amorphous deposits in Run B9 and B19. The micrographs of amorphous deposits with large magnification for other runs are similar, and are given in the Appendix 3. In the micrograph, spherical and near spherical aggregates, either existing in individual form or connected together through protuberances, are observed, suggesting the possible contribution of physical condensation. In condensation, a spherical droplet is formed because the spherical features are more stable than other kinds of shapes.

Based on the studies of Graff and Albright [34] for the coke deposition from acetylene, butadiene and benzene decomposition at 500~900°C, the morphology of formed deposits depends on several factors, i.e., the viscosity of the droplets, the wettability between liquid droplets and solid surface, the velocity of the gas stream near the droplet, and the rate of chemical reactions (e.g., cracking and dehydrogenation, etc.) in the liquid droplet or tar on the surface. The viscosity of the liquid droplets depends on the temperature and the chemical composition of the liquid. At lower temperature, the liquid droplets tend to be more viscous. The wettability depends on the composition of liquid droplets, and the material and roughness of the solid surface. For example, a stainless steel surface has a higher wettability for the hydrocarbon liquid droplets than a glass tube wall. Rapid chemical reactions in the droplets can also readily change the deposit morphology. Graff and Albright [34] argued that with the high velocity in industrial units there is a greater tendency for spreading of the droplets than in lab tests. This is believed to apply to the present case where the velocity in the industrial cyclone exit tube is \( \sim 40.6 \text{ m/s} \) compared to \( \sim 6.9 \text{ m/s} \) in the laboratory unit.

In the present laboratory case, the liquid droplets would tend to be more viscous at lower temperatures (<500°C), and would not easily spread at the low vapour velocity in the laboratory unit. Both factors favor the condensed tar droplets to keep their original shape. Therefore, the
spherical amorphous structures are observed to be predominant in the deposits at lower operating temperature conditions.

Fig. 4-5 SEM of the Amorphous Deposits in Exit Tube (Run B19, $T_{\text{wall}} = 428^\circ\text{C}$)

Fig. 4-6 SEM of the Amorphous Deposits in Exit Tube (Run B9. $T_{\text{wall}} = 460^\circ\text{C}$)
Fig. 4-7 and 4-8 are magnified micrographs of the platelet surface of Run B9 at different magnifications; similar structures of other runs are also shown in Appendix 3. There are many boulder-like droplets attached on the plate surface, although a small amount of amorphous deposit can also be noticed. This kind of deposit might form as follows. There can be a small part of tube surface area at a higher temperature because of uneven heat transfer characteristics. The droplets which first condense on these high temperature tube wall surfaces will have a low viscosity and a tendency to spread on the stainless tube wall, producing platelet structures. After the inner layer platelet deposits are formed, other droplets would condense on the platelet surfaces, which have a lower temperature compared with the inner layer. These viscous fluid droplets, with a high viscosity on the lower temperatures surface of the platelet deposit, are then shaped to boulder-like features by flowing gas above it before it solidifies.

![Fig. 4-7 SEM of the Platelet Deposits (Run B9, T_{wall} = 460°C)](image-url)
Fig. 4-8 Magnified SEM of the Platelet Deposits (Run B9, \( T_{\text{wall}} = 460^\circ\text{C} \))

However, the presence of droplet or spherical particles in the deposit cannot be exclusively attributed to physical condensation, because tar droplets could also be formed by chemical reactions [123]. Other experimental evidence in our previous work [5-7] such as vapour temperature and vapour velocity/residence time effects, do not support a major role of chemical reaction in deposit formation.

4.3.2 Deposit Formed in the Long Tube at Higher Temperature Conditions

Fig. 4-9 ~ 4-14 are SEM pictures of deposits in exit tube collected from different runs at high temperature operating conditions (\( T_{\text{w}} > 500^\circ\text{C} \)). From these pictures, it can be seen that, especially for those collected at temperatures above 600°C, there are much more platelet structures compared with those collected at lower temperature conditions. At high temperature conditions, the condensed tar droplets are less viscous and are more readily spread on the stainless tube wall surface even at low fluid velocity, and thus cause platelet deposits to be predominant.
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Fig. 4-9 SEM of the deposits in exit tube (Run B11, $T_w = 618^\circ C$)

Fig. 4-10 SEM of the Deposits in Exit Tube (Run B12, $T_w = 608^\circ C$)
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-11 SEM of the Deposits in Exit Tube (Run B16, $T_w = 603^\circ$C)

Figure 4-12 SEM of the Deposits in Exit Tube (Run B17, $T_w = 633^\circ$C)
Fig. 4-13 SEM of the Deposits in Exit Tube (Run B25, $T_w = 500^\circ C$)

Fig. 4-14 SEM of the Deposits in Exit Tube (Run B30, $T_w = 500^\circ C$)
Figure 4-15 ~ 4-17 are magnified SEM pictures of the platelet deposits, and Figure 4-18~4-20 amorphous ones from runs with wall temperature of over 600°C. Other similar pictures were collected from different runs but are shown in Appendix 4. Just as in low temperature operation conditions, there are many boulder-like droplets attached on the plate surface for the platelet deposits, and there are many different sized small spheres in the amorphous deposits. The formation mechanisms of plate-like and amorphous deposits are the same as those under lower temperature conditions. The only difference is that there is more high temperature tube surface available in the higher temperature conditions, which leads to more platelet deposit formation. Both kinds of morphology are consistent with physical condensation as main reason for the test tube fouling, however, chemical reactions may follow in long aging periods.

Fig. 4-15 SEM of the Platelet Deposits in Exit Tube (Run B12, \( T_w = 608°C \))
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-16 SEM of the Platelet Deposits in Exit Tube (Run B12, $T_w = 608^\circ$C)

Fig. 4-17 SEM of the Platelet Deposits in Exit Tube (Run B16, $T_w = 603^\circ$C)
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-18 SEM of the Amorphous Deposits in Exit Tube (Run B16, $T_w = 603^\circ$C)

Fig. 4-19 SEM of the Amorphous Deposits in Exit Tube (Run B17, $T_w = 633^\circ$C)
Table 4-4 gives the typical elemental composition of the deposit by EDAX measurement which represents different shape and different condition deposits. EDAX values for carbon, oxygen and sulfur which are point or area values in the deposits. Note that in EDAX hydrogen is not detected, and oxygen can be of either organic or inorganic form. Values smaller than 1% are subject to considerable error.

From Table 4-4, only carbon, oxygen and sulfur were detected for most deposits, although occasionally aluminum, silicon and metals were found. Compared with Table 4-1, the carbon content are ca. 4% higher than bulk analysis results in some selected points or areas. This is because there is about 4% hydrogen in the deposits which cannot be detected by EDAX, and accuracy of EDAX is not as good as bulk chemical analysis. EDAX is not as sensitive as XRF, thus much fewer metals were detected than those of XRF (Table 4-2). As discussed in Section 4.2, aluminum and silicon are possibly carried from the clays in the feedstocks or the ceramic filters wrapped around the expanded freeboard in front of the cyclone, and the metals are
believed to be carried from the bitumen feed. Together with the droplet, they condense or transport from the bulk and then condensed on the cooler wall to form the deposits.

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Run B9</th>
<th>Run B20</th>
<th>Run B30</th>
<th>Run B16</th>
<th>Run B11</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>89.96</td>
<td>85.42</td>
<td>89.58</td>
<td>90.05</td>
<td>80.66</td>
</tr>
<tr>
<td>O</td>
<td>5.41</td>
<td>0.21</td>
<td>5.21</td>
<td>5.16</td>
<td>4.23</td>
</tr>
<tr>
<td>S</td>
<td>4.63</td>
<td>5.24</td>
<td>4.67</td>
<td>4.12</td>
<td>6.10</td>
</tr>
<tr>
<td>Al</td>
<td>/</td>
<td>0.03</td>
<td>0.21</td>
<td>/</td>
<td>0.11</td>
</tr>
<tr>
<td>Si</td>
<td>/</td>
<td>/</td>
<td>0.33</td>
<td>/</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe</td>
<td>/</td>
<td>4.02</td>
<td>/</td>
<td>0.67</td>
<td>7.39</td>
</tr>
<tr>
<td>Ni</td>
<td>/</td>
<td>0.69</td>
<td>/</td>
<td>/</td>
<td>1.42</td>
</tr>
<tr>
<td>C+O+S</td>
<td>100</td>
<td>90.87</td>
<td>99.46</td>
<td>99.33</td>
<td>90.99</td>
</tr>
<tr>
<td>S/C (g/g)</td>
<td>0.052</td>
<td>0.061</td>
<td>0.052</td>
<td>0.046</td>
<td>0.075</td>
</tr>
</tbody>
</table>

* / means that the element was not detected.

4.3.3 Deposit Formed in the Filter

Fig. 4-21 and 4-22 give the SEM of the deposits in the reactor freeboard filter, and Figure 4-23, 4-24 show the magnified micrograph. The morphology of this kind of deposits is much simpler compared with those formed in the long test tube, and all the deposits are honeycomb structure or loose-plate shape. The fiber in Fig. 4-22 comes from the filter. The density of deposits is much lower than those in the long tube.

Many broken hollow spheres which are embedded in the honeycomb or loose-plate structures were observed (Fig. 4-23 and 4-24). These hollow spheres (cenospheres) are believed to be carried from the coking reactor, because cenospheres are typical morphology of the deposits.
formed in the coking reactor, as an example shown in Fig 4-25. The formation mechanism of cenospheres is well known from the combustion literature for heavy fuel oils [124-126]. In present case, cenospheres could form as follows. When the bitumen is injected into the fluid coker through the atomization nozzle, the temperature increase that is due to heating from surroundings leads to cracking reactions and possibly local formation of a more viscous or solid film on the surface of the droplets. The viscous or solid film is permeable to volatiles, which continue to evaporate from the droplet, eventually leaving a remaining hollow sphere. The so-formed structure cenosphere, ranges in size between 1~100 μm according to the literature [124-126]. The cenospheres carried from the reactor together with possibly the liquid droplets carried from the feed, whose diameter is bigger than the filter pore, deposit on the filter, which exhibits a honeycomb or loose-plate structures.

Fig. 4-21 SEM of the Deposits in Filter (Run B9)
Fig. 4-22 SEM of the Deposits in Filter (Run B16)

Fig. 4-23 Magnified SEM of the Deposits in Filter (Run B9)
Fig. 4-24 Magnified SEM of the Deposits in Filter (Run B16)

Fig. 4-25 Typical SEM of the Deposits in the Coking Reactor (Run B9)
**Table 4-5 EDAX Measurement of Deposits Collected from the Filter**

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Run B9</th>
<th>Run B9</th>
<th>Run B16</th>
<th>Run B16</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>89.69</td>
<td>86.99</td>
<td>87.54</td>
<td>83.94</td>
</tr>
<tr>
<td>O</td>
<td>3.73</td>
<td>2.29</td>
<td>1.69</td>
<td>9.03</td>
</tr>
<tr>
<td>S</td>
<td>6.06</td>
<td>9.86</td>
<td>9.90</td>
<td>5.27</td>
</tr>
<tr>
<td>Al</td>
<td>0.23</td>
<td>0.07</td>
<td>0.07</td>
<td>0.15</td>
</tr>
<tr>
<td>Si</td>
<td>0.30</td>
<td>0.19</td>
<td>0.20</td>
<td>1.61</td>
</tr>
<tr>
<td>Ca</td>
<td>/</td>
<td>0.23</td>
<td>0.23</td>
<td>/</td>
</tr>
<tr>
<td>V</td>
<td>/</td>
<td>0.36</td>
<td>0.37</td>
<td>/</td>
</tr>
<tr>
<td>S/C (g/g)</td>
<td>0.068</td>
<td>0.113</td>
<td>0.113</td>
<td>0.062</td>
</tr>
</tbody>
</table>

* / means that the element was not detected.

Table 4-5 gives the EDAX measurement results for typical deposits on the filter; and the deposits are mainly composed of carbon, oxygen and sulfur. Moszkowicz et al. [126] reported that there are approximately 90% carbon, 5-6% sulfur, 3-4% hydrogen, and minor concentration metals (up to 0.1%) in the cenosphere formed in the process of pyrolysis of heavy oil droplets. These are consistent with this investigation.

### 4.3.4 Deposits from Syncrude Industrial Unit

Two different Syncrude industrial samples were available for morphological eximantion, Sample B from cyclone snout outlet and Sample D from gas outlet tube. Based on direct visual examination, an obvious difference exists between the fresh laboratory and industrial deposits (as shown in Fig. 4-26): the fresh laboratory deposits looks like black tiny powder or flakes; whereas the industrial samples like a black bulk stone, without any loose powder or flakes. The density of Sample B is 1.35 g/ml, and Sample D is 1.70 g/ml. However, the packed densities of laboratory deposits are much smaller than those of industrial samples, between 0.50-0.70 g/ml.
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-26 Picture of Industrial and Laboratory Deposits

The SEM of industrial Sample B and D are given in Fig. 4-27 and 4-28. There is not much difference in the morphology of the two samples: both of them are like bulk stone, and were very different to break. Platelet or amorphous deposits are not found in the industrial samples. The reason for this is perhaps as suggested in [34], that the condensed tar droplets are readily spread on the wall under the shear force of the high vapour velocity characteristic of industrial conditions. As well, months or years of aging of the industrial deposits at high temperatures and in the presence of hydrocarbons contribute to the stone-like structure of industrial deposits. Table 4-6 gives the EDAX results of Samples B and D. Experimental results indicated that both are mainly composed of carbon, oxygen and sulfur, just like laboratory samples. However, Sample D has a higher carbon content than Sample B, and this is consistent with previous bulk elemental analysis results.
Fig. 4-27 SEM of Syncrude Industrial Deposits B (Cyclone Snout Outlet)

Fig. 4-28 SEM of Syncrude Industrial Deposits D (Gas Outlet Tube)
Table 4-6 EDAX Measurement of Industrial Deposits

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Syncrude Sample B</th>
<th>Syncrude Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>84.84</td>
<td>90.53</td>
</tr>
<tr>
<td>O</td>
<td>11.35</td>
<td>5.55</td>
</tr>
<tr>
<td>S</td>
<td>4.00</td>
<td>3.68</td>
</tr>
<tr>
<td>Al</td>
<td>0.05</td>
<td>0.12</td>
</tr>
<tr>
<td>Si</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>C+O+S</td>
<td>99.89</td>
<td>99.77</td>
</tr>
<tr>
<td>S/C (g/g)</td>
<td>0.047</td>
<td>0.041</td>
</tr>
</tbody>
</table>

4.4 Thermogravimetric Analysis of Different Deposits

As described in Chapter 3, TGA experiments were carried out with a TGA-50 thermogravimetric analyzer (Shimadzu, Japan) on 5~15 mg samples under nitrogen with a flow rate 50 ml/min, within the temperature range of ambient to 1000°C and a heating rate of 10°C/min. In the analysis of TGA curve, the weight loss below ca. 150°C is attributed to removal of the absorbed water (moisture) [64]. In all the experiments, the weight loss at any given temperature or time can be expressed as:

\[
\text{Weight loss} = \frac{W_0 - W_t}{W_0} \times 100\% \quad (4-1)
\]

Where \( W_t \) is the sample weight at any given temperature or time; \( W_0 \) is the sample initial weight.
4.4.1 Comparison of TGA Results Between Filter and Long Exit Tube Deposits

The TGA results of deposits from the filter and long test tube (Run B9) are given in Fig. 4-29. Data for moisture, the weight loss at different temperatures, i.e., 550°C, 750°C and 1000°C, is given in Table 4-7. Both deposits have little moisture (0.1~0.2%). There are much more volatiles in the deposits from the exit tube than those from the filter, especially at lower temperatures. For example, there are 8.92 wt% volatile components for the exit tube deposits from ambient to 550°C, whereas only 1.66 wt% in filter deposits. These indicate that the filter deposits are more coke-like. Cracking reactions must take place during the period from ambient to 1000°C in the deposits. The cracked products released with the nitrogen flow and caused the weight loss. Thermal characteristic difference between the deposits from filter and exit tube also indicates that their formation mechanisms may be different.

Fig. 4-29 TGA Results of Deposits from Long Exit Tube and Filter (Run B9)
(heating rate 10°C/min; N₂ atmosphere)
Table 4-7 Comparison of TGA Results of Deposits Collected
from Filter and Exit Tube (Run B9)

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Moisture</th>
<th>150–550°C</th>
<th>550–750°C</th>
<th>750–1000°C</th>
<th>150–1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td></td>
<td>(wt%)</td>
<td>(wt%)</td>
<td>(wt%)</td>
<td>(wt%)</td>
</tr>
<tr>
<td>Filter</td>
<td>0.20</td>
<td>1.66</td>
<td>4.33</td>
<td>5.89</td>
<td>11.88</td>
</tr>
<tr>
<td>Exit Tube</td>
<td>0.12</td>
<td>8.92</td>
<td>7.47</td>
<td>1.68</td>
<td>18.07</td>
</tr>
</tbody>
</table>

4.4.2 Comparison of the Deposits from Different Operation Conditions

The TGA results of deposits collected from cooling and heating operation conditions are given in Fig. 4-30 and 4-31, respectively. The TGA results of industrial samples at the same instrument conditions are shown in Fig. 4-32. The comparison of moisture, the weight loss at different temperatures, i.e., 550°C, 750°C and 1000°C, of different deposits is listed in Table 4-8.

![Fig. 4-30 Thermal Analysis Results of Deposits at Cooling Conditions](image)

(heating rate 10°C/min; N₂ atmosphere)
Fig. 4-31 Thermal Analysis Results of Deposits at Heating Conditions
(heating rate 10°C/min; N₂ atmosphere)

Fig. 4-32 TGA Results of Industrial Deposits
(heating rate 10°C/min; N₂ atmosphere)
For the fresh laboratory deposits from the exit tube, about 10–30% are volatile components up to 1000°C. No correlation between weight loss at different temperatures and exit tube wall temperature is found. Average weight loss values between the temperature of 150–550°C, 550–750°C, 750–1000°C and total weight loss are 10.09±7.74%, 5.40±2.09%, 3.92±0.85% and 19.40±6.79%, respectively. Excluding Run B16, which gave an inordinately high value, the corresponding averaged weight loss of long tube samples are 8.14±4.96%, 5.45±2.25%, 4.24±0.91% and 17.85±4.90%, respectively. Most volatile components in laboratory deposits are released below 750°C. The industrial samples have much less volatile components at all temperatures than the fresh laboratory deposits, and most volatiles are released at higher temperatures of 750–1000°C. This is perhaps because industrial samples have much longer aging time in the plant, which leads to more polyaromatic or graphitic structures in the deposits, and thus less volatile components. However, the TGA curve for Run B11 (Fig. 4-32), which had a high tube wall temperature of 618°C (and hence little deposit collected), was similar to industrial samples, with lower volatiles at all temperatures compared with other fresh laboratory deposits.

Table 4-8 also illustrates the reproducibility of the TGA experiments, where for the industrial deposits duplicate experimental weight loss values at each temperature agree with 97.3%.
### Table 4-8 The Moisture and The Weight Loss for The Deposits in Different Operation Conditions

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Moisture (wt%)</th>
<th>Weight loss (wt%)</th>
<th>T(_{\text{wall}}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>150~550°C</td>
<td>550~750°C</td>
</tr>
<tr>
<td>Run B9</td>
<td>0.12</td>
<td>8.92</td>
<td>7.47</td>
</tr>
<tr>
<td>Run B19</td>
<td>0.12</td>
<td>2.81</td>
<td>6.44</td>
</tr>
<tr>
<td>Run B20</td>
<td>0.72</td>
<td>7.66</td>
<td>6.96</td>
</tr>
<tr>
<td>Run B40</td>
<td>0.04</td>
<td>5.16</td>
<td>6.56</td>
</tr>
<tr>
<td>Run B25*</td>
<td>0.15</td>
<td>16.13</td>
<td>4.91</td>
</tr>
<tr>
<td>Lab Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run B30</td>
<td>0.20</td>
<td>10.47</td>
<td>5.62</td>
</tr>
<tr>
<td>Run B16</td>
<td>0.10</td>
<td>25.64</td>
<td>4.87</td>
</tr>
<tr>
<td>Run B11</td>
<td>0.71</td>
<td>2.68</td>
<td>0.85</td>
</tr>
<tr>
<td>Run B17</td>
<td>0.77</td>
<td>11.33</td>
<td>4.88</td>
</tr>
<tr>
<td>Average</td>
<td>0.33</td>
<td>10.09±7.74</td>
<td>5.40±2.09</td>
</tr>
<tr>
<td>Average**</td>
<td>0.35</td>
<td>8.14±4.96</td>
<td>5.46±2.25</td>
</tr>
<tr>
<td>Industrial Sample B</td>
<td>0.34</td>
<td>0.86</td>
<td>0.32</td>
</tr>
<tr>
<td>Industrial Sample</td>
<td>0.32</td>
<td>0.86</td>
<td>0.33</td>
</tr>
<tr>
<td>Sample D</td>
<td>0.84</td>
<td>0.58</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>0.60</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* With second steam addition; **Average without Run B16
4.5 DRIFTS Analysis of the Deposits

4.5.1 Comparison of DRIFTS between Deposits from Filter and Long Tube

Fig. 4-33 is the DRIFT spectra of the deposits collected from filter and long exit tube (Run B9). For both deposits, the detected bands all occur in two main frequency regions: 2800-3000 and 1300-1500 cm\(^{-1}\), and an intense band at ca. 1595–1560 cm\(^{-1}\) can also be distinguished. This observation is consistent with the literature related to coke deposition on catalysts [55-64, 127].

![DRIFT Spectra Comparison of Deposits in the Filter and Exit Tube (Run B9)](image)

In the range of the C-H stretching vibrations in alkanes (2800-3000 cm\(^{-1}\)), the bands occurring at 2862, 2917, and 2962 cm\(^{-1}\) are assigned to the symmetric vibrations of CH\(_2\) and CH\(_3\), the asymmetric vibration of CH\(_2\), and the asymmetric vibration of CH\(_3\), respectively [64,128]. The region 2800-3000 cm\(^{-1}\) is also called the paraffinic band [64]. The 3050 cm\(^{-1}\) band is probably due to the C-H stretching vibration in aromatics (or in polyalkenes) [128]. In the range of C-H bending vibrations (1300-1500 cm\(^{-1}\)) in paraffinic or olefinic compounds, the band at 1442 cm\(^{-1}\) originates from the asymmetric bend vibrations of aliphatic groups attached to aromatic rings, which usually replace the in-plane bending vibration of CH\(_2\) at ~1465 cm\(^{-1}\) when
aromatics are formed [64, 129], and ~1378 cm\(^{-1}\) are due to symmetric bending vibration of CH\(_3\);
~1324 cm\(^{-1}\) is an unknown absorption. The ~1600 cm\(^{-1}\) band is known as the coke band. It is
attributed to the stretching vibration of C=C in microcrystalline graphitic structures, which are
present in polycyclic aromatic compounds and might also constitute the carbonaceous deposits
[54-64, 128]. The absorption pattern in the fingerprint region, 1300~700 cm\(^{-1}\), is frequently
complex with bands originating in interacting vibration modes and is usually very difficult to
interpret. Absorptions at ~753 cm\(^{-1}\), ~811 cm\(^{-1}\) and ~866 cm\(^{-1}\) are all possibly due to the in-phase
out-of-plane wagging vibrations of hydrogen at different circumstances in substituted aromatic
rings [128,129]. The frequency of 866 cm\(^{-1}\) is possibly caused by C-H out-of-plane wagging
vibration of isolated hydrogen. The absorptions at the frequency of 811 cm\(^{-1}\) and 753 cm\(^{-1}\) are
possibly caused by C-H out-of-plane wagging vibrations of 2 and 4 adjacent hydrogenation
atoms, respectively [128, 129]. The absorption frequencies of typical carbonaceous deposits
described above are summarized in Table 4-9 as follows.

<table>
<thead>
<tr>
<th>Paraffinic bands (v(_{\text{C-H}}))</th>
<th>Coke Band (v(_{\text{C-C}}))</th>
<th>(\delta\text{C-H bands})</th>
<th>Fingerprint region ((\omega\text{C-H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3050 ~2962 ~2917 ~2862 ~1600 ~1442 ~1378 ~1324 ~751, 811, 866</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

v: stretching vibration; \(\delta\): bending vibration; \(\omega\): wagging vibration

From the spectra of Fig. 4-33, both deposits from the exit tube and the filter indicate a
typical coke band, but coke band of the filter deposits is in a lower wavenumber at ~1595 cm\(^{-1}\).
The coke band shift to a lower frequency indicates that there are more aromatic rings in the filter
deposits [64, 127]. As well, the stretching vibration of C-H in aromatics 3050 cm\(^{-1}\) band can be
noted for both. The strong paraffinic bands 2800-3000 cm\(^{-1}\) can be noticed for the exit tube
sample, however, the deposits in the filter only show very weak bands in this region.
Furthermore, C-H bending vibrations (1300-1500 cm\(^{-1}\)) of paraffinic or olefinic compounds for long tube deposits are much stronger than those in deposits from filter. Therefore, the DRIFT experimental results suggest that the deposits from the filter have more polyaromatic structures than those from the exit tube. This is consistent with the TGA results, which indicated that there are much more volatile components in the deposits formed in the exit tube, and H/C ratios.

4.5.2 Comparison of DRIFTs for Deposits in Different Operation Conditions

The typical DRIFT spectra of the deposits collected from exit tube under cooling (Run B19 and B25) and heating conditions (Run B12, B16, B17) are given in Fig. 4-34 and 4-35, respectively. The spectra of the deposits collected from cooling conditions are all similar with that of Run B9 as explained above, thus only Run B19 and B25 are given here, and the others (Run B20, B30, B40) are given in Chapter 5. It can be observed that the DRIFT spectra of deposits collected under both heating and cooling conditions show a very strong typical coke band at about 1600 cm\(^{-1}\), and a strong \(\nu_{\text{C-H}}\) in aromatics band at 3050 cm\(^{-1}\). However, there are some differences in the region of C-H bending bands (1000-1500 cm\(^{-1}\)) as shown in Fig. 4-35. In the spectra of deposits at heating conditions, the absorption at \(-1378\) cm\(^{-1}\), which is due to symmetric bending vibration of \(\text{CH}_3\), disappears for all deposits. This indicates that the deposits collected at heating conditions have less paraffinics. As well, the DRIFT spectra of Run B12 (\(T_w = 608^\circ\text{C}\)) indicates significantly weaker absorptions in paraffinic band region at the frequency between 2800-3000 cm\(^{-1}\) compared with those at cooling conditions.

The spectra of the deposits from high temperature Run B11 (\(T_w = 618^\circ\text{C}\)) show very different characteristics than those of other deposits, but close to those of industrial samples (Syncrude Sample B and D) and pure graphite (Aldrich, 99.999%) as given in Fig. 4-36, where small peaks at frequency 3500-4000 cm\(^{-1}\) are caused by moisture, and those at \(-2400\) cm\(^{-1}\) by CO2 impurities in the spectrometer. The DRIFT spectrum of graphite is almost featureless;
similar DRIFT or IR spectra of graphite had been obtained previously by Ianniello et al. [63] and Cannon [130]. The deposits of Run B11 show similar infrared characteristics with graphite. DRIFT spectra of industrial Sample B and D also exhibit similar characteristics to graphite, except there are non-obvious bumps at the frequency of \( \approx 1587 \text{ cm}^{-1} \), and \( \approx 3050 \text{ cm}^{-1} \). The absorption at 1857 cm\(^{-1}\) is the coke band [64], but shifted to a lower wave number compared with the fresh deposits. The industrial deposits have more polyaromatic characteristics, and the conjugative effects of polyaromatic compound because of the delocalization of the \( \pi \) bands cause the wave number shift to a lower number [128, 129]. It also can be noted that coke band at \( \approx 1587 \text{ cm}^{-1} \) of Sample B is a little stronger than Sample D, which indicated that Sample D has more graphitic characteristics.

Generally it can be stated that in terms of DRIFT spectra, laboratory deposits from higher temperature runs contain less aliphatic structures, and indicate more coke-like structures. The laboratory deposits are much different than industrial samples, and the latter indicate a typical graphitic structure. However, when the temperature is raised, the laboratory deposits appear more like those of the industrial units.

![Fig. 4-34 DRIFTs Comparison of The Deposits under Cooling Conditions](image-url)
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-35 Comparison of Deposit DRIFTs under Heating Conditions

Fig. 4-36 Comparison of DRIFTs of Industrial, High Temperature Deposits and Graphite
4.5.3 Comparison of DRIFTs for Fresh Deposits, Bitumen Feed and Asphaltene

To better elucidate the cause of deposition in fluid coker cyclone exit lines, FTIR spectra (in absorbance) of the bitumen feeds to the coker and DRIFT spectra of asphaltene, the heavy species present at 15% in the bitumen, were plotted, and compared with that of fresh laboratory deposits (see Fig. 4-37).

![DRIFT spectra comparison](image)

**Fig. 4-37 DRIFTs Comparison of Fresh Lab Deposit, Bitumen and Asphaltene**

From Fig. 4-37, some similarities can be noticed for the DRIFT spectra of bitumen, asphaltene and deposits: all of them have the absorption in paraffinic bands (2800~3000cm⁻¹), very strong in both bitumen and asphaltene, but the bitumen seems even much stronger; and all of them have νC-H in aromatics at 3050cm⁻¹, although they are overlapped by strong paraffinic
bands in bitumen and asphaltene; bands at \( \sim 1600\text{cm}^{-1} \) exist in all three samples, but the peaks in both bitumen and asphaltene are much weaker compared with that in deposits. In the C-H bending vibration region (1300–1500\text{cm}^{-1}), both the bitumen and asphaltene have absorption at the frequency of \( \sim 1460 \) and 1375 \text{cm}^{-1}, which are due to the asymmetrical and symmetrical bending vibration of C-H in \(-\text{CH}_3\), respectively; 1453\text{cm}^{-1} in bitumen is due to the symmetrical bending vibration of C-H in \(-\text{CH}_2\). However, only the absorption at 1375 \text{cm}^{-1} shows up in the deposits, and \( \sim 1442\text{cm}^{-1} \) peak, which originates from the asymmetric bend vibration of aliphatic groups attached to aromatic rings, replaces the bands at \( \sim 1460 \text{cm}^{-1} \) because aromatics are formed in deposits. Similarities also exist in the fingerprint region, although the absorption is weak for both bitumen and asphaltene. A weak absorption at \( \sim 727\text{cm}^{-1} \) can be observed for both bitumen and asphaltene, which is caused by the wagging vibration of C-H when there is over four \(-\text{CH}_2-\) group in the aliphatic chains, and it is an evidence for the existence of long aliphatic chains [128]. Nevertheless, there is no absorption for the deposits at the frequency of 727 \text{cm}^{-1}.

In general, it can be concluded from the DRIFT results that the bitumen and asphaltene indicate a more aliphatic characteristic than the laboratory deposits. The similarities of the DRIFT spectra for bitumen, asphaltene and fresh laboratory deposits are consistent with prior TGA and other results which suggest physical condensation rather than chemical reaction as the mechanism for the cyclone exit line fouling. If deposit formation arose from chemical reactions in the vapour, one would expect significant differences in the DRIFT results for the deposits.

### 4.6 Solid-state $^{13}$C NMR Analysis of Carbonaceous Deposits

As described at Section 3.4.7 in Chapter 3, $^{13}$C solid-state NMR spectra were collected using a 9.4 T Bruker spectrometer in the Department of Chemistry (UBC), and operated in the Fourier transform mode. Single pulse excitement (SPE) was used to obtain quantitative data. Adamantane was used as external reference for the chemical shift (\( \delta \)).
There is no overlap between the main peaks and the spinning side bands (ssb) in the $^{13}$C chemical shift region under our experimental conditions. Small spinning side bands (ssb) are often seen in a NMR spectrum [128], symmetrically disposed on both side of a strong absorption peak; these results from inhomogeneities in the magnetic field and in the spinning sample tube. They are readily recognized because of their symmetrical appearance and because their separation from absorption peak is equal to the rate of spinning. Paramagnetic species interact with the nuclei around them (e.g., $^{13}$C) by spin-spin interaction, causing a dramatic decrease in their transverse relaxation time, and results in extreme broadening of corresponding resonance lines, making them invisible to NMR. A simple paramagnetic compound, containing magnetic $^{13}$C, which may be present in the coke is graphite. Experimental results have verified that there is no signal detected by $^{13}$C NMR under our instrumental conditions for pure graphite (99.999%, Aldrich) under our experimental conditions. For pure graphite, the fact that there is absolutely no signal detected by $^{13}$C NMR has also been reported by Fonseca et al. [66-68].

The quantitative $^{13}$C NMR spectra of fresh Run B40, and industrial Samples B and D are given in Fig. 4-38 ~ 4-40, respectively. It can be observed that NMR spectra of fresh Run B40 exhibit a broad peak in the chemical shift range 110~200 ppm centered at 129 ppm, and an additional peak with relatively weak intensities in the 5~60 ppm region centered at the chemical shift 15ppm. They correspond to the resonances of aromatics and aliphatics, respectively [64-76, 131]. The broad peak in NMR indicates that the structure in the deposits are mainly condensed carbonaceous materials [70,72], because mobile species in the deposits normally exhibit narrow, well-resolved $^{13}$C resonance lines. The broad peak can be possibly ascribed to the presence of nonsubstituted aromatic carbons (110~129 ppm), carbon bridges between aromatic rings (130~140 ppm), substituted aromatic carbons (140~150 ppm), and carbonyl (150~230 ppm) [64-76, 131]; the centered peak at 129.2 ppm is attributed to nonsubstituted aromatic carbons of the
aromatic rings [131]. The signals appearing in the 5–60 ppm region are possibly attributed to the presence of methyl groups in aliphatics or aromatics (10–20 ppm), methylene groups (20–35 ppm), methylene carbons in α position to two aromatic rings (35–50 ppm), and methyl groups bound to heteroatomics (50–65 ppm) [64-76, 131]; the centered signal with the greatest intensity can be assigned to the methyl group in aliphatics [131]. It should be noted that the signals of carbons from aromatics and aliphatics are overlapped respectively to give the NMR spectra of the deposits.

For the $^{13}$C NMR spectra of industrial Sample B, there is only a broad peak at aromatic regions (110–200 ppm), but no peak in the aliphatic region. This indicates that its structures are mostly aromatic, and the small peaks of aliphatics are overlapped by broad signals of aromatics. As well, the integral intensity of this sample in aromatic regions is much weaker compared with laboratory fresh sample ($13.5 \times 10^7$ vs $9.04 \times 10^7$) as given in Table 4-10, which indicated there is more NMR-invisible graphite [66-68] in the industrial Sample B. For the industrial Sample D, the NMR spectra only exhibit a much narrow peak at aromatic regions, and no obvious peak can be observed in the aliphatic regions. Moreover, the integral intensity at this region of Sample D is even much weaker ($0.09 \times 10^7$), which indicated more graphitic structures in Sample D. As well, it can be observed that the centered peak of aromatic regions shift to a high field from ~129 to ~123 ppm for industrial samples. The reason for this is not clear, but might be that the aromatic structures in industrial samples are more condensed, and the shielding effect of π electrons cause the chemical shifts move to a high field.
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-38 Quantitative $^{13}$C NMR Spectrum of Fresh Laboratory Deposits (Fresh Run B40)

Fig. 4-39 Quantitative $^{13}$C NMR Spectrum of Industrial Deposits (Sample B)
As described in Section 2.3.2 and 3.4.7, all carbons except graphite in the test sample contribute equally to the intensity of $^{13}$C NMR spectra. Paramagnetic species, e.g., graphitic-like carbon, are invisible to NMR. Therefore, the proportion of aromatic and aliphatic carbons in the deposits observed by NMR can then be calculated by the integrals of different coke spectra through a calibration line of a reference sample. Moreover, the fractions of aliphatic ($f_p$), aromatic ($f_a$) and graphitic carbons ($f_G$) can be calculated from equation (3-3) to (3-5), respectively. To obtain quantitative spectra (i.e. correct line intensity and corresponding good integrals), a flat baseline is required. An effort was also made to find $f_p$, $f_a$ and $f_G$ in different samples in our experiments by using cholesterol as reference sample, however, it was found that the carbon contents are always over estimated compared with bulk elemental analysis results. The reason is perhaps that the signals of carbons from aromatics and aliphatics are overlapped. This leads to a non-flat baseline and more errors in integrals.
If one assumes there is no graphitic carbon in the fresh laboratory deposits Run B40, which means all the carbons in the fresh deposits are visible to $^{13}$C NMR, then this sample can be used as a reference standard (84.89 wt%, carbon contents). If the overlapped aliphatics are not considered, the calculated $f_a$, $f_p$ and $f_G$ based on the equation (3-3) to (3-5) are given in Table 4-10. In fact, all the fresh deposits have some graphitic carbons. It has been reported [67] there is about 40 wt% $^{13}$C NMR invisible carbon in the coke collected from the catalysts in hydrogenation process for atmospheric residue. Thus, if 40% graphitic carbon in the fresh laboratory deposits is considered, another set of values of $f_a$, $f_p$ and $f_G$ can be calculated. These are given in Table 4-10 as well.

Table 4-10 Spectrum Integral Intensity of Different Deposits and Their Corresponding Relative Contents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectrum intensity</th>
<th>Case 1*</th>
<th>Case 2**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aromatics aliphatics</td>
<td>$C_{rea}¥%$ $C_{NMR}¥%$ $f_a$ $f_p$ $f_G$</td>
<td>$C_{NMR}¥%$ $f_a$ $f_p$ $f_G$</td>
</tr>
<tr>
<td>B40 fresh</td>
<td>134899554 3201881</td>
<td>84.89 84.89 0.98 0.02 0</td>
<td>50.94 0.99 0.01 0.40</td>
</tr>
<tr>
<td>Sample B</td>
<td>90431048</td>
<td>0 88.75 42.88 1.0 0</td>
<td>48 0 0.01 0.62</td>
</tr>
<tr>
<td>Sample D</td>
<td>929407</td>
<td>0 87.85 0.57 1.0 0</td>
<td>0.99 0.34 1.0 0.99</td>
</tr>
</tbody>
</table>

*Case 1: assuming no graphitic carbon in fresh deposits; ** Case 2: assuming 40% graphitic carbon in fresh deposits

$C_{rea}$: Carbon content by elemental analysis results; $C_{NMR}$: Carbon content visible to $^{13}$C NMR

$C_{NMR} = C_{rea} \times \frac{\text{total intensity of sample}}{\text{total intensity of fresh Run B40}}$.

$f_G = 1 - \frac{C_{NMR}¥%}{C_{rea}¥%}; f_a = f_G + f^*_a (1 - f_G); f_p = f^*_p (1 - f_G)

where $f^*_a$ and $f^*_p$ are fraction of aromatic and aliphatic carbons considering only those detected by quantitative $^{13}$C NMR, respectively.

From Table 4-10, it can be observed there are about 98 wt% aromatic carbons in the fresh laboratory deposits, and the aliphatic carbon are very little, only 1–2 wt%. For industrial sample B, all the deposits are aromatic structures, and there are about 50–60 wt% graphitic carbons; the
graphitic structures dominate in industrial Sample D: up to 99 wt%. The $^{13}$C NMR results are consistent with previous DRIFT results. All of the results indicate graphitic structures dominate in the industrial samples, especially for Sample D; fresh laboratory deposits have both aromatic and aliphatic structures.

4.7 Extraction of Soluble Components of Deposits

Chloroform, toluene, pyridine and 1-methyl-2-pyrolidone (MPD) were selected as extraction solvents based on the literature [41-52], and the selected deposits were then Soxhlet-extracted for 24 hours. The extracted solutions (ca. 100ml) were evaporated in a fume hood at a low heat to concentrate them up to 2ml (ca.) and kept for further GS-MS or simulated distillation analysis. The detailed experimental procedures of solvent extraction are given in Section 3.4.1. It was found that MPD, whose boiling point is 202°C, is very different to evaporate, and pyridine (b.p. 115°C) has an unpleasant odor during evaporation. Although MPD and pyridine may have better soluble ability for the deposits, only chloroform (b.p. 61°C) and toluene (b.p. 110°C) were then chosen for further investigation. These, especially for chloroform [41, 46-50], are also more commonly used solvents for extraction of “soluble coke” in the literature. Initially, efforts were made to try and identify individual components in the soluble extracts by GC-MS as described in section 3.4.2. However, it was found that the soluble fraction of the deposits contains very heavy components, and no soluble components are eluted in gas chromatography. Therefore, high temperature GC simulated distillation is used for the boiling point distribution of soluble fractions of deposits.

4.7.1 Soluble Fractions in Deposits and Their Boiling Point Distribution

The above concentrated soluble extracts were dried under natural evaporation in the fume hood, and the solid extracts weighed to calculate the soluble fractions. The color changes during extraction and the percentage soluble fractions for the different deposits in chloroform or toluene
are given in Table 4-11. An obvious color change occurred during extraction of fresh deposits collected from the long test tube. For the Syncrude Sample B, an obvious solvent color changes was also observed when extracted, however, almost no color change occurs for the Syncrude Sample D. Chloroform appears to be a better solvent than toluene. From Table 4-11, it can be seen that there are much more soluble components in the fresh laboratory deposits, 11.05 wt% in chloroform and 3.46 wt% in toluene; however, much fewer for industrial sample B (0.57 wt%) and particularly fewer for sample D (0.01 wt%). This is consistent with abovementioned results of TGA, DRIFT and $^{13}$C NMR, all of which indicate that there are much more condensed structures in industrial samples.

### Table 4-11 Colour Changes and Soluble Fractions of Deposits in Soxhlet Extraction

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Chloroform</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposits</td>
<td>Fresh Lab Run B40</td>
<td>Fresh Lab Run B40</td>
<td>Syncrude B (cyclone snot outlet)</td>
<td>Syncrude D (gas outlet tube)</td>
</tr>
<tr>
<td>Soluble fraction (wt %)</td>
<td>3.46</td>
<td>11.05</td>
<td>0.57</td>
<td>0.01</td>
</tr>
<tr>
<td>Solvent color after extraction</td>
<td>Brown</td>
<td>Brown</td>
<td>Brown</td>
<td>Clear</td>
</tr>
</tbody>
</table>

The boiling point distributions of soluble components in toluene and chloroform for different deposits are given in Fig. 4-41. There are many heavy components in the extracts from all the deposits. With chloroform as solvent, about 65 wt% of the extract has boiling points higher than 550°C for the extracts from fresh laboratory deposits, and 52 wt% boils above 750°C. For the extracts from industrial sample B, there are about 45 wt% whose boiling points are higher than 550°C and 27 wt% whose boiling points are higher than 750°C. Much more heavier components are found in the extracts of industrial sample D, where 80 wt% boils above 750°C. For all the extracts from different deposits, 95 wt% have boiling points are higher than
400°C. The fact that soluble components have very high boiling points is consistent with the condensation mechanism for cyclone exit line fouling. One would expect high boiling material to crack during coking. However, since 30~80 wt% components in extracts have boiling points higher than 750°C, deposit formation appears to arise not just from condensation of vapours in the fluid, but also by carryover of bitumen droplets. Previous experimental results [6], where a modest increase in deposition rate occurred with increasing filter pore size, also suggested liquid droplets from the bitumen feed contribute to deposition.

Fig. 4-41 shows that there are more heavy components in the extracts of chloroform than those of toluene. For example, for laboratory deposits, there are 65 wt% whose boiling points are higher than 550°C for those chloroform as solvent, and 52 wt% whose boiling points are higher.
than 750°C. However, there are only 42 wt% whose boiling points are higher than 550°C for those toluene as solvent, and 23 wt% whose boiling points are higher than 750°C. Therefore, chloroform seems to be a better solvent than toluene in extraction of deposits.

4.7.2 The Morphology for the Deposits after Solvent Extraction

Fig. 4-42 is the micrograph of fresh lab deposits after extraction by toluene; Fig 4-43 and 4-44 are magnified micrographs of plate-like and amorphous deposits, respectively. There is no big change in the morphology of deposits after solvent extraction for 24 hours: there are many boulder-like droplets attached on the plate surface for the platelet deposits, and spherical and near spherical aggregates are observed for amorphous deposits. The same phenomena can be observed for those extracted by other solvents. This suggests that the deposits are formed by condensation from heavy components, and most of them are very stable, and do not dissolve at the temperatures around 110°C, the temperature of extraction solvent’s boiling point.

Fig. 4-42 SEM of the Deposits after Toluene Extraction (Run B9)
Fig. 4-43 SEM of the Amorphous Deposits after Toluene Extraction (Run B9)

Fig 4-44 SEM of the Platelet Deposits after Toluene Extraction (Run B9)
4.7.3 Comparison of Thermal Behaviour for Deposits Before and After Extraction

The TGA analysis results up to 1000°C for different deposits, i.e. from long test tube and filter, before and after extraction by toluene are given in Fig. 4-45 and 4-46, respectively. For the deposits collected from the long test tube, it can be seen that the thermal properties of fresh deposits are much different with those of solvent extracted deposits. There are much more volatile components in fresh deposits, especially at the temperature between 300~500°C. This indicates that the soluble components are mostly volatile components, which still have not formed to very condensed structures. The differences of volatile components between fresh and extracted deposits at different temperatures are given in Table 4-12. However, for the deposits collected from coker filter, the thermal properties are quite similar for deposits before and after extraction, and the TGA curves up to 1000°C are very close. From Fig. 4-46 and Table 4-12, there are even a little more volatile components (1~2%) for extracted filter deposits. This may be due to small amount of solvent absorbed in the capillary pore structures in the deposits and/or due to experimental errors. In general, we can conclude that there is very little soluble material in filter deposits. In fact, for filter deposits, there is no colour change observed for the solvent before and after 24 hours Soxhlet extraction. This suggests that the filter deposits are quite different than those from long test tube, and the latter contain much more volatile components.

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Moisture (wt%)</th>
<th>Weight loss (wt%)</th>
<th>150~550°C</th>
<th>550~750°C</th>
<th>750~1000°C</th>
<th>150~1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exit Tube</td>
<td>0.12</td>
<td>8.92</td>
<td>7.47</td>
<td>1.68</td>
<td>18.07</td>
<td></td>
</tr>
<tr>
<td>Extracted</td>
<td>0.46</td>
<td>2.29</td>
<td>5.26</td>
<td>3.02</td>
<td>10.57</td>
<td></td>
</tr>
<tr>
<td>Filter</td>
<td>0.20</td>
<td>1.66</td>
<td>4.33</td>
<td>5.89</td>
<td>11.88</td>
<td></td>
</tr>
<tr>
<td>Extracted</td>
<td>1.11</td>
<td>2.68</td>
<td>5.25</td>
<td>5.48</td>
<td>13.41</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4 Characterization of Deposits from Fluid Coker Cyclone Unit

Fig. 4-45 Comparison of Deposits from Long Tube before and after Extracted by Toluene

Fig. 4-46 Comparison of Deposits from Filter before and after Extracted by Toluene
4.7.4 Comparison of DRIFTs for Deposits Before and After Solvent Extraction

Fig. 4-47 is the comparison of DRIFT spectra for deposits from the long test tube before and after extraction with different solvents. The paraffinic bands (2800~3000 cm\(^{-1}\)) become a little weaker for the solvent extracted deposits, but the coke band at ~1600 cm\(^{-1}\) all remains very strong. As well, absorptions in the C-H bending vibration regions (1300-1500 cm\(^{-1}\)) presumably due to solvents remaining on the deposits can be observed. For the deposits extracted by MPD, a strong absorption at ~1690 cm\(^{-1}\) can be clearly noticed, which is caused by -C=O in the remaining MPD, and it overlaps the part of coke band at 1600cm\(^{-1}\). Therefore, it can be stated that the soluble components in the deposits are mostly paraffinics, even though it may also contains some less condensed polyaromatics.

![Fig. 4-47 DRIFTs Comparison of Long Tube Deposits Extracted with Different Solvents](image-url)
Fig. 4-48 is the comparison of DRIFT spectra for deposits from filter before and after extraction with different solvents. For the MPD extracted deposits, the absorption caused by solvents can be clearly noticed: a strong absorption at $\sim 1690 \text{ cm}^{-1}$ is caused by $-\text{C}=\text{O}$; strong absorption at paraffinic bands ($2800$–$3000 \text{ cm}^{-1}$) and C-H bending vibration region ($1300$–$1500 \text{ cm}^{-1}$) caused by MPD are also very obvious; a big bump at $\sim 3500 \text{ cm}^{-1}$ is caused by moisture. For other solvent-extracted deposits, no appreciable differences can be observed in the paraffinic bands ($2800$–$3000 \text{ cm}^{-1}$), but the absorption caused by solvents can still be noticed in the C-H bending vibrations ($1300$–$1500 \text{ cm}^{-1}$), especially for the pyridine extracted deposits, and the coke band at $1600 \text{ cm}^{-1}$ remains very strong. The above observations indicate that there is virtually no obvious change in the deposits structure before and after solvent extraction.

![Graph showing DRIFT spectra comparison](image_url)

**Fig. 4-48 DRIFTs Comparison of Filter Deposits Extracted with Different Solvents**
4.8 Summary of Deposits Characterization Results

Based on the deposit characterization results, the following conclusions can be drawn:

1. SEM experimental results indicate that there are mainly two kinds of morphology for the deposits formed in the laboratory studies: platelet and amorphous deposits. At lower temperature conditions, the amorphous deposits are predominant, however, platelet deposits are the main morphology at higher operating temperature conditions. The viscosities, the characteristics of the condensed tar droplets, the velocity of fluid gas above the droplets, wettability of the tube wall, and even the rate of chemical reactions in the tar droplets determine the morphology of the deposit, according to the literature. There are many droplets attached on the platelet deposits, and many small droplets aggregate together to form the amorphous deposits. These results support the physical condensation mechanism as the main reason for the cyclone exit line fouling in the laboratory study. However, the morphology of commercial deposits appeared to be unique, differing from anything seen in the laboratory samples. This is possibly due to extremely high velocity of fluid gas and long aging time under industrial conditions of high hydrocarbon concentration.

2. The properties for the reactor freeboard filter deposits are much different than those of the exit tube. TGA, DRIFT and solvent extraction experimental results indicate that the filter deposits have much more coke-like characteristics than those of exit tube, and have less volatile components. The cenophores carried from the coker reactor possibly together with the liquid droplets carried from the bitumen feed lead to the deposition on the filter, and the deposits exhibit honeycomb or loose-plate structures.

3. The similarities of the DRIFT spectra for fresh laboratory deposits, asphaltene and bitumen feed support the condensation mechanism for cyclone exit line fouling. The fact that the extracts from the deposits contain very high boiling point components (90%>400°C) also is
consistent with physical condensation causing deposit formation. However, the metals detected in XRF analysis and the facts that many components in extracts whose boiling points are higher than 750°C indicate that deposit formation is not just from condensation from vapour phase. Carryover from bitumen droplets also contributes to deposition.

4. All the characterization results, i.e., elemental analysis, SEM, TGA, DRIFT, $^{13}$C NMR and solvent extraction, etc., indicate that industrial samples are unique, much different than the fresh laboratory deposits. Graphitic structures dominate in industrial samples. There are both polyaromatic and aliphatic structures in fresh laboratory deposits, but mainly these deposits are polyaromatic structures. Deposits from high temperature operation conditions indicate more polyaromatic structures. When the operation temperature is raised, the laboratory deposits possibly can appear more like those of the industrial units.
Chapter 5 Aging Study of Fresh Deposits from Laboratory Fluid Coker Unit

From the experimental results of Chapter 4, it has been found that the industrial samples are very unique and much different than our laboratory fresh deposits. The fresh laboratory deposits were collected after six hours running from a bench-scale fluid coker unit, whereas the industrial samples had been in place aging at temperatures around 500°C for time periods up to months or even over one year in the presence of hydrocarbons. This leads to the question whether deposits collected from the bench-scale unit can be representative of industrial samples. In order to clarify this problem, and to examine the evolution of deposit structure over long time periods, an aging study of fresh deposits from laboratory units at the temperature about 550°C was conducted.

5.1 Laboratory Fresh Deposit Samples for Aging Study

The deposit samples from the long test tube were collected from bench-scale fluid coker cyclone fouling unit after running six hours (Run B19, Run B20, Run B30 and Run B40). The main corresponding operating conditions are given in Table 5-1. These four samples were collected under cooling operating conditions. Very small quantities of deposits could be collected under heating conditions, hence there was not enough for further aging experiments. Sample B19 and B20 are deposits from the same bitumen feed ATB-A, and Sample B30 and B40 are from another bitumen feed ATB-B. The properties of bitumen feed are listed at Table 3-1 in Chapter 3, in which the ATB-A has much more heavy fractions, more carbon residue and lower H/C atomic ratio than that of feed ATB-B.

The samples were placed in sealed reactors under nitrogen in the muffle oven under 550°C for different specific aging times of the order of days. The detailed aging procedures are given at the Section 3.5 in Chapter 3. After the samples were taken out and cooled, different analytical
techniques, i.e., elemental analysis, SEM, TGA, DRIFT, and \(^{13}\)C solid-state NMR, are used to characterize the composition and structure of the fresh and aged deposits.

### Table 5-1 Fresh Lab Deposits for Aging Study and Their Main Operating Conditions

<table>
<thead>
<tr>
<th>Run #</th>
<th>Reactor (°C)</th>
<th>Cyclone (°C)</th>
<th>Vapour in Long Tube (°C)</th>
<th>Long Tube Wall (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B19</td>
<td>535</td>
<td>535</td>
<td>448</td>
<td>428</td>
<td>cooling</td>
</tr>
<tr>
<td>B20</td>
<td>535</td>
<td>535</td>
<td>473</td>
<td>443</td>
<td>cooling</td>
</tr>
<tr>
<td>B30</td>
<td>535</td>
<td>535</td>
<td>520</td>
<td>500</td>
<td>cooling</td>
</tr>
<tr>
<td>B40</td>
<td>535</td>
<td>530</td>
<td>458</td>
<td>425</td>
<td>cooling</td>
</tr>
</tbody>
</table>

* Bitumen: 0.3kg/hr; steam: 0.3kg/hr; nitrogen: 2.7L/min

### 5.2 The Changes of H/C Atomic Ratio and Weight Loss during Aging Process

The elemental composition and H/C atomic ratio (analysed by Canadian Microanalytical Service Ltd.) of fresh and aged deposits under different aging times are given in Table 5-2A. It can be seen that the fresh deposits which were formed under cooling operation conditions (vapour temperature: 448–520°C; tube wall 425–500°C) have similar elemental compositions. For all 4 fresh deposits, the contents of carbon, hydrogen, sulfur and nitrogen are similar with each other, and H/C atomic ratio is about 0.54–0.59. Industrial deposits have much lower H/C atomic ratio (0.16–0.21) compared with fresh laboratory deposits. For the aged deposits (>2 days), the H/C atomic ratios approach those of the industrial samples. The changes of H/C atomic ratio of different deposits with aging time are shown in Fig. 5-1. Reproducibility is shown in Fig. 5-1 and Table 5-2B. In general, the standard deviation of H/C ratio is 12.1% of the mean. Scatter is expected at low H/C ratios because of analytical difficulties at low hydrogen values. It can be observed that the H/C atomic ratio decreases dramatically during the first two days, especially in the first day. After aging two days, the H/C ratios drop from 0.55–0.59 to 0.2–0.3,
and then do not change much. The drop of H/C ratio with the aging time can be approximately expressed by a first order exponential decay equation:

\[ H/C = 0.26 + 0.31 \exp\left(-\frac{t}{0.18}\right) \]  

(5-1)

![Graph showing changes of H/C atomic ratio with aging time](image)

**Fig. 5-1 Changes of H/C Atomic Ratio with the Aging Time**

Volatile components either initially present in the deposits or which crack off from the side chains in the deposits must be released during the aging period, because it can be observed that the colour of ceramic wool, which is used to plug the open end of glass tube, became black after the samples were taken out of the muffle oven. The volatile components in the deposits are presumably more paraffinic, and have a high H/C atomic ratio. Therefore, the release of volatile components of a high H/C atomic ratio must be the main reason which causes much lower H/C atomic ratio of the aged deposits. This process mainly happened in the first one or two days.
Table 5-2A Elemental Composition and H/C Ratio of Fresh, Aged and Industrial Deposits

<table>
<thead>
<tr>
<th>Deposits</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>S (wt%)</th>
<th>N (wt%)</th>
<th>C+H (wt%)</th>
<th>H/C atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run B19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>85.42</td>
<td>4.24</td>
<td>/</td>
<td>1.69</td>
<td>89.66</td>
<td>0.59</td>
</tr>
<tr>
<td>Aged 12 hours</td>
<td>82.85</td>
<td>2.41</td>
<td>/</td>
<td>1.76</td>
<td>85.26</td>
<td>0.35</td>
</tr>
<tr>
<td>Aged 1 day</td>
<td>86.44</td>
<td>2.35</td>
<td>/</td>
<td>1.73</td>
<td>88.76</td>
<td>0.33</td>
</tr>
<tr>
<td>Aged 2 days</td>
<td>82.92</td>
<td>1.78</td>
<td>/</td>
<td>1.81</td>
<td>84.70</td>
<td>0.26</td>
</tr>
<tr>
<td>Aged 8 days</td>
<td>86.33</td>
<td>1.84</td>
<td>/</td>
<td>1.61</td>
<td>88.17</td>
<td>0.26</td>
</tr>
<tr>
<td>Run B20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>85.54</td>
<td>4.05</td>
<td>6.44</td>
<td>/</td>
<td>89.59</td>
<td>0.57</td>
</tr>
<tr>
<td>Aged 1 day</td>
<td>87.82</td>
<td>2.48</td>
<td>4.62</td>
<td>/</td>
<td>90.30</td>
<td>0.34</td>
</tr>
<tr>
<td>Aged 10 days</td>
<td>84.83</td>
<td>1.96</td>
<td>3.66</td>
<td>/</td>
<td>86.79</td>
<td>0.28</td>
</tr>
<tr>
<td>Aged 18 days</td>
<td>83.68</td>
<td>1.38</td>
<td>4.20</td>
<td>/</td>
<td>85.06</td>
<td>0.20</td>
</tr>
<tr>
<td>Aged 23 days</td>
<td>81.35</td>
<td>1.73</td>
<td>4.21</td>
<td>/</td>
<td>83.08</td>
<td>0.26</td>
</tr>
<tr>
<td>Run B30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>84.92</td>
<td>4.10</td>
<td>6.27</td>
<td>/</td>
<td>89.02</td>
<td>0.58</td>
</tr>
<tr>
<td>Aged 5 hours</td>
<td>79.24</td>
<td>2.21</td>
<td>/</td>
<td>1.9</td>
<td>81.45</td>
<td>0.33</td>
</tr>
<tr>
<td>Aged 12 hours</td>
<td>87.53</td>
<td>1.80</td>
<td>/</td>
<td>1.83</td>
<td>89.33</td>
<td>0.25</td>
</tr>
<tr>
<td>Aged 1 day</td>
<td>81.24</td>
<td>1.84</td>
<td>/</td>
<td>1.70</td>
<td>83.08</td>
<td>0.27</td>
</tr>
<tr>
<td>Aged 3 days</td>
<td>86.92</td>
<td>1.84</td>
<td>1.95</td>
<td>/</td>
<td>88.76</td>
<td>0.25</td>
</tr>
<tr>
<td>Aged 13 days</td>
<td>85.22</td>
<td>1.74</td>
<td>/</td>
<td>1.74</td>
<td>86.96</td>
<td>0.21</td>
</tr>
<tr>
<td>Aged 20 days</td>
<td>75.50</td>
<td>1.80</td>
<td>/</td>
<td>1.80</td>
<td>77.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Run B40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>84.89</td>
<td>3.80</td>
<td>/</td>
<td>/</td>
<td>88.69</td>
<td>0.54</td>
</tr>
<tr>
<td>Aged 2 days</td>
<td>86.70</td>
<td>1.86</td>
<td>/</td>
<td>/</td>
<td>88.56</td>
<td>0.26</td>
</tr>
<tr>
<td>Aged 11 days</td>
<td>89.28</td>
<td>2.08</td>
<td>/</td>
<td>/</td>
<td>91.36</td>
<td>0.28</td>
</tr>
<tr>
<td>Aged 24 days</td>
<td>85.51</td>
<td>1.18</td>
<td>/</td>
<td>/</td>
<td>86.69</td>
<td>0.17</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syncrude B</td>
<td>88.75</td>
<td>1.57</td>
<td>/</td>
<td>/</td>
<td>90.32</td>
<td>0.21</td>
</tr>
<tr>
<td>Syncrude D</td>
<td>87.85</td>
<td>1.18</td>
<td>/</td>
<td>/</td>
<td>89.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* / means that the item was not determined.

Table 5-2B The Standard Derivation of H/C Atomic Ratio Analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>H/C atomic ratio</th>
<th>Number of data point</th>
<th>Std derivation/mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average and standard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.57±0.02</td>
<td>4</td>
<td>3.51</td>
</tr>
<tr>
<td>After 12 hrs</td>
<td>0.30±0.05</td>
<td>2</td>
<td>16.6</td>
</tr>
<tr>
<td>After 1 days</td>
<td>0.31±0.04</td>
<td>3</td>
<td>12.9</td>
</tr>
<tr>
<td>After 10±3 days</td>
<td>0.26±0.04</td>
<td>4</td>
<td>15.4</td>
</tr>
</tbody>
</table>
During the initial aging periods (1~2 days), chemical reactions of paraffinic species to form polyaromatics are not likely to be the cause of the much lower H/C atomic ratio deposits, because the rate for the formation of polyaromatic compound is quite low (e.g., 10 g/m²*h for hydrocarbon cracking [90-95]). However, this doesn't mean that there are no chemical reactions for polyaromatic compound formation taking place in the first 1~2 days. But, if those chemical reactions take place, they must be very slow and are unlikely to lead to dramatic change of H/C ratio.

Table 5-3 and Fig. 5-2 give the weight loss along with the aging time for the deposits of Run B30 and Run B40. The scatter of experimental data, and the one unexpectedly high weight loss at 13 days could arise from very tiny broken glass chips and the ceramic wool which was used to plug the open end of glass tube falling into the glass tube and mixing with the deposits. However, it still can be concluded from experimental results that the weight loss mostly happened during first two days. There is around 10wt% weight loss for the fresh deposits after aging over 5 hours, and it does not change much with the aging time.

![Graph](image-url)  
**Fig. 5-2 Deposit Weight Loss with the Aging Time**
Table 5-3 Weight Loss along with the Aging Time of Run B30 and Run B40 Deposits

<table>
<thead>
<tr>
<th>Aging time</th>
<th>5</th>
<th>12</th>
<th>24</th>
<th>2</th>
<th>3</th>
<th>11</th>
<th>13</th>
<th>20</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hrs</td>
<td>hrs</td>
<td>hrs</td>
<td>days</td>
<td>days</td>
<td>days</td>
<td>days</td>
<td>days</td>
<td>days</td>
</tr>
<tr>
<td>B30 Weight loss (wt%)</td>
<td>10.4</td>
<td>14.6</td>
<td>9.0</td>
<td>/</td>
<td>11.4</td>
<td>/</td>
<td>19.3</td>
<td>11.2</td>
<td>/</td>
</tr>
<tr>
<td>B40 weight loss (wt%)</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>12.3</td>
<td>/</td>
<td>9.8</td>
<td>/</td>
<td>/</td>
<td>10.6</td>
</tr>
</tbody>
</table>

* / means that the item was not determined.

All the above results substantiate that the release of volatile components which have a high H/C atomic ratio must be the main cause of much lower H/C atomic ratio of aged deposits, and this process mainly happens in the first one or two days.

5.3 Deposits Weight Loss along with the Aging Time in the First 12 Hours

To investigate how exactly the release of volatiles proceeds in the initial periods, TGA was employed to monitor the weight loss on line during the first 12 hours aging time. This process was carried out with TGA on 5~15 mg samples under nitrogen with a flow rate 50 ml/min. The temperature was first ramped to 550°C from ambient temperature at a heating rate of 10°C/min, and then kept at 550°C for 12 hours. The weight changes of the sample were recorded on-line, and the experimental data were processed by TA60 software. The weight losses of different fresh deposits along with the aging times in TGA are given in Fig. 5-3, respectively. As well, Table 5-4 gives the weight loss at different periods, (e.g., ambient temperature ~550°C, 12 hours aging period at 550°C), and the total weight loss in the whole period.
Fig. 5-3 Weight Loss of Fresh Deposits along with the Aging Time in TGA

Table 5-4 Weight Losses of Fresh Deposits at Different Aging Periods in TGA

<table>
<thead>
<tr>
<th>Feed</th>
<th>Sample</th>
<th>Weight Loss (wt%)</th>
<th>Weight loss ratio in ambient ~550°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ambient~550°C</td>
<td>12 hours aging at 550°C</td>
</tr>
<tr>
<td>Run B19</td>
<td></td>
<td>8.55</td>
<td>4.24</td>
</tr>
<tr>
<td>ATB-A</td>
<td>Run B20</td>
<td>9.57</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>Run B30</td>
<td>7.11</td>
<td>5.78</td>
</tr>
<tr>
<td>ATB-B</td>
<td>Run B40</td>
<td>6.91</td>
<td>6.13</td>
</tr>
</tbody>
</table>

From the experimental results, it can be observed that all the fresh deposits have similar thermal properties. For all the deposits, the weight loss curves show a sharp drop within the first 2 hours, and then decrease gradually in the following aging times. The total weight loss percentages (12~14 wt%) are consistent with the aging study in the muffle oven. From Table 5-
4, it can be found that about 50–70 wt% of deposits release in the heating period from ambient to 550°C, which is less than one hour, and lower weight loss (<50% or less) occurs in the following 12 hour aging period. The average weight loss rates of different deposits in heating periods and aging periods are listed in Table 5-5. It can be seen that the average weight loss rates in the initial heating period are about 15–30 times faster than those of aging period at 550°C.

However, it also can be observed from Fig. 5-3 that deposit samples Run B30 and B40, which are collected from the same bitumen feed (ATB-B), exhibit a very similar thermal characteristic; Run B19 and B20, which are collected from another bitumen feed (ATB-A), demonstrate a similar thermal characteristic but different with that of Run B30 and B40. Table 5-4 and 5-5 also indicate that Run B19 and B20, which used the heavier feedstock oil ATB-A, have more volatile components released in the heating period (8–9 wt%) compared with Run B30 and B40 (ca. 7 wt%), but less volatile components (ca. 4 wt%) in the isothermal aging period at 550°C compared with those of Run B30 and B40 (ca. 6 wt%).

Table 5-5 Average Weight Loss Rates of Different Deposits in Different Periods

<table>
<thead>
<tr>
<th>Feed</th>
<th>Sample</th>
<th>Ambient–550°C (wt%.hr⁻¹)</th>
<th>Aged at 550°C (wt%.hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATB-A</td>
<td>Run B19</td>
<td>9.84</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Run B20</td>
<td>10.83</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Run B30</td>
<td>7.65</td>
<td>0.48</td>
</tr>
<tr>
<td>ATB-B</td>
<td>Run B40</td>
<td>8.11</td>
<td>0.51</td>
</tr>
</tbody>
</table>

In order to know more detail about the weight loss in heating period (ambient–550°C) and in the aging period at 550°C, the weight loss with the temperatures in the heating period and the weight loss with aging time at 550°C are drawn as Fig. 5-4 and 5-5, respectively. Table 5-6 gives the weight loss at 300°C, 550°C and the weight loss ratio before 300°C.
Chapter 5 Aging Study of Fresh Deposits from Laboratory Fluid Coker Unit

Fig. 5-4 Weight Loss in the Heating Period from Ambient ~550°C in TGA for Different Deposits

Fig. 5-5 Weight Loss after the Heating period of Different Deposits Aging at 550°C in TGA
Table 5-6 Weight Losses at 300, 550°C and Weight Loss Ratio in Different Periods

<table>
<thead>
<tr>
<th>Sample</th>
<th>300°C (wt%)</th>
<th>550°C (wt%)</th>
<th>weight loss in 12 hrs aging period (wt%)</th>
<th>ratio of weight loss at 300°C to total weight loss (wt%)</th>
<th>ratio of weight loss from 300~550°C to total weight loss (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run B19</td>
<td>0.35</td>
<td>8.55</td>
<td>12.79</td>
<td>2.73</td>
<td>64.11</td>
</tr>
<tr>
<td>Run B20</td>
<td>1.28</td>
<td>9.57</td>
<td>14.02</td>
<td>9.12</td>
<td>59.13</td>
</tr>
<tr>
<td>Run B30</td>
<td>2.18</td>
<td>7.11</td>
<td>12.89</td>
<td>16.9</td>
<td>38.27</td>
</tr>
<tr>
<td>Run B40</td>
<td>1.52</td>
<td>6.91</td>
<td>13.04</td>
<td>11.66</td>
<td>41.33</td>
</tr>
</tbody>
</table>

From Fig. 5-4 and Table 5-6, it can be noted that there is very little weight loss before 300°C (<15 % or much less) and extensive weight loss during the heating period from 300 ~ 500°C (ca. 40~65%). During aging (Fig. 5-5), the weight loss mainly happens in the initial period, and then subsequently drops gradually at a very slow rate. Combined with all above TGA and H/C atomic ratio experimental results, it can be concluded that during the heating period below 300°C, very little weight loss occurred, thus the deposits have a good thermal stability under these low temperatures. In heating from 300~550°C and in the initial isothermal aging period at 550°C, a rapid weight loss occurred, causing over 50 wt% of deposits total weight loss based on the whole aging period. The weight loss is mainly caused by the release of higher H/C ratio volatile components, and leads to a dramatic drop in H/C atomic ratio for the aged deposits. Thermal cracking reactions of long aliphatic chains which either exist as side chains in polyaromatic rings or are initially present in the deposits takes place in this period, leading to much smaller molecule products, which are volatile and cause the dramatic weight loss. In the following long isothermal aging periods at 550°C in nitrogen atmosphere, there is still weight loss occurring, however, the weight loss rate is very low. The chemical reactions leading to more condensed structures, such as cracking of short side chains in the polyaromatic rings,
dehydrogenation, cyclization, skeleton re-arrangement, etc., must be taking place in this latter period. The release of volatile components is gradual, and the H/C atomic ratio continues to decrease at a low rate. Although the H/C atomic ratios are rather scattered in Table 5-2 because of analytical errors, however, this trend still is evident in Fig. 5-1. During this period, chemical reactions which lead to condensed aromatic structures are thought to be the main reason for the gradual weight loss.

5.4 The Aging Study in TGA for the Aged and Industrial Deposits

To investigate whether there are further chemical reactions or further volatile release for the pre-aged deposits, the different pre-aged deposits of Run B40 were placed in the TGA at 550°C under nitrogen atmosphere for another 12 hours, and their weight loss was monitored on line. The same experiments were done with industrial samples. Their weight loss along with aging time is given in Fig. 5-6. Table 5-7 gives the weight loss and average weight loss rates during the whole period.

![Fig. 5-6 TGA Results of Pre-aged and Industrial Deposits at 550°C for 12hours](image-url)
Experimental results indicated that there is still further weight loss for all the pre-aged and industrial deposits, although they had been aged for quite a long time, especially for the industrial ones. However, the weight loss (2~6 wt%) is much less than that of the fresh deposits on the same experimental conditions (13~14 wt%). From the curves, it also can be noticed that the weight loss occurs at a very low rate (<0.443 wt%/hr), and no dramatic weight loss happened compared with the case of fresh deposits. Chemical reactions to form condensed polyaromatic structures, such as cracking of the short chains in aromatics, cyclization, dehydrogenation, skeleton re-arrangement, etc. may be the main reason to cause the small weight loss.

From Fig. 5-6, it can be further noticed that there is a relatively fast weight loss in the initial period for the industrial samples. This is perhaps due to the fact that the deposit formation is a continuous process, and there are always some fresh deposits formed on the old deposit surface in the industrial plant. These fresh portion of the deposits, which have considerable amount of paraffinics, crack and release in the initial heating period, and cause the fast initial weight loss.

5.5 Comparison of Thermogravimetric Analysis of Fresh and Aged Deposits

Experiments were carried out with 5~15 mg samples under nitrogen with a flow rate 50 ml/min, within the temperature range of ambient to 1000°C and a heating rate of 10°C/min. The weight loss below ca. 150°C is attributed to removal of the absorbed water (moisture) [64]. Fig. 5-7~5-10 give the TGA weight loss comparison of different fresh, aged laboratory deposits (Run B19, Run B20, Run B30, Run B40) and industrial samples, respectively. From these
figures, it can be seen that the shapes of the weight loss curve for all fresh laboratory deposits are quite similar. All TGA curves for fresh deposits have a bigger gradient after 400°C compared with the aged laboratory deposits and industrial samples. The TGA curves of all aged deposits show a shape close to that of the industrial samples, which have a rather lower gradient, and the weight loss occurred mostly above 600°C. This means that thermal properties of all aged laboratory deposits are similar to those of industrial samples. The moisture and the total weight loss of different deposits at 550, 750, 1000°C are given in Table 5-8, and the curves of TGA weight loss at 550, 750, 1000°C of different fresh and aged laboratory deposits versus aging time are given in Fig. 5-11−5-13, respectively.

![Graph of TGA curves showing weight loss vs. temperature for fresh and aged deposits](image)

**Fig. 5-7 Comparison of Fresh, Aged Laboratory Deposits (Run B19) and Industrial Samples**
Fig. 5-8 Comparison of Fresh, Aged Laboratory Deposits (Run B20) and Industrial Samples

Fig. 5-9 Comparison of Fresh, Aged Laboratory Deposits (Run B30) and Industrial Samples
Chapter 5 Aging Study of Fresh Deposits from Laboratory Fluid Coker Unit

Fig. 5-10 Comparison of Fresh, Aged Laboratory Deposits (Run B40) and Industrial Samples

Fig. 5-11 TGA Weight Loss at 550°C for Fresh and Aged Deposits
### Table 5-8 Weight Loss for the Deposits before and after Aging

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Moisture (wt%)</th>
<th>Weight loss at 550°C (wt%)</th>
<th>Weight loss at 750°C (wt%)</th>
<th>Weight loss at 1000°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run B19</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.05</td>
<td>7.99</td>
<td>14.09</td>
<td>16.90</td>
</tr>
<tr>
<td>Aged 24 hrs</td>
<td>0.61</td>
<td>0.81</td>
<td>2.73</td>
<td>6.51</td>
</tr>
<tr>
<td>Aged 8 days</td>
<td>0.53</td>
<td>1.46</td>
<td>2.89</td>
<td>6.75</td>
</tr>
<tr>
<td><strong>Run B 20</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.72</td>
<td>7.66</td>
<td>14.62</td>
<td>24.11</td>
</tr>
<tr>
<td>Aged 1 day</td>
<td>0.35</td>
<td>0.13</td>
<td>5.17</td>
<td>11.40</td>
</tr>
<tr>
<td>Aged 10 days</td>
<td>0.30</td>
<td>1.18</td>
<td>2.49</td>
<td>6.75</td>
</tr>
<tr>
<td>Aged 18 days</td>
<td>0.20</td>
<td>1.54</td>
<td>3.25</td>
<td>10.42</td>
</tr>
<tr>
<td>Aged 23 days</td>
<td>0.29</td>
<td>0.02</td>
<td>2.36</td>
<td>9.56</td>
</tr>
<tr>
<td><strong>Run B30</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.20</td>
<td>10.47</td>
<td>16.09</td>
<td>18.41</td>
</tr>
<tr>
<td>Aged 5 hrs</td>
<td>0.45</td>
<td>0.84</td>
<td>4.34</td>
<td>8.86</td>
</tr>
<tr>
<td>Aged 12 hrs</td>
<td>0.27</td>
<td>0.35</td>
<td>3.84</td>
<td>9.15</td>
</tr>
<tr>
<td>Aged 24 hrs</td>
<td>0.14</td>
<td>0.39</td>
<td>2.25</td>
<td>5.48</td>
</tr>
<tr>
<td>Aged 3 days</td>
<td>0.20</td>
<td>0.08</td>
<td>2.65</td>
<td>7.42</td>
</tr>
<tr>
<td>Aged 13 days</td>
<td>0.06</td>
<td>0.57</td>
<td>2.09</td>
<td>7.08</td>
</tr>
<tr>
<td>Aged 20 days</td>
<td>0.09</td>
<td>0.08</td>
<td>0.55</td>
<td>3.36</td>
</tr>
<tr>
<td><strong>Run B40</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>0.04</td>
<td>5.16</td>
<td>11.72</td>
<td>16.55</td>
</tr>
<tr>
<td>Aged 2 days</td>
<td>0.21</td>
<td>0.24</td>
<td>1.59</td>
<td>4.75</td>
</tr>
<tr>
<td>Aged 11 days</td>
<td>0.15</td>
<td>0.00</td>
<td>0.95</td>
<td>4.08</td>
</tr>
<tr>
<td>Aged 24 days</td>
<td>0.38</td>
<td>0.18</td>
<td>1.17</td>
<td>5.19</td>
</tr>
<tr>
<td><strong>Industrial</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syncrude B</td>
<td>0.34</td>
<td>0.86</td>
<td>1.18</td>
<td>4.28</td>
</tr>
<tr>
<td>Syncrude D</td>
<td>0.84</td>
<td>0.58</td>
<td>0.70</td>
<td>2.22</td>
</tr>
</tbody>
</table>
From Table 5-8, all the fresh, aged and industrial deposits have a little moisture (<1%). Experimental results also indicate that the fresh deposits have about 17~25 wt% volatile components up to 1000°C. For the aged deposits, there are much less volatile components (4~11 wt % at 1000°C) than the fresh ones. The industrial samples have much less volatile components
(2~4%) than the laboratory samples and are close to aged deposits from the laboratory unit. This is because industrial samples have much longer aging time, which leads to heavier non-volatile components in the deposits.

From the Fig. 5-11~5-13, it can also be observed that the TGA weight loss for one or two days aged deposits are much lower than those of fresh deposits at 550, 750 and 1000°C. For example, the weight loss of fresh deposits at 500°C dropped from 5~11% to less than 2%; the weight loss at 750°C dropped from 12~16% to 1~5%; and the weight loss at 1000°C from 17~24% dropped to 4~11% after aging one or two days. For one specific deposit aged over one or two days, the TGA weight loss at 550, 750 and 1000°C does not change much. This is in line with above H/C atomic ratio and TGA aging study results. During the aging process, most volatile components are released in the first aging period, and it is the main reason for the dramatic H/C ratio decrease of aged deposits.

5.6 The Morphology of the Fresh and Aged Deposits

The SEM pictures of fresh deposits, 5 hours, 12 hours, 1 day, 3 days, 13 days, and 20 days aged deposits of Run B30 are given in Fig. 5-14~5-20, respectively. For the fresh Run B30 deposits, the platelet deposits are predominant, although amorphous deposits also exist in the deposits. As discussed in Chapter 4, the low viscosity and high wettablility of condensed tar droplet apparently cause platelet features to be predominant at high temperatures (>500°C). However, from Fig. 5-14~5-20, it seems that there are additional amorphous features produced along with the aging time. This indicates that volatile components in the deposits are thermally cracked and released during the aging process, and part of them are re-condensed or adsorbed on the deposit surface to cause the different morphology of deposits formed. The low wettability of glass tube wall and deposit surface, the stagnant gas atmosphere in the sealed reactor appear to result in the new deposits being mainly amorphous, although the temperature is quite high in the
aging process and the re-condensed or absorbed droplets would have a relatively low viscosity. Fig. 5-21~5-24 are magnified SEM pictures of Run B30 aged deposits, it can be seen that most of them are bead-like or fluffy deposits, which support the re-condensation or absorption mechanism for the formation of amorphous deposits in the furnace aging process. Furthermore, other chemical reactions might also occur during long time aging process, because conglomeration of deposits was observed for all above aged samples (as one of examples, see Fig. 5-26).

Fig. 5-14 SEM of Fresh Deposits (Run B30, Tw=500°C)

Fig. 5-15 SEM of Deposits after Aged 5 Hours (Run B30)
Fig. 5-16 SEM of Deposits after Aged 12 Hours (Run B30)

Fig. 5-17 SEM of Deposits after Aged 24 Hours (Run B30)
Fig. 5-18 SEM of Deposits after Aged 3 Days (Run B30)

Fig. 5-19 SEM of Deposits after Aged 13 Days (Run B30)
Fig. 5-20 SEM of Deposits after Aged 20 Days (Run B30)

Fig. 5-21 Magnified SEM of the 5-hour-aged Deposits (Run B30)
Fig. 5-22 Magnified SEM of the 3-day-aged Deposits (Run B30)

Fig. 5-23 Magnified SEM of the 13-day-aged Deposits (Run B30)
For the fresh laboratory deposits of Run B19, B20 and Run B40, the amorphous deposits are already predominant in all three samples as shown in Fig. 4-2-4-4 in Chapter 4. Fig. 5-26~5-29 are representative SEM pictures of aged deposits of Run B19, B20 and B40, the other similar
ones are given in Appendix 5. Similar to the aged deposits of Run B30, more amorphous features were produced at long aging time for the deposit samples collected at much lower temperatures (<450°C). Thus the morphology of aged deposits does not change much compared with the fresh one (See Fig.4-2~4-4). Fig. 5-30~5-32 are the representative magnified SEM pictures of aged deposits, the other similar ones are given in Appendix 5. Bead-like droplets or fluffy deposits can be observed on the surface of the aged deposits. All these substantiate the view that volatile components are released and thermally cracked during aging process, and then re-condensed or adsorbed at the deposits surface to cause amorphous bead-like or fluffy deposits, because of the low wettability of glass tube wall and deposits surface. However, no obvious conglomeration phenomena were observed for all the aged deposits of Run B19, B20 and Run B40.

![SEM of one-day-aged deposits (Run B19)](image)

**Fig. 5-26 SEM of one-day-aged deposits (Run B19)**
Fig. 5-27 SEM of eight-day-aged deposits (Run B19)

Fig. 5-28 SEM of 18 Days Aged Deposits (Run B20)
Fig. 5-29 SEM of 24 Days Aged Deposits (Run B40)

Fig. 5-30 Magnified SEM of the 8-day-aged deposits (Run B19)
Fig. 5-31 Magnified SEM of the 23-day-aged deposits (Run B20)

Fig. 5-32 Magnified SEM of the 24-day-aged deposits (Run B40)
5.7 DRIFT Analysis Comparison of Fresh and Aged Deposits

5.7.1 DRIFTs of Fresh and Aged Deposits with Different Aging Time

The DRIFT spectra of fresh and aged deposits of Run B20 (aged 1, 10, 18 and 23 days) are given in Fig. 5-33 and 5-34, respectively. Only the frequency regions which have characteristic absorptions are shown in the DRIFT spectra. For one-day-aged deposits, it can be observed that paraffinic bands 2800-3000\text{cm}^{-1} for C-H stretching vibration of -CH$_3$ or -CH$_2$- group almost cannot be noticed, but $\delta$C-H in aromatics 3050\text{cm}^{-1} still remains very strong; coke band remains strong, but shifts from 1598\text{cm}^{-1} to a lower wavenumber 1594 \text{cm}^{-1}. The detailed asymmetric and symmetric bend vibrations of -CH$_3$ or -CH$_2$- in the region of C-H bending vibrations (1300-1500\text{cm}^{-1}) cannot be differentiated, and become two broad adsorption centered at the frequency of 1424 and 1340\text{cm}^{-1}. All these observations indicate that most volatile components, mainly paraffinics which have a high H/C ratio, are thermally cracked and released at high temperatures during the first aging day. The shift of coke band to a lower number indicates more polyaromatic structures are formed during the aging process at high temperatures. The aged deposits have more polyaromatic characteristics, and the conjugative effects of polyaromatic compound because of the delocalization of the $\pi$ bands cause the wave number shift to a lower number [128, 129]. The same phenomenon was also observed by Rozwadowski et al. [64] and Eberly [127] when studying the coke structures on catalytic processes by IR spectroscopy. As well, it can be further noticed that, for one-day-aged deposits, the absorption at the frequency of 873 \text{cm}^{-1} in the fingerprint region, which is possibly caused by C-H out-of-plane bending vibrations of isolated hydrogen [128], becomes much stronger and shifts to a higher frequency compared with fresh deposits. The absorptions at the frequency of 814 \text{cm}^{-1} and 755 \text{cm}^{-1}, which are possibly caused by C-H out-of-plane bending vibrations of 2 and 4 adjacent hydrogenation
atoms respectively [128], become a little weaker compared with the fresh deposits. This suggests that dehydrogenation reactions took place in the aging process.

Fig. 5-33 DRIFTs Comparison of Fresh and Aged Laboratory Deposits (Run B20)

Fig. 5-34 DRIFTs of Aged Laboratory Deposits (Run B20)
The DRIFT spectra of 10, 18, and 23 days aged deposit are similar with one-day-aged deposits: no absorption can be observed in paraffinic bands in the region of 2800-3000cm\(^{-1}\); \(\delta_{\text{C-H}}\) in aromatics 3050cm\(^{-1}\) become weaker and weaker with the aging time going on; and the coke band shift to a further lower wave number for longer aged deposits. The shifts of coke band wave number with the aging time of Run B20 are given in Table 5-9. All these experimental results indicated that more volatile compound released during the aging process; slow chemical reactions (e.g., cracking, dehydrogenation, cyclization, skeleton re-arrangement, etc.) took place and produced more condensed polyaromatic structures with the aging time proceeded.

**Table 5-9 Shifts of Coke Band Frequency with the Aging Time (Run B20)**

<table>
<thead>
<tr>
<th>Aging Time (Days)</th>
<th>Fresh</th>
<th>1</th>
<th>10</th>
<th>18</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave Number (cm(^{-1}))</td>
<td>1598</td>
<td>1594</td>
<td>1591</td>
<td>1585</td>
<td>1580</td>
</tr>
</tbody>
</table>

The Kubelka-Munk model incorporates several requirements regarding the sample [132]. These assumptions are that the scattering coefficient is essentially constant throughout the sample, the front surface reflectance is minimized, the sample is infinitely thick, and the illumination of the samples is isotropic. These assumptions must be fulfilled as closely as possible to apply Kubelka-Munk theory. For all aged deposits, their packing density, grain size and isotropic properties are all changed, and thus the baselines of DRIFT spectra for all aged deposits are slanted compared with that of fresh deposits.

Fig. 5-35 and 5-36 are the comparison of DRIFT spectra of fresh, and aged laboratory deposits for Run B30. Similar results with those of Run B20 can be observed from the DRIFT spectra for deposits Run B30 after aging 5, 12, 24 hours, 3, 10 and 20 days. There is a big difference between 5 hours aged deposits and fresh laboratory deposits. The paraffinic bands 2800-3000cm\(^{-1}\) and \(\delta_{\text{C-H}}\) in aromatics 3050cm\(^{-1}\) become weaker for those with the longer aging
time, and the coke band remains strong but shifts to a lower wavenumber as the aging time proceeded, which indicates that the deposits have more polyaromatic characteristics with the time increases. As well, for aged deposits, the absorption at the frequency of $873\text{cm}^{-1}$ at fingerprint region becomes much stronger and shifts to a higher frequency compared with fresh deposits, which suggests that dehydrogenation reactions took place in the aging process. The same phenomena also can be observed for the fresh and aged deposits of Run B19 (Fig. 5-37). The shifts of coke band of run B19 and Run B30 with the aging time are given in Table 5-10 and 5-11, respectively.

<table>
<thead>
<tr>
<th>Table 5-10 Shifts of Coke Band Frequency with the Aging Time (Run B 19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging Time (Days)</td>
</tr>
<tr>
<td>Wave Number (cm$^{-1}$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5-11 Shifts of Coke Band Frequency with the Aging Time (Run B 30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging Time</td>
</tr>
<tr>
<td>Wave Number (cm$^{-1}$)</td>
</tr>
</tbody>
</table>

In general, the DRIFT studies indicate that the aged deposits have a more typical condensed polyaromatic structures compared with fresh deposits for reasons given above. These results are consistent with elemental analysis and TGA experiments. All above experimental results substantiate the view that most volatile compounds with high H/C ratio are released during the first aging period, and thus first-period-aged deposits show a much different characteristic than fresh deposits. With increasing aging times, slow chemical reactions for condensed polyaromatic structures formation still go on and produce more condensed polyaromatic structures in the deposits.
Fig. 5-35 DRIFTs Comparison of Fresh and Aged Deposits (Run B30)

Fig. 5-36 DRIFTs Comparison of Deposits (Run B30)
5.7.2 DRIFT Spectra Comparison of Fresh and TGA Aged Deposits

To investigate the structure and composition changes for the deposits in the early stage, the DRIFT spectra of fresh, 10min-aged, and 12 hour-aged deposits in the TGA are compared with each other. The comparison of DRIFTs spectra of Run B19, Run B20 and Run B30 with different aging times were given as Fig. 5-38–5-40, respectively. The shifts of coke band with aging time are given in Table 5-12.

### Table 5-12 Shifts of Coke Band with the Aging Time (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fresh</th>
<th>Aged 10 min</th>
<th>Aged 12 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run B19</td>
<td>1598</td>
<td>1598</td>
<td>1592</td>
</tr>
<tr>
<td>Run B20</td>
<td>1598</td>
<td>1598</td>
<td>1588</td>
</tr>
<tr>
<td>Run B30</td>
<td>1600</td>
<td>1598</td>
<td>1592</td>
</tr>
</tbody>
</table>
Chapter 5 Aging Study of Fresh Deposits from Laboratory Fluid Coker Unit

Fig. 5-38 DRIFTs Comparison of Fresh and TGA Aged Deposits (Run B19)

Fig. 5-39 DRIFTs Comparison of Fresh and TGA Aged Deposits (Run B20)
From the experimental results, it can be noted that the paraffinic bands (2800–3000 cm\(^{-1}\)) become much weaker when the temperature was ramped to 550°C for 10 min compared with the fresh deposits for Run B19 and B20, and the absorption at 1376 cm\(^{-1}\), which are due to symmetric bending vibration of \(-\text{CH}_3\), is very weak compared with fresh deposits. For Run B30, the paraffinic bands even almost cannot be noticed after the sample was kept at 550°C for 10 min, but the coke band is still at ca. 1600 cm\(^{-1}\). All these indicated that there are still obvious paraffinic components in all the deposits until this moment, although considerable volatile paraffinic components are released during the heating period from ambient to 550°C.

After the deposits were kept at 550°C for 12 hours in the TGA, the paraffinic bands (2800–3000 cm\(^{-1}\)) disappeared for all the deposit samples, and the coke band shifted to a much lower wave number (see Table 5-12), which indicates a much more polyaromatic characteristics. This suggests that after the deposits heating to 550°C, the paraffinic components continue to be released in the following several hours. However, slow chemical reactions which lead to the
formation of condensed polyaromatic structures are also taking place, and the deposits exhibit more and more polyaromatic characteristics.

5.7.3 Comparison of DRIFT Spectra for Fresh, Aged and Industrial Deposits

As those shown in Fig. 4-36 in Chapter 4, the DRIFT spectra of industrial samples seem much different from laboratory fresh and most aged deposits. The industrial samples indicated typical graphitic structures, and no paraffinic and coke bands show up at all. However, experimental results do indicate that the structures of long time aged laboratory deposits (e.g., about one month aging) can approach those of industrial samples. Fig. 5-41 is the comparison of DRIFT spectra for fresh, aged and industrial deposits, and from which the structure evolution of fresh deposits in the aging process can be clearly observed. In Fig. 5-41, it can be observed that the structure of 24 days aged laboratory deposits is similar to that of Sample B. For both of them, the coke band shifts to a much lower frequency (1587 cm\(^{-1}\)) and has much lower intensity, which indicated more condensed polyaromatic structures; the stretching vibration of C-H for aromatics are all very weak and almost cannot been noticed; the bend vibration of C-H for paraffinics cannot be differentiated and indicate a small bump at the region of 1300~1500 cm\(^{-1}\); the weak absorptions in fingerprint region indicate dehydrogenation reaction took place in the aging process.

Based on all above experimental results, the structural evolution of the deposits during aging process can be expressed as the follows: for the fresh deposits, which indicate typical paraffinic and polyaromatic structures, the long paraffinic chains which are either initially present or exist as the side chain of aromatics, crack and release in the first aging period (with 1~2 days) at high temperatures. This leads to a typical semi-polyaromatic structure for the aged deposits, which still show a little paraffinic structure but more polyaromatic characteristics. In the following aging period, slow chemical reactions, i.e., dehydrogenation, cyclization, skeleton
re-arrangement, etc., take place and cause more and more condensed polyaromatics formed in the deposits. Dehydrogenation and skeleton re-arrangement reactions take place in all the aging process and cause more and more graphitic structures in the deposits.

**Fig. 5-41 DRIFT Spectra of Fresh, Aged and Industrial Deposits**

**5.8 Solid Sate $^{13}$C NMR Spectra of the Aged Laboratory Deposits**

The quantitative solid-state $^{13}$C NMR spectra of 2-day-aged and 24-day-aged deposits are given in Fig. 5-42 and 5-43, respectively. The instrumental conditions are the same as those of Section 4.6 in Chapter 4, and single pulse excitement (SPE) method was used to obtain quantitative data. It can be observed that the NMR spectra of both aged deposits exhibit a broad peak in the chemical shift range 50–220 ppm centered at 128 ppm, which mainly correspond to aromatics, although perhaps the small peaks of aliphatics are overlapped by broad signals of aromatics. The broad peak in NMR indicates that the structures in the aged deposits are mainly condensed carbonaceous materials [70, 72]. It also should be noted that the integral intensity of
24-day-aged deposits is much weaker than that of 2-day-aged deposits (16.02×10^7 vs 7.86×10^7), which indicates that there is more NMR invisible graphite in 24-day aged deposits. Using the same method as mentioned in Section 4.6 in Chapter 4, the calculated results of aromatic fraction \( f_a \), aliphatic fraction \( f_p \) and graphitic fraction \( f_G \) for two aged laboratory deposit are given in Table 5-13, and compared with fresh and industrial samples. Two circumstances are assumed in the calculation when using fresh deposits as reference standard (84.89 wt%, carbon content): no graphitic carbon or 40 wt% graphitic carbon in the fresh deposits. The comparison of fresh, aged, and industrial quantitative 13C NMR spectra are given Fig. 5-44.

**Table 5-13 Spectrum Integral Intensity of Different Deposits and Their Corresponding Relative Contents**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectrum intensity</th>
<th>Case 1(^*)</th>
<th>Case 2(^**)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aromatics aliphatics</td>
<td>C_{rea}%</td>
<td>C_{NMR}%</td>
</tr>
<tr>
<td>B40 fresh</td>
<td>134899554 3201881</td>
<td>84.89</td>
<td>84.89</td>
</tr>
<tr>
<td>B40 aged 2 days</td>
<td>160175459 0</td>
<td>86.70</td>
<td>98.46</td>
</tr>
<tr>
<td>B40 aged 24 days</td>
<td>78634446 0</td>
<td>85.51</td>
<td>48.69</td>
</tr>
<tr>
<td>Sample B</td>
<td>90431048 0</td>
<td>88.75</td>
<td>42.88</td>
</tr>
<tr>
<td>Sample D</td>
<td>929407 0</td>
<td>87.85</td>
<td>0.57</td>
</tr>
</tbody>
</table>

\(^*\) Case 1: assuming no graphitic carbon in fresh deposits; \(^**\) Case 2: assuming 40% graphitic carbon in fresh deposits

From Table 5-13, for 2 day aged deposits, the \(^{13}\text{C} \) NMR detected carbon is similar to that of fresh deposits in both calculation cases, but without aliphatic carbons in the aged deposits. For 2-day-aged deposits, it can be noted that the \(^{13}\text{C} \) NMR detected carbon is 13.5 wt% higher than that of the elemental analysis results. This is reasonable considering that there are about 10% errors for \(^{13}\text{C} \) NMR quantitative analysis, and the integral errors caused by non-well resolved broad NMR spectra peak. However, for 24-day-aged deposits, more graphitic structures are formed
during long aged periods, and their structure are similar with industrial Sample B: 40–60 wt% graphitic structures in both of the deposits.

Fig. 5-42 Quantitative $^{13}$C NMR of Aged Laboratory Deposits (2 day aged, Run B40)

Fig. 5-43 Quantitative $^{13}$C NMR of Aged Laboratory Deposits (24 day aged, Run B40)
Fig. 5-44 Comparison of Quantitative $^{13}$C NMR of Fresh, Aged and Industrial Deposits

Generally, it can be concluded from $^{13}$C NMR analytical results that the structure of short time aged laboratory deposits is similar to fresh deposits except that the aged deposits have less aliphatic structures. For the long time aged laboratory deposits, their structure can be similar with industrial samples: graphitic structures dominate in both. This is consistent with the results of DRIFT analysis.

5.9 Solvent Extraction for Soluble Components in the Aged Deposits

Chloroform was used as extraction solvent, because it is a much better solvent than toluene and much more deposits can be soluble in it based on the experimental results in Section 4.7. It is also much easier to be evaporated from residue deposits than other solvents. A 125ml Soxhlet apparatus is employed for the extraction process. About 0.1000g of 11-day-aged deposits (Run B40) were used for extraction. The detailed experimental procedures are given in the Section 3.4.1. It can be noted that there is almost no color change for the 11-day-aged deposits during
extraction process, and their soluble fraction in the chloroform after 24 hours extraction is less than 0.05 wt%. This is consistent with abovementioned results of DRIFT and $^{13}$C NMR, and all of them indicate that there are much more condensed structures in long time aged deposits, similar with industrial samples.

![Boiling Point Distributions of Extracts from 11-day-aged Deposits (Run B40)](image)

**Fig. 5-45 Boiling Point Distributions of Extracts from 11-day-aged Deposits (Run B40)**

The boiling point distribution by simulated simulation of soluble components in chloroform for 11-day-aged deposits are given in Fig. 5-45. It can be noted that there are many heavy components in the extracts for 11-day-aged deposits: there are over 95 wt% whose boiling points are higher than 750°C. This indicates that almost all the structure in the long time aged laboratory deposits is condensed polyaromatics, even in the solvent soluble fractions. In Section 4.7.1, it was noticed that there are more soluble fractions and more lower boiling point components in the extracts of industrial deposits than those of long time aged laboratory deposits. The reason for the presence of a small amount of soluble fractions and low boiling components in the industrial samples, which have already indicated a typical graphitic structure, is attributed to continuous nature of the deposit formation process. There are always a few “new” part of deposits to be condensed on the “old” deposits surface. When the deposits were taken out
of the tube wall, these “new” deposits still have not been aged to polyaromatic or graphitic structures, and these fresh formed deposits are soluble in the chloroform solvent. TGA aging results (Section 5.4) of industrial samples also support this conclusion; it can be noticed that there are ca. 3% weight loss for the industrial deposits aging in TGA for 12 hours.

5.10 Summary of Laboratory Deposits Aging Study

Based on the experimental results of laboratory deposit aging study, the following conclusions can be drawn:

1. Elemental analysis results from furnace aging tests indicate that the H/C atomic ratio of fresh laboratory deposit with H/C~0.6 decreases dramatically to H/C~0.3 during the first day of aging, and then does not change much. For the aged deposits, the H/C atomic ratios approach those of industrial deposits. The release of volatile components which have a higher H/C atomic ratio must be the main reason to cause much lower H/C atomic ratio of aged deposits, and this process mainly happened in the first aging period.

2. SEM experimental results indicated that deposits are more amorphous with increased aging time. This probably means that some volatile components evolved during the aging process, thermally cracked and then re-adsorbed at the deposit surface to cause amorphous bead-like or fluffy droplets under stagnant atmosphere because of the low wettability of the glass tube wall and the deposit surface.

3. TGA results indicate thermal properties of aged deposits from laboratory units have a close resemblance to those of the industrial samples. The weight loss tests substantiate the elemental analysis from the furnace aging test. In the first several hours of aging, weight loss is mainly caused by the release of higher H/C ratio volatile components, which leads to dramatic H/C atomic ratio drops for the aged deposits. In the following aging time, the weight of deposits decreases gradually at a very low rate.
4. DRIFT experimental results substantiate the TGA and elemental analysis results. The shift of coke band wave number to lower values indicates that chemical reactions for the formation of condensed polyaromatics took place in the deposits as the aging time proceeded. The long time aged laboratory deposits indicate a typical graphite characteristic, which structure is similar with those of industrial samples.

5. Solid-state quantitative $^{13}$C NMR analytical results indicate that the structure of short time aged laboratory deposits is similar to fresh deposits except that the aged deposits have less aliphatic structures. For the long aged laboratory deposits, their structure can be similar with industrial samples: graphitic structures dominate in both of them.

6. Solvent extraction indicates that there is almost no soluble portion for the long time aged laboratory deposits, but a small soluble portion exists in the industrial samples. This suggests that polyaromatic deposits were formed during long aging time, and deposits formation is possibly a continuous process. In industrial operation conditions, there are always some fresh deposits to be condensed on the “old” deposit surface.

7. The structural evolution of the deposits can be expressed as the following: At high temperatures, fresh deposits (soft coke) which have some obvious paraffinic structures and polyaromatic characteristics first, through release of volatile components by thermal cracking of long aliphatic chains in the deposits, form semi-polyaromatic deposits which still show a little paraffinic structure but more polyaromatic characteristics, and then slow chemical reactions, such as cyclization, dehydrogenation, skeleton re-arrangement, etc. become predominant to cause more and more polyaromatic structures (hard coke). Dehydrogenation and re-arrangement reactions take place throughout the aging process and cause more and more graphitic structures in the deposits.
Chapter 6 Kinetic Models for Aging of Deposits at High Temperatures

During aging of cyclone fouling deposits, the composition and structure of deposits change with the time. As described in Chapter 5, a considerable amount of volatile components were released with increasing aging time, especially during the initial aging period. This process includes complex chemical reactions, such as thermal cracking, dehydrogenation, cyclization, skeleton re-arrangement, etc., and finally leads to more condensed polyaromatic and graphitic structures. Therefore, the reaction process is quite complex, and no mechanism and kinetics has been proposed in the literature for deposit aging. Previous analysis results by elemental analysis, TGA, DRIFT, $^{13}$C NMR, etc. indicate that the fresh laboratory deposits are composed mostly of fused aromatic rings carrying some aliphatic chains, which can be cracked, and volatilize at high temperatures, as in a pyrolysis process. In this chapter, the deposit aging kinetics will be studied through thermogravimetric analysis.

6.1 Experimental Methods

An aging study was carried out using a TGA on 5–10 mg samples under nitrogen with a flow rate 50 ml/min as in Chapter 5. The temperature was first ramped to 550°C from ambient temperature at a heating rate of 10°C/min, and then kept at 550°C for 8~12 hours. To investigate deposit aging kinetics at different temperatures, final aging temperatures of 500°C and 600°C were also studied. The weight changes of the sample were recorded on line, and the recorded data were analyzed by TA60 software.

In addition to examining the difference between the fresh deposits and industrial samples, thermogravimetric measurement were also made on pre-aged deposits, which had been collected from Run B40 and then placed at 550°C under nitrogen atmosphere in a muffle oven for different times (2, 11 and 24 days). These samples appeared to represent material whose structure and
composition were between the fresh lab deposits and graphitic plant deposits. The detailed pre-
aging procedures were given in Section 3.5, Chapter 3.

6.2 Experimental Samples

As those in Chapter 5, fresh deposit samples (Run B19, Run B20, Run B30 and Run B40) from the long exit tube were collected from the UBC fluid coker cyclone fouling unit after running six hours. Sample B19 and B20 are deposits from bitumen feed ATB-A, and Sample B30 and B40 are from bitumen ATB-B, in which the ATB-A has much more heavy fractions, more carbon residue and lower H/C atomic ratio. The corresponding operation conditions of each run are given in Table 5-1 in Chapter 5. Deposit B and D are industrial samples provided by Syncrude Canada, Ltd.

6.3 TGA Experimental Results

6.3.1 Fresh Laboratory Deposits

The changes of volatile components \((V^*-V, \%)\) in the different laboratory fresh deposits with the time and temperature during the total TGA aging period are given in Fig. 6-1, in which the final aging temperature is 550°C. Fig. 6-2 gives details of volatile component changes with the temperature during heat-up period from ambient to 550°C at a heating rate 10°C/min, which needs about 50 minutes, and Fig. 6-3 demonstrates the detail of the volatile component changes with aging time at long time isothermal (550°C) aging period. In these figures, \(V^*\) is the maximum volatile content released at final aging time in each designated stage, and \(V\) is the volatile content released at any given time \(t\). Thus,

\[
V^* = \frac{W_0 - W_f}{W_0} \times 100\% \quad (6-1)
\]

\[
V = \frac{W_0 - W_t}{W_0} \times 100\% \quad (6-2)
\]
Where $W_t$ is the sample weight at the time $t$, and $W_0$ is the sample initial weight, $W_f$ the sample weight at the final time of each stage.

Fig. 6-1 shows that the deposits from the same bitumen feed have similar response to thermal treatment, and there is a notable difference between the deposits from different bitumen feeds. For example, deposit samples Run B19 and B20, from the heavier bitumen feed (ATB-A), exhibits similar thermal characteristics; Run B30 and B40, which are collected from the lighter feed ATB-B, demonstrate similar thermal characteristics but different with those of Run B19 and B20. This difference exists in spite of the similar H/C ratios (Table 5-2A). This conclusion can be more clearly seen in Fig. 6-2 and Fig. 6-3, where the heating period and isothermal aging period are plotted separately. Run B19 and B20 release more volatile components in the heating period, but less volatile components in the isothermal aging period at 550°C compared with those of Run B30 and B40. The quantitative data are given in Table 6-1, in which the comparison of maximum volatile components $V^*$ (%) of different deposits in different periods are listed. The small discrepancy between Run B30 and B40 in heating period is perhaps because the Run B30 was collected from a much higher temperature (520°C).

On the other hand, all deposit samples have some common characteristics. In Fig. 6-1, the shapes of all the curves are basically similar; there is a dramatic drop for the volatile components which occurs at the temperature around 550°C. The drop is much sharper for the deposits of Run B19, and B20. The maximum volatile contents $V^*$ of all the samples are similar, which is in the range of 12–14 wt%, as given in Table 6-1. In Fig. 6-2, for all the samples, it can be observed that there is a short period in which the amount of volatile components does not change with the temperature, i.e., 150–200°C. After this period, the volatile components begin to decline, first at slow rate, and then drop sharply. In Fig. 6-3, during the long isothermal aging period, the amount
of volatile components declines dramatically with the aging time in the initial periods, and then it declines at a near constant rate.

Fig. 6-1 Changes of Volatile Components in Different Fresh Deposits with Aging Time in the TGA

Fig. 6-2 Changes of Volatile Components with the Temperature in Heating Periods
Fig. 6-3 Changes of Volatile Components with the Time in Aging Period at 550°C

Table 6-1 Maximum Volatile Components in Different Aging Stages of Different Samples

<table>
<thead>
<tr>
<th>Feed</th>
<th>Sample</th>
<th>$V^*_{\text{heating}}$ (wt%)</th>
<th>$V^*_{\text{aging}}$ (wt%)</th>
<th>$V^*_{\text{total}}$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run B19</td>
<td>7.55</td>
<td>5.18</td>
<td>12.73</td>
</tr>
<tr>
<td>ATB-A</td>
<td>Run B20</td>
<td>8.43</td>
<td>5.87</td>
<td>14.16</td>
</tr>
<tr>
<td></td>
<td>Run B30</td>
<td>7.05</td>
<td>6.12</td>
<td>13.17</td>
</tr>
<tr>
<td>ATB-B</td>
<td>Run B40</td>
<td>6.04</td>
<td>7.11</td>
<td>13.15</td>
</tr>
</tbody>
</table>

For fresh deposits Run B20 and B40, different final aging temperatures, 500 and 600°C, were also studied in addition to the data at 550°C described above. In this case, the deposits were only aged for 8 hours rather than 12 hours at final temperatures. The changes of volatile components in deposits with the time and temperature during TGA aging process are given in Fig. 6-4, in which only 8 hours aging data were provided for those aging at 550°C. Table 6-2
gives the comparison of maximum volatile contents in different designated stages for deposits aging at different final temperatures for 8 hours. For both samples, there is a bigger volatile component content in both total heating period and aging period when there is a higher final aging temperature. However, there is not much difference for the volatile components in isothermal aging period for the deposits aging at different temperatures.

![Graph showing changes of volatile components with aging time when deposits aging in different final temperatures for 8 hours.]

**Table 6-2 Maximum Volatile Components in Different Aging Stages of Different Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run B20</th>
<th>Run B40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500°C</td>
<td>550°C</td>
</tr>
<tr>
<td>V*&lt;sub&gt;heating&lt;/sub&gt; (%)</td>
<td>5.55</td>
<td>8.34</td>
</tr>
<tr>
<td>V*&lt;sub&gt;aging&lt;/sub&gt; (%)</td>
<td>5.44</td>
<td>4.92</td>
</tr>
<tr>
<td>V*&lt;sub&gt;total&lt;/sub&gt; (%)</td>
<td>11.99</td>
<td>13.26</td>
</tr>
</tbody>
</table>
6.3.2 Pre-aged Laboratory and Industrial Deposits

The laboratory pre-aged samples have been shown (Chapter 5) to have properties between fresh deposits and industrial deposits. The changes of volatile components in the different laboratory pre-aged deposits (Run B40) with the time and temperature during TGA aging process are given in Fig. 6-5. Almost no volatile components are released during the heating periods, except for the 2-day-aged deposits, which has very few (<0.1%). This indicated that there are almost no chemical reactions taking place below the temperature of 550°C. For the isothermal aging period at 550°C (which is the temperature of pre-aging), the volatile components decline gradually at a near constant rate. For the low H/C materials (H/C ~0.25) the volatilization is much lower than that of the fresh deposits (H/C ~0.60).

![Fig. 6-5 Changes of Volatile Components in Pre-aged Deposits with Aging Time in TGA](image)

The maximum volatile components of each aged sample in the final time are given in Table 6-3. It can be seen that there are much less volatile components (ca. 4–5%) in the aged deposits compared with those of fresh deposits (ca.13–14%). This means that much volatile components
were released or changed into non-volatile components in the long pre-aging time at high temperatures in the muffle oven, but there are still some volatile components left in the deposits after the long time pre-aging.

**Table 6-3 Maximum Volatile Components in Different Aged Deposits (Run B40)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aged 2 days</th>
<th>Aged 11 days</th>
<th>Aged 24 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^*_{total}$ (%)</td>
<td>5.73</td>
<td>4.03</td>
<td>5.21</td>
</tr>
</tbody>
</table>

Fig. 6-6 gives the changes of volatile components in the industrial deposits with the time and temperature during the TGA aging process. A very small quantity of volatile components are released in the heating period from ambient to 550°C, 1.72% and 0.66% for sample B and D, respectively. Just as explained in Chapter 5, this is perhaps because there are always some fresh deposits formed on the surface of “old” deposits, and this new surface has some paraffinic structures which can lead to thermal cracking reactions taking place. The total maximum volatile components for sample B and sample D in the whole aging period are 4.23% 2.40% respectively, which are close to those of the samples pre-aged for 11 and 24 days (Table 6-3).

![Fig. 6-6 Changes of Volatile Components in Industrial Deposits with Aging Time in TGA](image-url)
6.4 The Methodology of Kinetic Models for Deposits Aging

Typical experimental results for fresh laboratory deposits are illustrated in Fig. 6-7. During the heating period (Region 1) from ambient to final temperatures (ca. 0–50 min), a non-isothermal kinetic model, which is widely used in pyrolysis processes, will be used. At the final temperatures, two regions are evident. In Region 2, the amount of volatile components declines dramatically with time (ca. 50–200 min), and then in Region 3 at longer times (>200 min) the volatile components decline at a near constant rate. Thus, two different isothermal kinetic models will be applied to characterize Region 2 and 3. However, for the aged and industrial deposits, only Region 1 and 3 were evident.

![Fig. 6-7 Different Kinetic Models and Their Corresponding Reaction Time Regions](image-url)
6.5 Kinetic Models in Heating Periods

6.5.1 Introduction to Non-isothermal Overall First Order Reaction Model

The overall first order reaction mechanism is widely used to describe pyrolysis processes of coal, oil shale, bitumen, biomass and other hydrocarbons, due to its mathematical simplicity [133-135]. This model assumes that devolatilization takes place as a single first-order reaction at a rate proportional to the remaining volatile content \((V^* - V)\). The mechanism does not change during pyrolysis. The general expression for the first-order mechanism is given as:

\[
\frac{dV}{dt} = k_0 \exp^{-E_a/RT} (V^* - V) \tag{6-3}
\]

Under the nonisothermal conditions employed in the TGA experiments, the temperature at any time during the heating period is given by the following expression:

\[
T = Ct + T_0 \tag{6-4}
\]

where \(T_0\) is the initial temperature of the experiment, and \(C\) is the heating rate. Substituting the time differential \(dt\), with the temperature differential \(dT\), i.e. \(dT = Cdt\), the general expression is then given as:

\[
\frac{dV}{dT} = \frac{k_0}{C} \exp^{-E_a/RT} (V^* - V) \tag{6-5}
\]

A number of methods have been suggested to extract values of \(k_0\), and \(E_a\) for Equation (6-5) from experiments in which \(V\) is measured as a function of \(T\) at a constant heating rate. These methods are summarized in Appendix 6, and their key equations are listed in Table 6-4. In this table, \(Y\) represents the function for each model which should give a linear plot with \(1/T\) to yield the activation energy.

In the Coats-Redfern method, it is assumed that the activation energy \(E_a \gg 2RT\), which is a special case of the integral method and may not be valid in this case. For the Friedman model, it
is very easy to lead to erroneous kinetic parameters when differentiating the raw TGA data. Thus, the above two methods will not be applied to our cases. The more complex Anthony and Howard model which allows for a distribution of activation energy, includes a very cumbersome mathematical operation, and was found not suitable to the pyrolysis of pitch from heavy oil upgrading process [133], and so is also avoided here. Therefore, only the integral method and Chen-Nuttall method are applied to the aging process of cyclone fouling deposits.

**Table 6-4 Summary of the Analysis Methods Used in Constant Heating Rate Pyrolysis [133]**

<table>
<thead>
<tr>
<th>Method</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integral [135,136]</td>
<td>$Y = \ln(\frac{-C \ln(1 - \frac{V}{V^*})}{RT^2}) - \ln(1 - \frac{2RT}{E_a}) \approx \ln \frac{k_0}{E_a} - \frac{E_a}{RT}$ (6-6)</td>
</tr>
<tr>
<td>Coats- Redfern[137]</td>
<td>$Y = \ln(\frac{-C \ln(1 - \frac{V}{V^*})}{RT^2}) \approx \ln \frac{k_0}{E_a} - \frac{E_a}{RT}$ (6-7)</td>
</tr>
<tr>
<td>Friedman [138]</td>
<td>$Y = \ln(\frac{C}{V} \frac{dV}{dT}) - \ln(1 - \frac{V}{V^*}) = \ln k_0 - \frac{E_a}{RT}$ (6-8)</td>
</tr>
<tr>
<td>Chen-Nuttall [139]</td>
<td>$Y = \ln(\frac{-C(E_a + 2RT)}{RT^2} \ln(1 - \frac{V}{V^*})) = \ln k_0 - \frac{E_a}{RT}$ (6-9)</td>
</tr>
<tr>
<td>Anthony-Howard [140]</td>
<td>$V = V^*(1 - \frac{1}{\sigma(2\pi)^{0.5}} \int \exp{\frac{k_0 RT^2}{CE_a} (\exp(-\frac{E_a}{RT}) (1 - \frac{2RT}{E_a}))}$ (6-10)</td>
</tr>
</tbody>
</table>

$$\exp[-0.5\left(\frac{E_a - E_{a0}}{\sigma}\right)^2]dE_a$$
6.5.2 Testing of Overall First Order Reaction Model of Integral and Chen-Nuttall Methods

Both the integral and Chen-Nuttall methods were used to fit the experimental data. The activation energy $E_a$ and pre-exponential factor $k_0$ was determined for each sample by non-linear multiple regression (Levenberg-Marquart algorithmic analysis) with a MATLAB program (example in Appendix 7), after inputting initial estimates of the two parameters based on the literature [133-135]. The values of $E_a$ and $k_0$ for different samples are listed in Table 6-5, in which the standard variation error $\sigma$ is calculated by the equation (6-11), where $V_{i,exp}$ is the experimental volatile content, $V_{i,fit}$ is the model predicted volatile content at data point $i$ and $n$ is the total number of data points.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (V_{i,exp} - V_{i,fit})^2}{n - 2}}$$ (6-11)

From Table 6-5, for all the fresh deposits, the apparent activation energy falls in a narrow range (22~37 kJ/mol). The range of apparent pre-exponential factors is wider (1~30 min$^{-1}$). There is close agreement between the $E_a$ values obtained in this study and those typically reported for the pyrolysis of pitch, oil shale, etc. (e.g., $E_a$=30~35 kJ/mol, $k_0$=35~150 min$^{-1}$ for pitch pyrolysis) [135,137]. Having obtained the kinetic parameters, the comparison of experimental and predicted volatile contents of different samples, which are calculated by equation (6-12) and (6-13) respectively, can then be given in Fig. 6-8, 6-9 and Fig. 6-11, respectively.

$$V_{\text{integral}} = V^* \left\{ 1 - \exp\left[ -\frac{k_0RT^2}{CE_a} \exp\left( -\frac{E_a}{RT} \right) \left( 1 - \frac{2RT}{E_a} \right) \right] \right\}$$ (6-12)

$$V_{\text{Chen-Nuttall}} = V^* \left\{ 1 - \exp\left[ -\frac{k_0RT^2}{C(E_a + 2RT)} \exp\left( -\frac{E_a}{RT} \right) \right] \right\}$$ (6-13)
Table 6-5 Kinetic Parameters of Overall First Order Reaction for Different Deposits Aging in the Heating Period by Integral and Chen-Nuttall Method

<table>
<thead>
<tr>
<th>Samples</th>
<th>Method</th>
<th>$k_0$ (min$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B19, 550°C</td>
<td>Integral</td>
<td>30.28</td>
<td>36.71</td>
<td>0.0786</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>22.55</td>
<td>35.76</td>
<td>0.0748</td>
</tr>
<tr>
<td>B20, 550°C</td>
<td>Integral</td>
<td>2.84</td>
<td>22.46</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>1.24</td>
<td>20.01</td>
<td>0.0874</td>
</tr>
<tr>
<td>B30, 550°C</td>
<td>Integral</td>
<td>9.96</td>
<td>24.57</td>
<td>0.0165</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>5.31</td>
<td>22.74</td>
<td>0.0196</td>
</tr>
<tr>
<td>B40, 550°C</td>
<td>Integral</td>
<td>13.14</td>
<td>28.51</td>
<td>0.0706</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>8.34</td>
<td>27.15</td>
<td>0.0731</td>
</tr>
<tr>
<td>B20, 500°C</td>
<td>Integral</td>
<td>4.91</td>
<td>23.64</td>
<td>0.0463</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>2.69</td>
<td>21.99</td>
<td>0.0437</td>
</tr>
<tr>
<td>B20, 600°C</td>
<td>Integral</td>
<td>5.21</td>
<td>26.60</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>2.84</td>
<td>24.75</td>
<td>0.112</td>
</tr>
<tr>
<td>B40, 500°C</td>
<td>Integral</td>
<td>12.36</td>
<td>26.33</td>
<td>0.0418</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>7.68</td>
<td>25.00</td>
<td>0.044</td>
</tr>
<tr>
<td>B40, 600°C</td>
<td>Integral</td>
<td>7.89</td>
<td>27.97</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>4.69</td>
<td>26.38</td>
<td>0.059</td>
</tr>
<tr>
<td>Sample B</td>
<td>Integral</td>
<td>6.74</td>
<td>20.37</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>2.62</td>
<td>17.72</td>
<td>0.019</td>
</tr>
<tr>
<td>Sample D</td>
<td>Integral</td>
<td>6.03</td>
<td>15.87</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>0.96</td>
<td>10.87</td>
<td>0.036</td>
</tr>
</tbody>
</table>
Fig. 6-8 Comparison of Model Prediction and Experimental Volatiles for Different Samples with a Final Temperature of 550°C by Single-stage First Order Reaction Model

From Fig. 6-8 and 6-9, it can be observed that the predicted volatile contents at all temperature ranges by both the integral and Chen-Nuttall methods are fitted reasonably well. However, both models failed to accurately predict the volatile contents of fresh deposits Run B19, B20 and B40 at temperatures higher than 350°C, even though the values of kinetic parameters are well within the expected range for hydrocarbon pyrolysis and agree well with the
literature. The discrepancy at high temperatures was also found by Yue [133], Thakur and Nuttall [139], and Schucher [141]. The reason for this is that the chemical nature of the reactants in the sample changes continuously as the pyrolysis progresses. All the above authors reported two sets of kinetic parameters were required to fit their experimental data over the whole range.

Fig. 6-9 Comparison of Model Prediction and Experimental Volatiles for Different Samples with Final Temperature of 500°C and 600°C by Single-stage First Order Reaction Model
In examining the $Y$ values of above fresh samples for each overall single reaction model, it is clear that the relations between $Y$ and $1/T$ are not linear, as shown in Fig. 6-10. Inflection points are observed at $1/T$ value of 0.0014 (ca. 440°C), and the same point was also observed by Yue [133]. Therefore, first order single step reaction models fail to apply over the whole temperature range of the above samples.

Fig. 6-10 Comparison of Model-predicted and Experimental $Y$ Results of Fresh Deposits with a Final Temperature of 550°C by Single-stage First Order Reaction Model
Even though the overall single stage model fails to predict the volatile contents of most fresh deposits at high temperatures, from Fig. 6-11, it can be noted that the both the integral and Chen-Nuttall methods can very successfully predict the volatile contents in all temperature ranges for industrial samples and the fresh deposits of Run B30, which was collected at much higher temperature (520°C) than the others. This suggests that the chemical nature of the reactants in industrial samples and deposits collected at high temperatures does not change much as the pyrolysis progresses, and differs from the chemical nature of the fresh deposits collected at
lower temperatures. One set of kinetic parameters is enough to fit their experimental data over the whole temperature range, from ambient to 550°C.

In examining the Y values of samples B, D and Run B30 for each overall single reaction model, the Y values and 1/T have a good linear relationship, as shown in Fig. 6-12. This suggests that both the single-stage integral and Chen-Nuttall methods can predict the volatile contents of industrial and high temperature lab deposits very well.

Fig. 6-12 Comparison of Model-predicted and Experimental Y Results of Industrial Samples and High Temperature Lab Deposits with a Final Temperature of 550°C by Single-stage First Order Reaction Model
From Table 6-5, it is also notable that when the activation energy $E_a$ is low, the pre-exponential factor $k_0$ is also low. The low values of activation energy would be compensated by low values of the pre-exponential factors to give the same rate constant $k$ value. This mutual dependence of apparent Arrhenius parameters is known as kinetic compensation effect, and will be discussed later in this section.

6.5.3 Two-stage First Order Reaction Model of Integral and Chen-Nuttall Methods

In section 6.5.2, it was noted that overall first order reaction model is not suitable for the fresh lab deposits collected at lower temperatures. From the literature, multi-steps behavior has been clearly identified for the pyrolysis process of oil shale, pitch and heavy residuum fractions [133]. Here, the pyrolysis of fresh cyclone fouling deposits collected at lower temperatures is assumed as a two-step, first order thermal decomposition with regard to the volatile content remaining in the residue. At a critical temperature, the kinetic parameters are assumed to undergo a change as the reaction shifts from one stage to another stage of the pyrolysis process. In each stage, only one type of reaction dominates, and the kinetic parameters remain relatively constant. Thus, each stage of the reaction can be modeled as a single first order reaction. As the reaction proceeds and the temperature increases, the chemical nature of the active reacting matrix gradually undergoes changes due to the depletion of the component which dominated the reaction behavior in that stage. This causes the significant change of the reaction behavior. Based on above analysis in Section 6.5.2, this critical temperature which changes the pyrolysis behavior should be at about 440°C. Then, the two-stage pyrolysis mechanism of fresh laboratory deposits can be expressed as follows,

$$
\frac{dV}{dT} = \sum_{i} C \alpha_i k_{0,i} \exp\left(-\frac{E_{a,i}}{RT}\right)(V^* - V)
$$

where $\alpha_1 = 1$, $\alpha_2 = 0$ when $T < 440^\circ$C, and $\alpha_1 = 0$, $\alpha_2 = 1$, when $T \geq 440^\circ$C.
The TGA data were therefore divided into two stages: stage 1 corresponds to the first stage of the pyrolysis reaction in the temperature range of ambient ~ 440°C, and the stage 2 corresponds to the second stage of reaction in the temperature range of 440°C to the final aging temperatures. Data from each stage were fitted to the model by integral and Chen-Nuttall method; respectively. The calculated kinetic parameters are listed in Table 6-6 for the each sample.

Table 6-6 Kinetic Parameters of Two-stage First Order Reaction for Different Deposits Aging in the Heating Period by Integral and Chen-Nuttall Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>( k_{0,1} ) ( \text{min}^{-1} )</th>
<th>( E_{a,1} ) ( \text{kJ/mol} )</th>
<th>( \sigma )</th>
<th>( k_{0,2} ) ( \text{min}^{-1} )</th>
<th>( E_{a,2} ) ( \text{kJ/mol} )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B19, 550°C</td>
<td>Integral</td>
<td>7.428</td>
<td>30.88</td>
<td>0.011</td>
<td>6.806 ( \times 10^4 )</td>
<td>81.40</td>
<td>0.0031</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>5.252</td>
<td>29.85</td>
<td>0.011</td>
<td>6.284 ( \times 10^4 )</td>
<td>81.08</td>
<td>0.0031</td>
</tr>
<tr>
<td>B20, 550°C</td>
<td>Integral</td>
<td>1.227</td>
<td>19.17</td>
<td>0.023</td>
<td>5.435 ( \times 10^4 )</td>
<td>80.27</td>
<td>0.0057</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>0.513</td>
<td>16.89</td>
<td>0.029</td>
<td>5.005 ( \times 10^4 )</td>
<td>79.93</td>
<td>0.0058</td>
</tr>
<tr>
<td>B40, 550°C</td>
<td>Integral</td>
<td>9.732</td>
<td>26.96</td>
<td>0.068</td>
<td>1.385 ( \times 10^3 )</td>
<td>56.24</td>
<td>0.0076</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>10.516</td>
<td>28.02</td>
<td>0.085</td>
<td>1.167 ( \times 10^3 )</td>
<td>55.55</td>
<td>0.0075</td>
</tr>
<tr>
<td>B20, 500°C</td>
<td>Integral</td>
<td>3.159</td>
<td>22.03</td>
<td>0.020</td>
<td>3.429 ( \times 10^6 )</td>
<td>99.63</td>
<td>0.0044</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>1.733</td>
<td>20.47</td>
<td>0.023</td>
<td>3.268 ( \times 10^6 )</td>
<td>99.44</td>
<td>0.0044</td>
</tr>
<tr>
<td>B20, 600°C</td>
<td>Integral</td>
<td>1.236</td>
<td>20.89</td>
<td>0.026</td>
<td>5.784 ( \times 10^3 )</td>
<td>68.52</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>Chen-Nuttall</td>
<td>0.778</td>
<td>20.05</td>
<td>0.038</td>
<td>5.124 ( \times 10^3 )</td>
<td>68.01</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>Integral</td>
<td>9.237</td>
<td>25.01</td>
<td>0.037</td>
<td>6.875 ( \times 10^4 )</td>
<td>75.75</td>
<td>0.0089</td>
</tr>
<tr>
<td>B40, 500°C</td>
<td>Chen-Nuttall</td>
<td>7.490</td>
<td>24.89</td>
<td>0.044</td>
<td>6.309 ( \times 10^4 )</td>
<td>75.41</td>
<td>0.0089</td>
</tr>
<tr>
<td></td>
<td>Integral</td>
<td>6.469</td>
<td>27.13</td>
<td>0.061</td>
<td>205.68</td>
<td>48.01</td>
<td>0.011</td>
</tr>
<tr>
<td>B40, 600°C</td>
<td>Chen-Nuttall</td>
<td>5.041</td>
<td>26.60</td>
<td>0.065</td>
<td>158.7</td>
<td>46.94</td>
<td>0.010</td>
</tr>
</tbody>
</table>
The values of the kinetic parameters $E_{a,1}$, $k_{0,1}$, $E_{a,2}$ and $k_{0,2}$ determined by both of the two-stage reaction methods are in reasonable agreement. Table 6-6 also indicates the expected significant change of kinetic parameters between the first and second stage reactions. The activation energies of the second stage are about 2~4 times than those of the first stage. The kinetic compensation effects, low activation energy associating with low exponential factor, are also observed in the Table 6-6, and will discussed in detail later.

![Graph](image)

**Fig. 6-13** Comparison of Model Prediction and Experimental Volatiles for Samples with a Final Temperature of 550°C with Two-stage First Order Reaction Model

Having obtained these parameters, the predicted volatile contents were calculated according to both methods, and the predicted results plotted along with the experimental results in Fig. 6-13
and 6-14. Both of the methods have good prediction of the volatile content over the whole range of temperatures for samples of Run B19 and B20. This suggests that both the two-stage integral and Chen-Nuttall models adequately describe the reactions in the above two samples during the heating period. For the sample of Run B40, the predicted and experimental volatile contents are fitted very well except in the range of 250~450°C. Perhaps, more stages are needed to model the sample of Run B40.

![Comparison of Model Prediction and Experimental Volatiles for Samples](image)

**Fig. 6-14 Comparison of Model Prediction and Experimental Volatiles for Samples with a Final Temperature of 500°C and 600°C by Two-stage First Order Reaction Model**

In examining the Y values of above samples for each two-stage reaction model, the Y values and 1/T have a good linear relationship for sample Run B19 and B20 aging at a final
temperature of 550°C, as shown in Fig. 6-15, however, the Y values and 1/T have a good linear relationship only in the high temperature range for Run B40. The discontinuity arises at the temperature of about 440°C where first stage ends and the second stage begins. The relationship of Y values and 1/T of the above samples at other final temperatures is similar with those of Fig. 6-15, and thus are not given here.

Fig. 6-15 Comparison of Model-predicted and Experimental Y Results of Samples with a Final Temperature of 550°C with Two-stage First Order Reaction Model
6.5.4 Compensation Effects of Kinetic Parameters in the Heating Period

On determining the kinetic parameters from the TGA curves of solid-state reactions, it has been often encountered that when the activation energy $E_a$ is low, the pre-exponential factor $k_0$ is also low. Thus the low values of activation energy would be compensated by low values of the pre-exponential factors to give the same rate constant $k$ value. This mutual dependence of apparent Arrhenius parameters is known as the kinetic compensation effect and is expressed by:

$$\ln k_0 = \alpha + \beta E_a$$

(6-15)

Equation (6-15) indicates that the linear dependence between the apparent values of the logarithmic pre-exponential $\ln k_0$ and activation energy $E_a$ with the constant $\alpha$ and $\beta$. The simple relationship of Equation (6-15) is reproduced on the Arrhenius coordinate, $\ln k$ vs. $1/T$, with an intersection point called the isokinetic point $(1/T_{iso}, \ln k_{iso})$. Using the isokinetic relationship, equation (6-15) is rewritten as:

$$\ln k = a + b \frac{1}{T}$$

(6-16)

The equation (6-16) is a special case of the equation (6-15). The existence of equation (6-16) guarantees the existence of equation (6-15) and the compensation effect. However, the existence of equation (6-15) guarantees the existence of compensation effect, but not the equation (6-16).

Numerous papers have dealt with the kinetic compensation effects, and the causation of the mutual dependence of the Arrhenius parameters was classified into three categories by N. Koga [142]: (a) physico-chemical properties of the samples and reaction processes; (b) experimental procedural factors in the TGA measurements; (c) mathematical consequences of general kinetic calculation. Recognition of the kinetic compensation effect will give some insights to the relationship between the logarithm of pre-exponential factor, $\ln k_0$, and activation energy $E_a$, and
further give guidelines of application and explanation of the kinetic parameters. Because of the
existence of kinetic compensation effects, the magnitude of the rate constant is therefore of more
importance than that of each kinetic parameters $k_0$ and $E_a$.

Kinetic compensation effects appear to exist for all the deposits in heating up period. When
plotting the logarithm of pre-exponential factors $k_0$, which were determined either by overall one
stage first order reaction model or a two-stage model, versus the reciprocal temperature $1/T$ for
all different deposit samples in Fig. 6-16 and 6-17, it can be observed that there is an
approximately linear relation for all the point in one stage model, and much better linear relation
for all data in the two-stage model, especially at high temperatures. This indicates that the same
kind of chemical reactions take place for different deposits in the same stage, but the kinetic
parameters of different deposit samples analyzed by first order reaction nonisothermal model do
not reproduce with each other. However, the parameters of different samples follow the
compensation effect.

On the other hand, an isokinetic temperature is not observed. As an example, for the
parameters determined by two-stage model, the lines of ln$k$~$1/T$ do not intersect at one single
point for different samples from Fig. 6-18. This suggests that the existence of compensation
effect does not guarantee the isokinetic point.
Fig. 6-16 Plot of $\ln k_0$ and Activation Energy Values for Different Deposit Samples in Overall One-stage Model
Fig. 6-17 Plot of ln$k_0$ and Activation Energy Values for Different Deposit Samples in Two-stage Model
6.5.5 Results Discussion in Heating Period

Although the phenomena of volatile release of cyclone fouling deposits under TGA conditions are complex, adequate kinetic description is possible by using the first order non-isothermal reaction model. For the industrial deposits and the laboratory deposits collected at high temperatures (>500°C), in which small amounts volatile components exist, a single stage kinetic model of low activation energy barrier and low pre-exponential factor can describe their thermal properties very well. It has been reported [133, 143-145] that this model was developed
for relatively low volatile content materials and processes such as coal pyrolysis. For the laboratory fresh deposits collected at low temperatures (<500°C), kinetic description is made possible by a two-stage model, a first stage kinetic model of low activation energy barrier and low pre-exponential factor, and a second stage of higher activation energy and pre-exponential factor. The two-stage model reflects changes in chemical constitution or structures as conversion proceeds by using two sets of kinetic parameters. Both the integral and Chen-Nuttall analysis method can be used to find the kinetic parameters, and the analysis results by above two methods are in reasonable agreement.

The calculated apparent activation energies (17~100 kJ/mol) in this study are in the same magnitude with thermal cracking of hydrocarbon mixtures (ca. 50 kJ/mol) [146], pitch pyrolysis (18~100 kJ/mol) [133] and oil shale decomposition (38~62 kJ/mol) [139], etc., especially similar with those of the Athabasca pitch (+ 524°C fraction) pyrolysis reported by Yue [133]. This suggests that thermal cracking reactions taking place during the process of cyclone fouling deposit aging. The close thermal cracking kinetic phenomena with pitch, oil shale, etc. indicate the similar components exist in the cyclone fouling deposits.

For the fresh laboratory deposits collected at the temperature below 500°C, there is more heavy oil content expected in the deposits based on the condensation mechanism. At lower temperatures (<440°C) in TGA, the chemical reactions with lower energy barrier, e.g. the cracking of long aliphatic chains connected with the polyaromatic rings, etc., dominate the aging process, and thus exhibit a lower apparent activation energy. However, at higher temperatures (>440°C), the more difficult reactions which need much more energies, e.g., cracking of short chains of polyaromatic rings, dehydrogenation, skeleton re-arrangement of polyaromatics, etc. will dominate the aging process, and a higher apparent activation energy is observed. For the industrial samples and the deposits collected at higher temperatures (>500°C), most volatile
components have already been released when they were in the plant. Only small amount of the
dressest deposits condensed on the surface of “old” deposit can be cracked, and exhibits a low
apparent activation energy.

6.6 Kinetic Models in Isothermal Aging Period

Initially, irreversible reactions were assumed taking place in the deposits isothermal aging
process, and the overall reaction can be expressed as:

\[-r = - \frac{d(V^* - V)}{dt} = k(V^* - V)^\alpha\]

(6-17)

where \(-r\) is the disappearing rate of volatile components, and \(k\) the reaction rate constant, \(\alpha\)
reaction order. After taking the natural logarithm of both side of equation (6-17),

\[\ln\left(- \frac{d(V^* - V)}{dt}\right) = \ln k + \alpha \ln(V^* - V)\]

(6-18)

the slope of a plot of left hand side as a function of \(\ln(V^* - V)\) is the reaction order, and reaction
constant can be got from the intercept on \(y\) axial direction. The activation energy of the reaction
can be determined by Arrhenius equation when reaction constants at different temperatures are
available.

However, it was found that several different reaction stages were required to apply these
equations, and reaction parameters were different for various samples and stages. There was not
a universal kinetic equation which could be used to express the reaction phenomena for different
deposits.

To simplify the mathematical operation for the kinetic models of deposit aging,
dimensionless manipulation is introduced in present study. Dimensionless manipulation is
widely used for complex kinetic phenomena, such as gasification of coal char [147-150], etc.
Based on the thermal characteristics in isothermal period, two different kinetic models in the
isothermal period will be applied separately for fresh deposits, but one model is enough to
describe the kinetic phenomena for aged and industrial deposits. Following the approach of Mahajan [147], it can be assumed that:

\[ \omega = \frac{V^* - V}{V^*} \times 100\% \]  \hspace{1cm} (6-19)

and

\[ \theta = \frac{t_i - t_0}{t_{1/2}} \]  \hspace{1cm} (6-20)

where \( V^* \) is the maximum volatile component at each designated stage in the isothermal period. \( t_0 \) is the reaction beginning time in each stage, and \( t_i \) is the reaction time, \( t_{1/2} \) the time needed when the \( \omega \) reaches to 50% conversion. \( \omega \) is the dimensionless volatile content, and \( \theta \) the dimensionless reaction time.

Assuming it is an irreversible reaction in the deposits isothermal aging process, and the overall dimensionless reaction rate can be expressed as:

\[ -\Gamma = -\frac{d\omega}{d\theta} = f(k_i, \omega) \]  \hspace{1cm} (6-21)

where \(-\Gamma\) is the dimensionless release rate of volatile components, and \( k_i \) the reaction rate constant.

6.6.1 Kinetic Models on Initial Isothermal Aging Stage

The volatile component changes with reaction time in the initial isothermal period at different temperatures (ca. 50~200min) are given as Fig. 6-19, and it can be observed that all the curves have similar shape. To simplify the mathematical process, dimensionless \( \omega, \theta \) are introduced as described in equation (6-19) and (6-20). After dimensionless manipulation, the relationship of dimensionless volatile content \( \omega \) and dimensionless time \( \theta \) for all the samples are given in Fig. 6-20. All curves appear to collapse to a unique curve which appears similar to an exponential day curve, only one sample (Run B40 aging at 500°C) has a little variation. The
volatile component changes of all samples with reaction time approximately follow the same 2\textsuperscript{nd} order exponential decay equation as follows,

\[
\omega = Ae^{-\alpha_1\theta} + Be^{-\alpha_2\theta}
\]  \hspace{1cm} (6-22)

where \(A = 32.28\), \(B = 65.32\), \(\alpha_1 = 0.39\) and \(\alpha_2 = 3.00\). From the slope of every \(\theta\) point, the dimensionless volatile components release rate can be determined, correspondingly. Thus,

\[
-\Gamma = -\frac{d\omega}{d\theta} = k_1e^{-\alpha_1\theta} + k_2e^{-\alpha_2\theta}
\]  \hspace{1cm} (6-23)

where \(k_1\) and \(k_2\) are rate constant, and \(k_1=A/\alpha_1=82.77\) and \(k_2=B/\alpha_2=21.74\), respectively. Therefore, the reaction rate changes with the dimensionless time \(\theta\) also follows a 2\textsuperscript{nd} order exponential decay equation but with a much faster decay rate as given in equation (6-23) and Fig. 6-21. It can be observed that the volatile components release rate drops dramatically at the very beginning, and gradually slows down to a very low rate.

Based on above analysis, only one reaction rate equation is recommended to describe the kinetic phenomena for all samples aging at different temperatures in this period. This suggests that the volatile component release rate is the same at all temperatures. The reasons for this are perhaps that the thermal reaction rate is very fast in this period for all samples, and that more reactants had been released in the heating period for samples aging at a higher temperature before it reached the final aging temperature, which counteracts the temperature effects.
Fig. 6-19 Volatile Component Changes with The Reaction Time in Initial Isothermal Period

\[ \omega = 33.28 \exp(-\theta/0.39) + 65.32 \exp(-\theta/3.00) \]

\[ R^2 = 0.9793 \]

Fig. 6-20 The Dimensionless Kinetic Curves of All Deposit Samples in Initial Isothermal Period
6.6.2 Kinetic Models in The Second Isothermal Period

In the first isothermal period (Fig. 6-7), the volatile components decrease dramatically with the aging time, then in the second isothermal period slow down and come to a near zero order reaction with respect to volatile components. In fact, the latter is a very slow reaction, and only ca. 1.5~4.0% volatile components were released in about 10 hours. To simplify the kinetic model, the dimensionless manipulation by the equation (6-19) and (6-20) are also used here, and the relationship of dimensionless volatile content $\omega$ and dimensionless time $\theta$ ($\theta$ > 200 min) at the temperature of 550°C for Run B19, B20, B30 and B40 are given in Fig. 6-22, respectively. It can be observed that all the data are close to one linear equation. Thus, the volatile component release rate for all samples can be described approximately by a zero order dimensionless reaction as follows,

$$ -\Gamma = -\frac{d\omega}{d\theta} = 47.72 $$

(6-24)
Fig. 6-22 Dimensionless Kinetic Curve of All Deposit Samples at 550°C in The Second Isothermal Period

For the samples (Run B20 and B40) aging time at 500°C and 600°C, after the dimensionless manipulation, the relationship of dimensionless volatile content $\omega$ and dimensionless time $\theta$ are given in Fig. 6-23, respectively.

Fig. 6-23 Dimensionless Kinetic Curve of All Deposit Samples in 2nd Isothermal Period
It can be observed that the dimensionless volatile component $\omega$ changes with the dimensionless time $\theta$ follow zero order reaction for both deposits aging isothermally at 500 and 600°C, and dimensionless reaction rate are 46.00 and 54.71, respectively. According to Arrhenius equation,

$$\ln k = \ln k_0 - \frac{E_a}{RT}$$

the reaction apparent activation energy of deposits isothermal aging can be determined by the reaction rate constant at the temperature of 500, 550 and 600°C as shown in Fig. 6-24. From Fig. 6-24, the apparent activation energy $E_a$ and dimensionless pre-exponential factor $k_0$ are 9.61 kJ/mol and 201.54, respectively. This low apparent activation energy reflects that the volatile release rate in this period is not sensitive to temperature.

![Fig. 6-24 Relationship of lnk and 1/T at Different Temperatures](image)

6.6.3 Kinetics of Pre-aged Laboratory Deposits and Industrial Deposits

For the pre-aged and industrial deposits, the volatile components decline gradually at a near constant rate in all isothermal conditions, without the fast initial period found for the fresh deposits. Based on this characteristic, one model can describe the kinetic phenomena for pre-
aged and industrial deposits. After dimensionless manipulation, the relationship of dimensionless volatile components $\omega$ and dimensionless time $\theta$ for aged laboratory deposits and industrial deposits are given in Fig. 6-25 and 6-26, respectively.

---

**Fig. 6-25 Dimensionless Kinetic Curve of Aged Laboratory Deposits**

**Fig. 6-26 Dimensionless Kinetic Curve of Industrial Deposits**
It can be noted that both of the reaction kinetics of both pre-aged laboratory deposits and industrial samples can be expressed by zero order reactions, which corresponding dimensionless rate are 60.47 and 52.19 respectively, although some curvature exists for the former (Fig. 6-25). The volatile component release rates of aged fresh deposits and industrial deposits are very close, which reflects their similar characteristics.

### 6.7 Overall Kinetic Equations of Fresh, Aged Laboratory Deposits and Industrial Samples

Based on all above TGA kinetic analysis results, different kinetic models have been applied to different aging periods. The kinetic picture for the aging of deposits is clearly very complex. The apparent kinetic equations and their applied period of different fresh, aged laboratory and industrial samples can be summarized in Table 6-7.

**Table 6-7 Overall Kinetic Equations of Fresh, Aged Lab Deposits and Industrial Samples**

<table>
<thead>
<tr>
<th>Period</th>
<th>Kinetic equation</th>
<th>TGA time (min)</th>
<th>Fresh lab</th>
<th>Aged lab</th>
<th>Industrial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-isothermal</td>
<td>Integral model (one or two stages) [ \ln(\frac{-C \ln(1 - \frac{V}{V^*})}{RT^2}) - \ln(1 - \frac{2RT}{E_a}) \approx \ln \frac{k_o}{E_a} - \frac{E_a}{RT} ]</td>
<td>ca. 0–50</td>
<td>N/A</td>
<td>ca. 0–50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>or Chen-Nuttall model (one or two stages) [ \ln(\frac{-C(E_a + 2RT)}{RT^2} \ln(1 - \frac{V}{V^*})) = \ln k_o - \frac{E_a}{RT} ]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial isothermal</td>
<td>dimensionless 2(^{nd}) order exponential decay equation [ \Gamma = -\frac{d\omega}{d\theta} = k_1 e^{-\frac{\theta}{\alpha}} + k_2 e^{-\frac{\theta}{\alpha_2}} ]</td>
<td>ca. 50–200</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>where: [ \omega = \frac{V' - V}{V^*} \times 100% ; ; ; \theta = \frac{t_i - t_0}{t_{i/2}} ]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(^{nd}) isothermal</td>
<td>dimensionless zero order equation [ \Gamma = -\frac{d\omega}{d\theta} = \text{constant} ]</td>
<td>(&gt;\text{ca. 200})</td>
<td>(&gt;\text{ca. 50})</td>
<td>(&gt;\text{ca. 50})</td>
<td></td>
</tr>
</tbody>
</table>

The definition of \(\omega\) and \(\theta\) is the same with above.
For the fresh laboratory deposits, they have three kinetic periods in Table 6-7. However, for the laboratory pre-aged deposits, almost no chemical reactions take place in the heating period, and one dimensionless zero order equation is enough to describe its kinetic phenomena. For industrial samples, there are also no initial isothermal period, but there are cracking reactions taking place in the heating period, because there are always fresh deposits formed on the surface of aged deposits in industrial plant.

6.8 Structure Evolution of Lab Fresh Deposits and Industrial Samples in the Aging Process

According to previous analysis results, it can be concluded that fresh laboratory deposits are composed of mostly polyaromatic structures with some aliphatic chains; for the pre-aged laboratory deposits, it is mainly the polyaromatic structures. However, the industrial samples which have been aging in plant for months demonstrate mostly graphitic structures combined with a few fresh deposit characteristics. TGA kinetic study results indicate there are mostly thermal cracking reactions of aliphatic chains taking place in the heating period and initial isothermal period. In the following long aging period, more complex slow reactions taking place to produce more condensed polyaromatic structures, and finally lead to graphitic structures.

Marsh and Griffiths [151] proposed a model of the structural evolution in carbonization/graphitization process based on their XRD and TEM experimental results, as illustrated in Fig. 6-27. This generally applies at much higher temperature than the current work. In the carbons from lowest heat treatment temperature (HTT, 1100K) of pitch coke, a conglomerate structure is found, which is not truly lamellar and does not have a good stacking arrangement. On increasing the HTT to 1500 and 1700K, the original molecules apparently join together to create larger structural units and the ordering, although better defined, is certainly not parallel. In fact because of extensive curvature as if caused by stress, it is called ripple material.
It is not until a temperature of 2000K is reached that significant parallel stacking is to be found in the graphitic material.

Based on the Marsh-Griffiths model, the structural evolution model of cyclone fouling deposit aging is proposed as illustrated in Fig. 6-28. Compared with the heat treatment of pitch coke, the current study of cyclone fouling deposits aging, takes place at a much lower temperature but with a much longer reaction time. The fresh laboratory deposit has a structure similar to the conglomerate structure but with much longer aliphatic chains. During the heating period and initial isothermal aging process, thermal cracking reactions of aliphatic chains takes place and produces more condensed polyaromatic structures with or without short aliphatic groups. As aging proceeds, dehydrogenation and carbon skeleton re-arrangement happens and leads to graphitic structures. The structure of pre-aged deposits represents a transition state between the polyaromatic and graphitic structures.
For industrial cokers, the fresh deposits which form in the early running of the cyclone coker unit are expected to have similar structure to those in the laboratory unit. During long times on stream, the deposits age in the plant at about 500°C. Similar thermal cracking, dehydrogenation and carbon skeleton re-arrangement reactions, etc. take place as with lab fresh deposits and eventually lead to more ordered graphitic structures. The difference between the industrial samples and the laboratory fresh deposit aging is that the industrial process is a continuous process, and there are always fresh deposits being formed at all times. The deposits are baked isothermally at about 500°C for much longer times, up to over one year; and no heat up period occurs compared with those aged in the TGA.

Fig. 6-28 Structure Evolution model for Cyclone Fouling Deposits in Aging Process following Marsh-Griffiths Model [151]
6.9 Summary of Deposit Aging Kinetic Models

Based on the TGA kinetic study of laboratory fresh, aged deposits and industrial samples, the following conclusions can be drawn:

1. It was not possible to construct a single mathematical model to describe the weight loss behavior of all deposits during the entire thermogravimetric heating process. Kinetic models were developed to describe reactions in different aging periods based on thermal behavior of deposits. During the heating period from ambient to final temperatures, a first order non-isothermal kinetic model was used to describe the de-volatilization reaction properties of cyclone fouling deposits. Isothermal kinetic models were used to characterize the weight loss phenomena with time at different final temperatures.

2. In the heating period, for the laboratory deposits collected at low temperatures (<500°C), a two-stage model is used. The first stage has a low activation energy barrier and low pre-exponential factor, and the second stage a higher activation energy and pre-exponential factor. However, for the industrial deposits and the laboratory deposits collected at high temperatures, a single stage kinetic model of low activation energy barrier and low pre-exponential factor can well describe their thermal behavior. Both the integral and Chen-Nuttall analysis method can be used to find the kinetic parameters. Kinetic compensation effects were observed for different samples.

3. The values of apparent activation energies in the heating period suggest that thermal cracking reactions taking place. Similar thermal cracking kinetic phenomena observed by others with pitch, oil shale, etc. indicate the same kind of components exist in the cyclone fouling deposits.
4. In the long time isothermal aging process, the kinetics can be divided into two different periods. In the initial period, the dimensionless release rate of volatiles, which declines dramatically with reaction time, was described by a 2\textsuperscript{nd} order exponential decay equation:

\[- r = - \frac{d\omega}{d\theta} = k_1 e^{-\frac{\theta}{a_1}} + k_2 e^{-\frac{\theta}{a_2}}\]

A zero order reaction model could be used to describe the subsequent slow aging reaction period, in which the apparent activation energy is 9.61 kJ/mol.

5. The aged laboratory deposits and industrial deposit samples have similar but not identical characteristics. There are thermal cracking reactions taking place for industrial samples in heating period, but not for the pre-aged laboratory deposits. In the isothermal aging period, one zero order reaction model is sufficient to describe the total slow reaction aging kinetics, without a fast initial period.

6. A structural evolution model of cyclone fouling deposits aging is proposed based on this study. For the fresh laboratory deposit, its structures are similar to the conglomerate structure of Marsh and Griffiths consisting of a fused aromatic structure with much longer aliphatic chains. After the heating period and initial isothermal aging process, more condensed polyaromatic structures are formed. As aging proceeds, dehydrogenation and carbon skeleton re-arrangement occur and lead to more ordered graphitic structures. The structure of pre-aged deposits represents a transition state between the polyaromatic and graphitic structures.
Chapter 7 Droplet Mass Transfer Deposition Model

Previous experimental results, both the tests of process variables on deposition rate and the characterization of deposits, support the argument that physical condensation from the vapour phase on the wall is the main reason for cyclone exit line fouling in laboratory conditions. However, the fact that a modest increase in deposition rate occurred with increasing filter pore size [6], suggests that the entrainment of liquid droplets also contributes to the deposit formation, although it is not the primary reason. As well, metals detected in deposits by XRF analysis and the fact that many components in extracts whose boiling points are higher than 750°C indicate that deposit formation is not only just from condensation from vapour phase, but carryover of bitumen droplets also contributes to deposition. Condensation in the bulk would lead to additional droplet formation. Simulation of cyclone product stream using HYSIS by Jankovic [116] shows that some liquids should be present in the vapour fluid. The major objectives of this work are to simulate the deposition rate based on liquid droplet mass transfer, predict the deposition rate changes with the tube diameter and droplet sizes, and compare results to the experimental data and the simulation results of physical condensation model [7].

7.1 Model Development

The geometry of the droplet mass transfer model configuration is shown in Fig. 7-1. The model is one dimensional in space and assumes plug flow. This implies the neglect of radial concentration gradients and axial dispersion. In this model, a viscous fluid of hydrocarbon vapours, containing liquid droplets of specified size flowing parallel to an adjacent tube surface in a smooth circular tube of radius \( d \), is considered. Before the fluid enters the tube, the fluid temperature is uniform at the temperature \( T_0 \). There is a constant heat flux at the wall, which can be either negative or positive. The droplet can transport from the bulk to the tube wall surface to
cause deposition through the droplet mass transfer mechanism. It is assumed that there is no re-entrainment of deposits into the bulk stream. Other assumptions include inertness of the bulk vapour fluid, hydrodynamically smooth surface, ideal gas mixture behavior, no hydrodynamic or thermal entrance region effects, and the viscosity and thermal conductivity of vapour phase do not change with the tube length.

![Fig. 7-1 Differential Element of an Exit Tube](image_url)

Given the above assumptions, the following design equations can be written for a plug flow tubular system. The energy balance gives the axial fluid temperature profile,

\[ \frac{dT}{dz} = \frac{q \pi d}{F_{\text{droplet},0} (1 - x) \hat{C}_p,\text{droplet}} + F_{\text{vapour}} \hat{C}_p,\text{vapour} \]  

(7-1)

The droplet component mass balance equation is:

\[ \frac{dx}{dz} = \frac{R_d \pi d}{F_{\text{droplet},0}} \]  

(7-2)

where \( F \) represents molar flow rate (mol/s), fraction conversion \( x \) is defined as the fraction of droplets converted into deposits, and \( R_d \) the droplet deposition flux (mol/m² s). The deposit thickness \( \delta_c \) is calculated from the deposition flux as described later, which is in general form,

\[ \delta_c = \delta_c(z,t) \]  

(7-3)
The model is pseudo-steady-state with respect to time. In other words, the solution of equations (7-1) and (7-2) is assumed constant over a time step, and the effects of the deposit accumulation through equation (7-3) are updated explicitly at the end of each time step. This pseudo-steady-state assumption would be indeed valid as long as the deposit formation rate does not change appreciably over a sufficient small time step.

### 7.1.1 Deposit Formation Rate Due to Droplet Mass Transfer

The transport of liquid droplets from the mainstream to the deposition surface can be expressed as:

$$R_d = k_i (C_b - C_s) = k_d C_b$$

(7-4)

in which $C_b$ is the bulk concentration of liquid droplets, and $C_s$ is concentration of droplets in suspension adjacent to deposition surface. If it is assumed that all droplets that arrive at the tube surface adhere to it, $C_s = 0$ and the transport coefficient $k_i$ becomes identical to the deposition coefficient $k_d$. Given the effects of temperature (assuming ideal gas) and droplet concentration changes along the tube length, the deposition rate \[152\] at a specified location $z$ can be expressed as,

$$R_{d,z} = k_i C_{b,z} = k_i C_{b,0} (1 - x) \frac{T_0}{T_z}$$

(7-5)

If the fluid is in the regime of laminar flow, suspended liquid droplets move with the fluid and are carried to the wall by Brownian motion of the fluid molecules. The submicron droplets can then be treated as large molecules, so $k_i$ becomes equivalent to the conventional mass transfer coefficient $k_m$, which can be obtained from relevant empirical correlations or theoretical equations for convection mass transfer in the literature. To use these relations requires knowledge of Brownian diffusivity, which for a dilute suspension of spheres, is given by the Stokes-Einstein equation \[153\],

$$D_e = \frac{k_b T}{3\pi \mu d_p}$$

(7-6)
In laminar flow regime with established velocity profile, e.g., the following empirical equation [154] can be used to calculate mass transfer coefficient:

\[
Sh = \frac{k_m d}{D_e} = 1.62\left(\frac{Pe}{L}\right)^{\frac{1}{3}} \quad (7-7)
\]

where \(0 < Re < 2000\), \(Pe(d/L) > 200\) and \(Pe = \frac{dv}{D_e}\).

For fully developed turbulent flow, mass transport of droplets from suspensions flowing parallel to tube wall can occur via diffusion, inertia, and impaction as summarized by N. Epstein [155]. The dominant mechanism is determined by droplet relaxation time, \(t_p^+\):

\[
t_p^+ = \frac{\rho_p d^2 v^2}{18 \mu v} \quad \text{and} \quad v_* = \sqrt{\frac{f}{2}} \quad (7-8)
\]

where \(\rho_p\) is droplet density; \(d_p\) is the droplet diameter; \(v_*\) is the friction velocity; \(\mu\) and \(v\) are fluid viscosity and kinematic viscosity, respectively. The ranges of each mechanism are given slightly different, depending on the source. Bott [159] lists the boundaries as \(t_p^+ \sim 0.1\) and 10 which were used in this calculation, whereas Epstein [155] lists \(t_p^+ \sim 0.2\) and 20.

\[
t_p^+ < \sim 0.1-0.2 \quad \text{diffusion} \quad k_i = k_m = \frac{0.0847 v_*}{Sc^{2/3}} \quad (7-9)
\]

\[
\sim 0.1-0.2 < t_p^+ < \sim 10-20 \quad \text{inertia} \quad k_i = 0.00035(t_p^+)^2 \quad (7-10)
\]

\[
t_p^+ > \sim 10-20 \quad \text{impact} \quad k_i = 0.18 v_* \quad (7-11)
\]

In equation (7-9), the diffusivity of droplets can also be calculated by equation (7-6). Because in the diffusion regime, suspended droplets also can be regarded as being carried to the tube wall by Brownian motion of fluid molecules in the turbulent flow. For smooth pipe line flow [156],

\[
f = \frac{0.0791}{Re^{0.25}} \quad (7-12)
\]

The average deposition rate can be expressed as,

\[
R_{d,\text{avg}} = \frac{1}{L} \int_0^L R_d dz \quad (7-13)
\]
Hydrodynamic and thermal entrance region effects are ignored in the present study. The hydrodynamic entrance length \( x \) [156, 157] for laminar flow and turbulent flow can be approximately expressed by equation \( \frac{x}{d_{\text{lam}}} \approx 0.05 \text{Re} \) and \( 10 \leq \frac{x}{d_{\text{urb}}} \leq 60 \), respectively. In fact, all the fluids are in entrance region in this study. In the entrance region, the mass transfer coefficient could be obtained by the application of the analogy of heat transfer results. For example, equation (7-14) and (7-15) are Nusselt number for laminar flow and turbulent flow regime [156,157], respectively.

\[
Nu_e = 1.86(\text{Pe} \frac{d}{l})^{\frac{1}{3}} \quad \text{where } 0.48 < Pr < 167000
\]  

\[
\frac{Nu_e}{Nu_{fd}} = 1 + a/(x/d)^b \quad \text{where } \begin{cases}  
a = 23.99 \text{Re}^{-0.230} \\
 b = -2.08 \times 10^{-6} \text{Re} + 0.815
\end{cases}
\]  

where the subscript \( e \) means entrance region, \( fd \) means fully developed condition, and \( x \) is the entrance region length. The variables \( a \) and \( b \) are a function of Reynolds number [157].

### 7.1.2 Deposit Thickness

The deposit thickness changes, \( \Delta \delta_c \), over a time step, \( \Delta t \), can be expressed as follows:

\[
\Delta \delta_c = \frac{M_c R_d}{\rho_c} \Delta t
\]  

where \( M_c \) and \( \rho_c \) are the molecular weight and the density of deposits, respectively. In this case, the density of deposit is assumed as 1.10 g/cm\(^3\), and the molecular weight is the same as that of the liquid droplets. The equation is to be solved at each time step for the change of deposit thickness at each axial position. This change can be added to the previous value to update the total deposit thickness for the subsequent time steps. The deposition rate is very low in most of our conditions (ca. \( 10^{-5} \sim 10^{-7} \) g/m\(^2\)s in lab conditions), and hence the tube diameter does not change much due to droplet mass transfer deposition in six hours running process (\( 10^{-4} \sim 10^{-5} \) mm
deposit thickness in lab conditions). Therefore, the tube diameter changes due to deposition are
omitted in most of the calculations, and most of the deposit thickness in the exit line is calculated
according to the initial deposition rate.

7.1.3 Heat Capacity of Hydrocarbon Vapours and Liquid Droplets

The heat capacity of hydrocarbon vapours and liquid droplets on a mass basis can be
calculated by empirical equations [2] as follows,

\[ C_p = a + bT + cT^2 \] (7-17)

\[ a = -0.32646 + 0.02678K - CF(0.084773 - 0.080809d^{15^\circ C}) \] (7-18)

\[ b = -[1.3892 - 1.2122K + 0.0383K^2 - CF(2.1773 - 2.0826d^{15^\circ C})]\times10^{-4} \] (7-19)

\[ c = -[(1.5393 + CF(0.78649 - 0.70423d^{15^\circ C})]\times10^{-7} \] (7-20)

where \( CF = [(12.8/K - 1)(10.0/K - 1)\times100]^2 \) for \( 10 \leq K \leq 12.8 \)
\[ CF = 0 \] otherwise

in which \( CF \) is an empirical coefficient, and \( K \) is the Watson characterization factor for the
mixture. \( K \) can be calculated as:

\[ K = \frac{1.246T_b^{1/5}}{d^{15^\circ C}} \] (7-21)

in which \( T_b \) is the mean average boiling point, and \( d^{15^\circ C} \) is the specific gravity at \( 15^\circ C \) relative to
water. For the mixture heat capacity of vapour phase on a molar basis \( (\hat{C}_p = C_p \times M_w) \) is:

\[ \hat{C}_{p,vapour} = y_{\text{hydrocarbon}} \hat{C}_{p,\text{hydrocarbon}} + y_{\text{steam}} \hat{C}_{p,\text{steam}} + y_{\text{N}_2} \hat{C}_{p,\text{N}_2} \] (7-22)

In the present case, based on the flows to the lab unit, \( y_{\text{hydrocarbon}} = 0.017, y_{\text{N}_2} = 0.275, y_{\text{steam}} = 0.708 \)

The average molecular weight of liquid droplet in typical industrial conditions was taken to
be 1227, as reported in the simulation results of Jankovic [116]. Based on analysis results of
different bitumen pitch and vacuum residue by the Hong E [118], the following values can be
estimated for droplets: \( d^{15^\circ C} = 1.0678, K = 11.63 \). Thus, from equation (7-17) to (7-21),
\[ \dot{C}_{p,\text{droplet}} = (-11.997 \times 10^{-2} + 1.8 \times 7.436 \times 10^{-4} T - 3.24 \times 1.608 \times 10^{-7} T^2) \times 1227 \quad (7-23) \]

However, the contribution of droplet heat capacity was omitted in laboratory conditions in order to compare with previous simulation results according to condensation mechanism. In fact, it is reasonable when considering its very low concentration present in the vapour phase (molar fraction of droplet \( \sim 10^{-5} \)).

The average molecular weight of hydrocarbon can be assumed as 750 [116], whence \( d^{15}C = 0.993, K = 11.77 \) [118]. Thus,

\[ \dot{C}_{p,\text{hydrocarbon}} = (-1.910 \times 10^{-2} + 1.8 \times 7.762 \times 10^{-4} T - 3.24 \times 1.690 \times 10^{-7} T^2) \times 750 \quad (7-24) \]

For steam [158], \( \dot{C}_{p,\text{steam}} = 29.16 + 14.49 \times 10^3 T - 2.022 \times 10^6 T^2 \quad (7-25) \)

For nitrogen [158], \( \dot{C}_{p,\text{N}} = 27.32 + 6.226 \times 10^3 T - 0.9502 \times 10^6 T^2 \quad (7-26) \)

### 7.1.4 Heat Transfer Considerations

In case of constant heat flux at the tube wall, it is assumed that the heat flux is 1157 W/m\(^2\) for laboratory conditions, and 4934 W/m\(^2\) for industrial conditions [7]. In case of constant wall temperature, the overall heat transfer coefficient can be expressed as [106]:

\[
\frac{1}{U} = \frac{1}{h_i d_i} + \frac{\delta_e d_e}{k_e d_e} + \frac{\delta_d d_d}{k_d d_d}
\]

(7-27)

where \( i \) and \( o \) indicate inside and outside tube respectively, \( d_m \) is the logarithmic mean tube diameter. The last two terms can be neglected in the case that the tube wall and coke thickness are very thin, and the overall heat transfer coefficient equals to the convective heat transfer coefficient inside the tube. For the fully developed laminar flow, uniform tube surface temperature, the corresponding heat transfer equation is:

\[
Nu = 1.62 (Pe \frac{d}{L})^{1/3}
\]

(7-28)

Thermal conductivity of bulk vapour is calculated using the following expression [106]:
\[ k = \frac{\mu}{M} (1.537 \times 10^4 + 1.273 \hat{C}_v) \quad (7-29) \]

where

\[ \hat{C}_v = \hat{C}_p - 8314 \quad (7-30) \]

Then the heat flux can be expressed as follows,

\[ q = U(T - T_w) \quad (7-31) \]

### 7.2 Properties of Fluid and Basic Operation Parameters

The properties and operation conditions of vapour fluid and droplet in laboratory conditions are assumed the same with those of previous simulation process based on wall condensation mechanism [7], in order to compare predicted trend for droplet transport. In the laboratory unit, the input flowrate of bitumen, water and nitrogen are 5g/min, 5g/min and 7.4L/min at 540°C, respectively. The molar fraction of droplet in vapours is assumed as about \(8.93 \times 10^{-5}\). The property data of fluid and droplet in industrial conditions, such as the viscosity of vapour, the density of vapour and droplets, the molecular weight of vapour, and bitumen, etc., are based on the simulation results of Syncrude fluid coker unit by Jankovic [116]. The mass flowrate of droplet and vapour in industrial conditions are 16211 kg/hr and \(5.30 \times 10^5\) kg/hr, respectively; the ratio of mass flowrate for droplet and vapour in the cyclone exit line is 0.031. The geometry data of the industrial coker cyclone exit line are given in the reference [116]. The heat capacities are calculated according to the equation (7-17) to (7-26). For comparison, the physical properties and basic operation conditions of laboratory and industrial units are summarized in Table 7-1.

From Table 7-1, the liquid droplet molar fraction in laboratory operation conditions is very close to that of industrial conditions, but the density of vapour and droplet in laboratory unit are different with those of industrial conditions, and causes a much higher droplet molar concentration in the vapour phase under industrial conditions. However, this difference would not affect the prediction trend of the simulation results. The main difference between the
laboratory and industrial unit is in hydrodynamic conditions, i.e., the fluid is in laminar flow regime rather than turbulent flow in the laboratory unit.

**Table 7-1 The Physical Properties and Operation Conditions for Lab and Industrial Units**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Laboratory</th>
<th>Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of vapours (kg/m.s)</td>
<td>3.38×10⁻⁵</td>
<td>3.11×10⁻⁵</td>
</tr>
<tr>
<td>Density of vapour (kg/m³)</td>
<td>0.497</td>
<td>1.715</td>
</tr>
<tr>
<td>Density of droplets (kg/m³)</td>
<td>1270</td>
<td>760</td>
</tr>
<tr>
<td>Molecular weight of vapour</td>
<td>33.13</td>
<td>58.6</td>
</tr>
<tr>
<td>Molecular weight of hydrocarbon</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>Molecular weight of droplet</td>
<td>1907</td>
<td>1227</td>
</tr>
<tr>
<td>Initial heat capacity of vapour (J/mol K)</td>
<td>77.02</td>
<td>77.02</td>
</tr>
<tr>
<td>Initial heat capacity of droplet (J/mol K)</td>
<td>NA</td>
<td>3753.87</td>
</tr>
<tr>
<td>Molar Fraction of Droplet in vapours</td>
<td>8.93×10⁻⁵</td>
<td>1.46×10⁻⁴</td>
</tr>
<tr>
<td>Initial droplet concentration (mol/m³)</td>
<td>1.34×10⁻³</td>
<td>4.28×10⁻²</td>
</tr>
<tr>
<td>Molar flowrate of vapour (mol/s)</td>
<td>6.666×10⁻³</td>
<td>418.70</td>
</tr>
<tr>
<td>Molar flowrate of droplet (mol/s)</td>
<td>5.947×10⁻⁷</td>
<td>0.612</td>
</tr>
<tr>
<td>Volumetric flowrate of vapour (m³/s)</td>
<td>4.442×10⁻⁴</td>
<td>14.31</td>
</tr>
<tr>
<td>Diameter of the tube (m)</td>
<td>5.8~15.7×10⁻³</td>
<td>0.67</td>
</tr>
<tr>
<td>Tube length (m)</td>
<td>0.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Inlet temperature (°C)</td>
<td>540</td>
<td>540</td>
</tr>
<tr>
<td>Linear velocity of vapours (m/s)</td>
<td>2.3~16.8</td>
<td>40.58</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>529~1434</td>
<td>1.5×10⁶</td>
</tr>
<tr>
<td>Pe(d/L)</td>
<td>&gt;9.1×10⁶</td>
<td>&gt;9.1×10⁹</td>
</tr>
</tbody>
</table>
A MATLAB program uses Runge-Kutta Cash-Karp method (see Appendix 8) was written to solve two simultaneous first order initial value ordinary differential equations (7-1) and (7-2), in which the deposition rate, heat capacity, and heat transfer were incorporated by their corresponding equations as discussed above, respectively. The simulation results of different running conditions are given in a CD available from the author and the supervisor, and to be discussed in the following different sections.

7.3 Laboratory Conditions with Constant Heat Flux

In this case, a constant heat flux, 1157 W/m², at the tube wall is assumed based on reference [7]. First, the liquid droplet diameter is taken as 1 μm, and the three different tube diameters used in the experiments, i.e., 5.8, 9.0 and 15.7 mm, were tested to indicate the tube diameter effect on deposition rate at specified droplet size and mass flowrate of vapour. Then, the exit tube diameter was assumed as 9 mm, which is the same size of the usual laboratory unit exit tube. Different droplet sizes, i.e., 0.1, 1, 10, 50 and 100 μm, were assumed to predict the droplet size effect on the deposition rate, although the maximum droplet size from the cyclone cut point in [116] were considered to be 11 μm.

7.3.1 Tube Diameter Effect on the Deposition Rate

If the droplet size is 1 μm, the temperature distribution along the tube length for different diameter tubes is shown as Fig. 7-2. At the heat flux and mass flowrate stated, the outlet fluid would rise to a much higher temperature for the bigger diameter tube. For a vapour fluid whose inlet temperature is 540°C, the outlet temperature can rise up to 638°C, 597°C and 576°C for the tube diameter 15.7, 9.0 and 5.8 mm, respectively. However, no such large increases in temperature were actually observed, probably due to variation in heat flux. Fig. 7-3 gives the distribution of liquid droplet concentration along the tube length for three different diameter tubes, which indicates that the outlet droplet concentration gradually decreases along the tube
length and the outlet droplet concentrations are similar with each other for different diameter tubes. Fig. 7-4 and Fig. 7-5 are the transport coefficient and deposition rate distribution along the tube length. Both of them do not change much along the tube length, and the deposition rate caused by droplet mass transfer is very slow \((2\sim6\times10^{-6} \text{ g/m}^2\text{s})\). The transport coefficient increases a little along the tube length because of the increase of temperature, and the deposition rate decreases along the tube length a little because of the temperature effect and the consumption of liquid droplets, both of which lead to a lower droplet concentration. It can be noticed that the larger the tube diameter, the much lower the transport coefficient and deposition rate \((\text{g/m}^2\text{s})\). However, there is not much difference in deposit mass collected at a specified time for different diameter tubes (Table 7-2).

---

\[\text{Fig. 7-2 Vapour Temperature Distribution of Different Diameter Tubes (d}_p=1\mu\text{m) at Constant Mass Flow and Heat Flux}\]
Fig. 7-3 Droplet Concentration Distribution of Different Diameter Tubes ($d_p=1\mu m$)

Fig. 7-4 Transport Coefficient Distribution in Different Diameter Tubes ($d_p=1\mu m$)
Fig. 7-5 Deposition Rate Changes along the Tube Length (d_p=1μm)

The comparison of bulk fluid velocity, Reynolds number, average transport coefficient and deposition rate of different diameter tubes in case of droplet size 1 μm is given in Table 7-2, and Fig. 7-6 demonstrates that the smaller diameter tube has a higher deposition flux in laminar flow regions. The deposit thickness distribution of different diameter tubes in laboratory conditions is given in Fig. 7-7 after six hours running. It can be noticed that the deposition is not serious for all the cases (ca. 4~11 \times 10^{-5} \text{mm}) under laminar flow range, and the deposit thickness distribution is rather uniform along the tube length. For these conditions, the deposit would be less than one particle diameter thick, which implies a fractional surface coverage less than unity.

Table 7-2 Average Deposition Rate Changes with the Tube Diameter (d_p=1μm)

<table>
<thead>
<tr>
<th>Tube diameter (mm)</th>
<th>5.8</th>
<th>9.0</th>
<th>15.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid linear velocity (m/s)</td>
<td>16.81</td>
<td>6.98</td>
<td>2.29</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>1434</td>
<td>924</td>
<td>530</td>
</tr>
<tr>
<td>Transport coefficient (\times 10^{-6} \text{m/s})</td>
<td>2.61</td>
<td>1.69</td>
<td>0.99</td>
</tr>
<tr>
<td>Deposition rate (\times 10^{-6} \text{g/m}^2 \text{s})</td>
<td>6.52</td>
<td>4.19</td>
<td>2.38</td>
</tr>
<tr>
<td>Deposition mass rate (mg/h)</td>
<td>0.385</td>
<td>0.384</td>
<td>0.380</td>
</tr>
</tbody>
</table>
Fig. 7-6 Average Deposition Rate Changes with the Tube Diameter
(Total Vapour Flow Constant)

Fig 7-7 Deposit Thickness along The Tube Length after Six Hours
7.3.2 Droplet Size Effect on the Deposition Rate

The exit tube diameter is assumed to be 9 mm, which is same size of the usual laboratory unit exit tube, and different droplet sizes, e.g., 0.1, 1, 10, 50 and 100 μm, are assumed to predict the droplet size effect on the deposition rate. The temperature and droplet concentration changes with the tube length in case of different droplet sizes have already been calculated in Fig. 7-2 and Fig. 7-3 for tube diameter of 9 mm for the one micron droplet. For vapour inlet temperature at 540°C, the outlet temperature raises up to 597°C (Fig. 7-2). The changes of droplet concentration along the tube for different size droplets are also similar, and shown previously in Fig. 7-3. The droplet concentration dropped slowly from 1.34 to 1.25 mol/L at the tube outlet for all different size droplets.

The transport coefficient changes for different size droplets along the tube length are given in Fig. 7-8 and Table 7-3. For all different size droplets, the transport coefficient increases a little along the tube length due to temperature effect. However, there is a big difference for the transport coefficient among different size droplets. As expected, the smaller the droplet size is, the bigger the transport coefficient. For the droplet sizes from 0.1~100 μm, the transport coefficient changes from $79 \times 10^{-7}$ m/s to $0.79 \times 10^{-7}$ m/s, which is 100 times difference. This difference causes the average deposition rate (see Table 7-2, Fig 7-9 and 7-10) to drop from $19.4 \times 10^{-6}$ g/m²·s to $0.19 \times 10^{-6}$ g/m²·s for a droplet size from 0.1 to 100 μm, which is also 100 times difference.

Fig. 7-11 gives the deposit thickness distribution along the tube wall after six hours running. Deposits are much thicker for the smaller sized droplets. The larger sized droplets cause much less deposition, e.g., less than $7 \times 10^{-5}$ mm deposit thickness for droplets sized bigger than 1 μm after running six hours. The deposit is less than one particle diameter thick, which implies a fractioned surface coverage less than unity. The deposit thickness is quite uniform through the
length of the tube wall for all different size droplets, and the deposition is very minor for all different size droplets in the laboratory conditions.

Fig. 7-8 Transport Coefficient Changes for Different Droplet Sizes (D=9mm)

Fig. 7-9 Deposition Rate of Different Size Droplets along The Tube Length (D=9mm)
Table 7-3 Average Deposition Rate Changes With the Droplet Size

<table>
<thead>
<tr>
<th>Droplet size (μm)</th>
<th>0.1</th>
<th>1.0</th>
<th>10</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport coefficient ($\times 10^{-7}$ m/s)</td>
<td>78.62</td>
<td>16.94</td>
<td>3.65</td>
<td>1.25</td>
<td>0.79</td>
</tr>
<tr>
<td>Deposition rate ($\times 10^{-6}$ g/m² s)</td>
<td>19.43</td>
<td>4.19</td>
<td>0.90</td>
<td>0.31</td>
<td>0.19</td>
</tr>
<tr>
<td>Mass deposition rate (mg/h)</td>
<td>1.779</td>
<td>0.383</td>
<td>0.083</td>
<td>0.028</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Fig. 7-10 Average Deposition Rate Changes with the Droplet Size (D=9mm)

Fig. 7-11 Deposit Thickness along the Tube Length after Six Hours (D=9mm)
7.4 Laboratory Conditions with Constant Wall Temperature

If the tube temperature is kept constant, e.g. 500°C, during the operation process, the vapour temperature will drop from 540°C to 520°C because of the heat transfer (see Fig. 7-12). The droplet concentration increases slightly along the tube length because of temperature effects for ideal gas, and the transport coefficient decreases a very small extent along the tube wall (see Fig 7-13 and 7-14). Therefore, the deposition rate and the deposit thickness distribution along the tube length are quite uniform (Fig. 7-15 and 7-16), and they are of the same magnitude with constant heat flux conditions, correspondingly. As stated above, the fact that deposit thickness is less than one particle diameter after six hours implies that only a fraction of the tube surface is covered by the deposits.

![Temperature Distribution along the Tube Length](image)

Fig. 7-12 Temperature Distribution along the Tube Length for Constant Wall Temperature of 500°C
Fig. 7-13 Droplet Concentration Changes with The Tube Length
for Constant Wall Temperature of 500°C

Fig. 7-14 Transport Coefficient Changes with The Tube Length
for Constant Wall Temperature of 500°C
Chapter 7 Droplet Mass Transfer Deposition Model

Fig. 7-15 Deposition Rate Changes With the Tube Length for Constant Wall Temperature of 500°C

Fig. 7-16 Deposit Thickness along The Tube Length after Six Hours for Constant Wall Temperature of 500°C
7.5 Deposition Due to Droplet Mass Transfer and Physical Condensation in Lab Conditions

To clarify the extent of liquid droplet mass transfer contributing to the deposition in cyclone exit line, the comparison of the simulation results of liquid mass transfer model, physical condensation model and experimental data was conducted. For the droplet mass transfer model, the properties of vapour, droplet and the operation parameters are the same with those of corresponding condensation model.

![Graph showing experimental data and simulation results of vapour temperature effects on the deposition rate by condensation model](image)

**Fig. 7-17 Experimental Data and Simulation Results of Vapour Temperature Effects on the Deposition Rate by Condensation Model [7]**

Fig. 7-17 is the comparison of experimental data and simulation results of vapour temperature effects on the deposition rate according to the physical condensation model. With the vapour temperature increase, both the model simulation results and experimental data show that the deposition rate would decrease. Fig. 7-18 is the simulation results of the vapour temperature effects on deposition rate if the deposition is caused by droplet mass transfer mechanism, in which the molar fraction of droplet is assumed as $8.93 \times 10^{-5}$. Fig. 7-18 indicates that the deposition rate changes very little with increasing vapour temperatures, and is about three orders of magnitude smaller than the results predicted by the condensation model and the
experimental data \((10^{-7} \sim 10^{-6} \text{ vs } 3.4 \times 10^{-4} \sim 1.4 \times 10^{-2} \text{ g/m}^2\text{s})\). To reach a deposition rate of \(3 \times 10^{-3} \text{ g/m}^2\text{s}\) corresponding to a temperature of 500°C in Fig. 7-17, for 1 \(\mu\text{m}\) diameter droplets the droplet molar fraction have to reach \(-8 \times 10^{-2}\). This means that the deposition caused by droplet mass transfer mechanism in the cyclone exit line fouling is very minor under laboratory conditions, if it contributes to the deposition.

**Fig. 7-18 Droplet Mass Transfer Mechanism Simulation Results of Vapour Temperature Effects on the Deposition Rate at Constant Inlet Molar Fraction**

Fig. 7-19 is the comparison of experimental data and simulation results of secondary steam/nitrogen addition effects on the deposition rate by physical condensation mechanism. The decrease of the calculated deposition rate by physical condensation mechanism is due to the lower concentration of fouling precursor in the stream because of the addition of secondary steam or nitrogen. The addition of secondary steam or nitrogen would also cause the deposition rate to drop slightly according to the droplet mass transfer mechanism (as shown in Fig. 7-20). In Fig. 20, \(R_{d0}\) is the deposition rate without addition of secondary steam or nitrogen. For all different size droplets, the deposition rate decreases at the same ratio in case of same amount of
nitrogen or steam added. The transport coefficient would increase a little because of the higher vapour flowrate with the addition of secondary steam or nitrogen. However, the droplet concentration would be diluted by the addition of secondary steam or nitrogen, which is the reason for the deposition rate to decrease.

**Fig. 7-19 Comparison of Experiment and Simulation Results of Secondary Steam/Nitrogen Addition Effects on the Deposition Rate by Physical Condensation Model [7]**

**Fig. 7-20 Simulation Results of Secondary Steam/Nitrogen Addition Effects on the Deposition Rate by Mass Transfer Model**
Fig. 7-21 shows the predicted tube diameter effects on the deposition rate, together with experimental data. In this figure, the deposition rate is g/s rather than g/m²·s to avoid the inclusion the tube diameter in unit conversion. The physical condensation model predicts no effects of the tube diameter on the deposition rate, in agreement with the experimental data. From Fig. 7-22, the tube diameter effects on the deposition rate based on droplet mass transfer model are also not obvious. The larger diameter tube would cause a slightly reduced predicted deposition rate in the laboratory laminar flow conditions. The magnitude of the effect is very small, however. As an example, for 10μm size droplets, decreasing the tube diameter from 9 to 5mm raises the deposition rate by ~0.5 wt%, and increase the tube diameter from 9 to 15mm decreases the deposition rate by ~0.8 wt%.

![Graph showing tube diameter effect on deposition rate](image)

**Fig. 7-21 Comparison of Condensation Model Prediction and Experimental Data of Tube Diameter Effect on the Deposition Rate [7]**
7.6 Industrial Conditions with Constant Heat Flux

In industrial conditions, the bulk vapour fluid is in the regime of turbulent flow. For turbulent flow [155], mass transport of droplets from suspensions flowing parallel to tube wall can occur via diffusion, inertia, and impaction. The dominant mechanism is determined by droplet relaxation time, $t_p^+$. Therefore, the droplet deposition rate will be calculated based on the dominant mechanism.

For industrial conditions, it is assumed that the tube diameter is 0.67 m, and the tube length is 5.2 m, so that the ratio of $L/D \approx 7.8$, and the linear velocity of bulk fluid about 40m/s, which is similar with previous simulation conditions [7]. A constant heat flux 4934 W/m$^2$ is assumed to exert on the tube wall. See Table 7-2 for the other operation conditions and the properties of vapour phase and liquid droplets.
7.6.1 Droplet Deposition Due to Diffusion Mechanism

For the size of 0.1 to 0.8 μm diameter droplets, the calculated droplet relaxation time, $t_p^+$, is smaller than 0.1 (see Table 7-5). Equation (7-9) is used to calculate the transport coefficient. The temperature and the droplet concentration distribution along the tube wall are given in Fig. 7-23 and 7-24, respectively. The vapour temperature and the droplet concentration distribution are almost the same for the two different size droplets. The vapour temperature increases by less than 2°C, when it passes through the exit tube. Thus, in the absence of pressure effects, it is very reasonable to assume all the properties of the vapour phase do not change along the exit tube. The droplet concentration also decreases very little along the tube length (around 0.2 mol/L consumed along the tube). The calculated deposition rate distribution along the tube length is given as Fig. 7-25, and the Fig. 7-26 indicates the deposits thickness distribution along the tube after running six hours. In this situation, the deposition rate (ca. $4.63 \times 10^{-3}$ g/m$^2$ s for 0.1 μm droplet) is much faster than those of the same size droplets in laminar flow (e.g., ca. $1.94 \times 10^{-5}$ g/m$^2$·s in 9mm dia. tube). The reason for this is that, in turbulent flow, the droplet has much a higher transport coefficient than in laminar flow (ca. $8.83 \times 10^{-5}$ vs ca. $0.786 \times 10^{-5}$ m/s for 0.1 μm droplet), and also there is a higher droplet molar concentration in industrial conditions. As well, the small size droplet has a bigger transport coefficient and deposition rate in the diffusion regime.

Table 7-4 is the comparison of average droplet transport coefficient and deposition rate between laminar flow and turbulent flow ranges of the same size droplet ($d_p = 0.1$ μm). In this case, the deposition in turbulent flow becomes more serious than that in laminar flow because of a much higher transport coefficient, but the deposit distribution in the tube wall is still quite uniform.
Table 7-4 Comparison of Transport Coefficient and Deposition Rate in Laboratory and Industrial Conditions ($d_p=0.1\mu m$)

<table>
<thead>
<tr>
<th></th>
<th>Re</th>
<th>$k_t \times 10^5$ m/s</th>
<th>$R_d$ (g/m$^2$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory conditions</td>
<td>964</td>
<td>0.786</td>
<td>$1.94 \times 10^{-5}$</td>
</tr>
<tr>
<td>Industrial conditions</td>
<td>$1.499 \times 10^6$</td>
<td>8.83</td>
<td>$4.63 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 7-23 Temperature Distribution along the Tube Length in Diffusion Regime

Fig. 7-24 Droplet Concentration Distribution along the Tube Length in Diffusion Regime
Chapter 7 Droplet Mass Transfer Deposition Model

Fig. 7-25 Deposition Rate Changes with The tube Length in Diffusion Regime

Fig. 7-26 Deposit Thickness Distribution after Six Hours in Diffusion Regime
7.6.2 Droplet Deposition Due to Inertia Mechanism

For the 0.9–8 μm droplet, the calculated droplet relaxation time (Table 7-5), $0.1 < \tau_p^+ < 10$, thus equation (7-10) for the inertia regime can be used to calculate the transport coefficient. The temperature and droplet concentration distribution in this regime are similar with those of the diffusion regimes, as shown in Fig. 7-23 and 7-24. However, the deposition rates of different size droplets are much different with those in the diffusion regime. In the inertia regime, the deposition rate is in proportion with the square of relaxation time, and this causes deposition rates of different size droplets to be much different and have a wide range distribution (Table 7-5). For example, the deposition rate of 5 μm droplet is about 625 times as large as that of 1 μm droplet, and the deposition rate of 1 μm droplet is even smaller than that in diffusion regime. From Fig. 7-28, the deposit thickness can rise up to ca. 0.007–4.37 mm after running six hours, but the deposits distribution is quite uniform along the tube length.

Fig. 7-27 Deposition Rate Changes with The Tube Length in Inertia Regime
7.6.3 Droplet Deposition Because of Impaction Mechanism

If the droplet diameter is larger than 8 \( \mu \text{m} \), the calculated droplet relaxation time, \( t_p^+ > 10 \), and equation (7-11) will be used to calculate the transport coefficient. In this impaction regime, the deposition rate is proportion to the friction velocity \( v^* \), and it does not change with the droplet size. For all different size droplets whose diameter is bigger than 8 \( \mu \text{m} \), the distribution of vapour temperature, droplet concentration, deposition rate and the deposit thickness are all the same with each other. The temperature distribution along the tube in this regime is similar with that of the diffusion and inertia ranges, as shown in Fig. 7-23. However, the droplet concentration drops from 42.8 mol/L to 35.40 mol/L at the tube outlet in the impaction regime. This is because there is a much higher deposition rate if the deposit is formed through impaction, and many more droplets are removed from the vapour phase along the exit tube. The comparison of transport coefficient and deposition rate in different regimes is given in Table 7-5. The deposition rate becomes over 2500 times faster in impact regime than those in diffusion ranges. Fig. 7-30 and 7-31 are the deposition rate and deposit thickness distribution along the
tube length. Both the deposition rate and deposit thickness decrease with the tube length. In this case, the calculation shows that deposits build up very quickly, and would cause serious tube blockage problems, especially at the tube entrance. The values shown at $d_p > 8 \, \mu m$ are clearly orders of magnitude above industrial experience.

![Graph of droplet concentration changes with tube length](image1)

**Fig. 7-29** Droplet Concentration Changes with the Tube Length in Impact Regime

![Graph of deposition rate changes with tube length](image2)

**Fig. 7-30** Deposition Rate Changes with the Tube Length in Impact Regime
7.6.4 Discussion of Droplet Deposition in Turbulent Flow Range

Based on above discussion, the relationship between droplet transport coefficient and droplet size in the present industrial conditions can be approximately expressed by Fig. 7-32 for the clean tube. The transitions are shown as sharp boundaries whereas in reality changes in regime would be spread over a range of particle size [159]. A similar curve but based on $t_p^+$ was also drawn by N. Epstein for particle deposition [155]. For the droplet size from ca. 0.1–0.8 μm,
the deposition is caused by diffusion mechanism. The droplet transport coefficient is quite small ($\sim 10^{-5}$ m/s) and decreases with increasing particle size. For the droplet from 0.9-8 $\mu$m, the transport coefficient increases dramatically with the droplet size in this inertial regime. If the liquid droplet size becomes much bigger (>8 $\mu$m), the mass transport of droplets to the tube wall would occur via impaction mechanism. In the impaction regime, the deposition rate would not change with the droplet sizes, and maintains an excessively value. Bigger size droplet (e.g., >8 $\mu$m) should be avoided to achieve reasonable operation times in fluid cyclone coker based on the above discussion.

Smaller diameter tube would lead to a higher linear velocity of bulk fluid and a bigger Reynolds number (see Table 7-2) for a specified volumetric flow. Therefore, both of bigger size droplets (e.g., >8 $\mu$m) and small diameter tubes can enhance the droplet deposition based on the analysis of equation (7-8) to (7-11), and these should be avoided in the industrial operation.

![Fig. 7-32 Liquid Droplet Transport Regime in the Industrial Conditions ($\nu = 40$ m/s)](image_url)
7.7 Application of Droplet Mass Transfer Model to Industrial Cyclone Exit Line Fouling

The droplet concentration present in the bulk vapour fluid entering the cyclone exit tube would change with the fluid temperature, because the amount of liquid phase would decrease as the temperature was raised. However, this factor is not considered in the calculations of Section 7.6. Based on the HYSIS simulation results of Jankovic [116], liquid droplets would be present in the vapour fluid. However, over all temperatures typical of industrial practice, this temperature effect is relatively small (see Fig. 7-33). Therefore, it is acceptable that the changes in liquid fraction due to temperature are not considered in the modeling process, and this does not affect the model predicted trends.

![Temperature Effects for the Droplet Concentration in The Vapour Fluid](image)

**Fig. 7-33 Temperature Effects for the Droplet Concentration in The Vapour Fluid**

In industrial practice, the fluid coker unit is normally operated well over one year before shutting down to clean the fouled tubes. The deposition effect would cause the diameter of cyclone exit tube to become smaller with increased running time, and lead to increases in the linear velocity of the bulk fluid as follows,

\[
\frac{V_{\text{fouled}}}{V_{\text{clean}}} = \frac{D^2}{(D - 2\delta_c)^2}
\]

(7-32)
Chapter 7 Droplet Mass Transfer Deposition Model

The change of the linear velocity of bulk fluid and the reduction in diameter could affect deposition rate, and even cause a shift of deposition mechanism from one to another regime in turbulent flow, which could lead to major deposition rate changes with the unit running time. Therefore, the effect of deposit buildup must to be considered in the industrial practice. Also, it should be emphasized that these calculations assume that all droplets transported to the surface stick to the surface. As velocity becomes higher, this assumption may no longer hold.

For the large droplets, i.e., >8 μm, the deposition rate would be very high in the turbulent flow region, and cause the blockage problems in the first several running hours or days in the absence of removal effect. This must be avoided in the fluid coker operation. With the consideration of deposit-buildup effects, the changes of linear velocity of bulk fluid, transport coefficient, average deposit thickness with the running time are calculated for the different size droplets, i.e., 0.1, 0.5, 1.0 μm. In the simulation, the tube diameter is updated explicitly at the end of a time step (1~10 days), which means that solution of equation (7-1) and (7-2) is constant over a time step. The operation temperature, and droplet concentration are taken to be the same with those at tube entrance, which is reasonable when considering that there are little changes for either the droplet concentration or the temperature along the tube length in industrial conditions. Based on the equation (2-31), the ratio of pressure drop of fouled tube with that of clean tube can be expressed as follows if tube roughness is neglected:

\[
\frac{\Delta P_{\text{fouled}}}{\Delta P_{\text{clean}}} = \frac{D^5}{(D - 2\delta_c)^5}
\]  

(7-33)

Fig. 7-34 is the relationship of the tube pressure drop ratio (\(\Delta P_{\text{fouled}}/\Delta P_{\text{clean}}\)) with the deposit thickness. It can be seen that the pressure drop in the exit tube increases with the deposit thickness in an exponential order, which means that the deposition would cause the exit tube pressure increase dramatically. In plant operation, the available pressure drop is limited. In the
calculation which follows, the final area blockage is considered to be 90%, where $\delta_c = 229 \text{mm}$, and $\Delta P_{\text{fouled}}/\Delta P_{\text{clean}}$ equals 315.3.

![Graph showing relationship between tube pressure drop and deposit thickness.](image)

**Fig. 7-34 Relationship of the Tube Pressure Drop with The Deposit Thickness**

For the 0.1, 1 and 2 $\mu$m diameter droplet, the simulation results with consideration of deposit accumulation effecting under industrial conditions are given in Fig. 7-35 ~ 7-37, respectively. For the 0.1 $\mu$m droplet, the initial droplet deposition rate caused by diffusion mechanism will increase gradually with time, as does the bulk fluid velocity, transport coefficient, deposit thickness and pressure drop. After running 320 days, the pressure drop becomes so high ($\Delta P_{\text{fouled}}/\Delta P_{\text{clean}} > 100$) after 300 days, and the coker unit has to be shut down at this time in the industrial operation.
Fig. 7-35 Changes of Vapour Linear Velocity, Transport Coefficient, Deposition Thickness and Pressure Drop with The Running Time for Diffusion Regime in Industrial Unit

For 1 μm droplets, the deposition is in the inertia regime. The transport coefficient is very small for 1 μm droplet ($6.80 \times 10^{-6}$ m/s), even smaller than that of in diffusion regime. Thus, the bulk fluid velocity, transport coefficient and pressure drop would increase gradually with the running time in a very slow rate over a very long period (>1400 days, see Fig. 7-36) before the tube is blocked by depositions. It is an ideal situation in industrial practice.
Fig. 7-36 Changes of Vapour Linear Velocity, Transport Coefficient, Deposition Thickness and Pressure Drop with The Running Time in Industrial Unit (d_p=1 µm)

For the 2 µm droplets, the transport coefficient is much bigger than that of 1 µm droplets (1.09×10^{-4} m/s versus 6.80×10^{-6} m/s), although the deposition for both cases is in inertia regime. The deposition phenomena are similar with 1 µm droplets except that the deposit accumulation is much faster in the tube (see Fig. 7-37). All the parameters would increase much faster after the running time of 85 days, and eventually the deposition mechanism shifts from inertia to impact regime. The deposition rate increases dramatically in the impact regime and immediately leads to tube blockage in several hours. Therefore, based on above simulation results, only very small
diameter liquid droplets (ca. 1μm) would not cause the blockage problems in the long time industrial operation.

![Diagram of changes in vapour linear velocity, transport coefficient, deposition thickness, and pressure drop with running time in an industrial unit (dp=2 μm).]

**Fig. 7-37 Changes of Vapour Linear Velocity, Transport Coefficient, Deposition Thickness and Pressure Drop with The Running Time in Industrial Unit (dp=2 μm)**

### 7.8 Summary of Droplet Mass Transfer Deposition Model

A liquid droplet mass transfer model to describe the deposition in fluid coker cyclone exit line fouling has been developed. The model incorporates a deposit formation equation which is based on the droplet transport mechanism to predict the deposition rate in both laboratory and industrial conditions. All droplets which reach the surface are assumed to stick there. Based on the simulation results, the following conclusions can be drawn:
1. In the laminar flow range, at a constant vapour flowrate and temperature, the smaller droplet size will enhance the droplet deposition. The deposition rate is quite low for different size droplets in laminar flow range, and the deposits distribute uniformly along the tube length. The tube diameter effect on the deposition rate is very weak; the larger exit tube diameters only slightly alleviate the deposition caused by liquid droplet transport mechanism.

2. The droplet mass transfer model simulation results were compared with the laboratory experimental data and the results of the physical condensation model. The comparison results indicate that under laboratory conditions the deposition caused by the droplet mass transfer mechanism in the cyclone exit line fouling is very minor compared with physical condensation on the surface, if it contributes to the deposition. Physical condensation on the tube wall appears to be the primary reason for the fluid coker cyclone fouling based on the simulation results under laboratory conditions.

3. In the turbulent flow, mass transport of droplets can occur via diffusion, inertia, and impaction. The larger size droplets will cause the deposition mechanism to shift from diffusion regime to the impaction regime, which will accelerate the droplet deposition rate dramatically and cause much more deposits in the tube entrance region. In this case, small droplet size and large diameter exit tube will mitigate the deposition problem in fluid cyclone coker operation. Temperature effects are minimal.

4. With the consideration of deposit-buildup effects, the changes of linear velocity of bulk fluid, transport coefficient, and deposit thickness with the running time are simulated for the different size droplets, which indicate that the mass transfer also can cause serious deposition and blockage of tube line in industrial operation conditions, especially for the larger size droplets (i.e., >1 μm).
Chapter 8 Conclusions

Cyclone exit line fouling is a chronic problem for all fluid cokers and is a key process limitation to achieving longer run length. It has been a subject of detailed process studies at UBC [5-7]. The overall aims of this work were to elucidate the causes of deposit formation via extensive coke characterization with a range of techniques, examine the evolution of deposit composition and structure over time, compare the difference between the laboratory deposits and industrial samples, and propose a model of deposit structure evolution during the aging process based on kinetics of the deposit aging process and above characterization results. Since previous modeling ignored condensation in the bulk vapour, a mathematical model was to be developed based on the deposition of liquid droplets mass transfer, for comparison to predictions of the surface physical condensation model.

8.1 Characterization and Aging Study of Deposits from Fluid Coker Cyclone Unit

Samples of fresh deposits recovered from the laboratory bench-scale cyclone fouling unit and aged laboratory deposits have been compared with samples from the snout region and exit tube of an industrial fluid coker in this study. Extensive characterization studies using modern analytical techniques, e.g., elemental analysis, X-ray Fluorescence (XRF), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Diffusive Reflection Infrared Spectroscopy (DRIFT), and Solid-state $^{13}$C Nuclear Magnetic Resonance ($^{13}$C NMR), etc., were conducted. Simulated distillation was also applied to solvent extracts of deposits. Volatile release was quantified. The following conclusions are drawn from these extensive characterization results of cyclone fouling deposits:

1. SEM experimental results indicate that there are mainly two kinds of morphology for the deposits formed in the laboratory studies: platelet and amorphous deposits. At lower temperature
Chapter 8 Conclusions

conditions (≤500°C), the amorphous deposits are predominant, however, platelet deposits are the main morphology at higher operating temperature conditions (>500°C). There are many droplets attached on the platelet deposits, and many small droplets aggregate together to form the amorphous deposits. These results support physical condensation mechanism as the main reason for the cyclone exit line fouling in the laboratory study.

2. The similarities of the DRIFT spectra for fresh laboratory deposits, asphaltene and bitumen feed also support the physical condensation mechanism for cyclone exit line fouling. The fact that the extracts from the deposits contain very high boiling point components (90%>400°C) also substantiates condensation causing deposit formation. However, the metals detected in XRF analysis, and the fact that many components exist in extracts from Soxhlet extraction whose boiling points are higher than 750°C indicate that carryover from bitumen droplets also contributes to deposition.

3. All the characterization results, i.e., elemental analysis, SEM, TGA, DRIFT, $^{13}$C NMR and solvent extraction, etc., indicate that industrial samples are much different than the fresh laboratory deposits. Graphitic structures dominate in industrial samples. There are both polyaromatic and aliphatic structures in fresh laboratory deposits, but mainly these deposits are polyaromatic structures. When the operation temperature is raised, the laboratory deposits are increasingly polyaromatic, and possibly can appear more like those of the industrial units.

4. Aging studies were conducted in which fresh deposits were maintained at cyclone temperature for periods up to 24 days. The H/C atomic ratio of fresh laboratory deposit with H/C~0.6 decreases dramatically to H/C~0.3 during the first day of aging, and then decreases gradually to about 0.2, which was close to the values found in plant deposits. The release of volatile components which have a higher H/C atomic ratio must be the main reason to cause much lower H/C atomic ratio of aged deposits; this process mainly happened in the first aging
period. TGA results indicate weight-loss behavior of aged laboratory deposits closely resemble those of the industrial samples.

5. For laboratory deposits, there are additional amorphous features produced during aging. Volatile components evolve during the aging process, are thermally cracked and then re-adsorb on the deposit surface to cause these amorphous features under laboratory condition of near stagnant atmosphere, and low wettability of the glass tube wall and the deposit surface. There was no experimental explanation for the differences in morphology of the industrial samples with the aged lab samples. From the literature, the differences appear to be due to the differences in hydrodynamic conditions during deposit laydown.

6. DRIFT experimental results substantiate the TGA and elemental analysis results. The shift of coke band wave number to lower values indicates that chemical reactions for the formation of condensed polyaromatics took place in the deposits as the aging time proceeded. Solid-state quantitative $^{13}$C NMR analytical results indicate that the structure of short-time aged laboratory deposits is similar to fresh deposits except that the aged deposits have less aliphatic structures. Both DRIFTs and $^{13}$C NMR showed that the long-time aged laboratory deposits indicate a typical graphite characteristic, which structure is similar with those of industrial samples. The various techniques studied yielded a consistent picture of the evolution from the heavy fluid phase components when initially deposit from the vapour to the final massive graphitic coke-like deposit formed in the industrial coker cyclone exit tube.

7. Solvent extraction indicates that there is almost no soluble portion for the long-time aged laboratory deposits, but a small soluble portion exists in the industrial samples. This suggests that polyaromatic deposits were formed during long aging times, and deposit formation is a continuous process. During industrial operation, there is always some fresh deposit being condensed on the "old" deposit surface.
8.2 Kinetics of Deposit Aging at High Temperatures

During the aging process of fresh lab deposits, a considerable amount of volatile components is released, especially in the initial aging period. Complex chemical reactions occur during this process, and finally lead to more condensed polyaromatic and graphitic structures. It was not possible to construct a single mathematical model to describe the weight loss behavior of all deposits during the entire thermogravimetric heating process. Kinetic models were developed to describe reactions in different aging periods based on thermal behavior of deposits. During the heating period from ambient to final temperatures, a first order non-isothermal kinetic model was used to describe the de-volatilization reaction properties of cyclone fouling deposits. Isothermal kinetic models were used to characterize the weight loss phenomena with time at different final temperatures. The following conclusions were drawn based on the kinetic studies:

1. In the heating period, for the laboratory deposits collected at low temperatures (<500°C), a two-stage model is used. The first stage has a low activation energy barrier and low pre-exponential factor, and the second stage a higher activation energy and pre-exponential factor. However, for the industrial deposits and the laboratory deposits collected at high temperatures, a single stage kinetic model of low activation energy barrier and low pre-exponential factor can well describe their thermal behavior. Both the integral and Chen-Nuttall method can be used to find the kinetic parameters. Kinetic compensation effects were observed for different samples.

2. The values of apparent activation energies in the heating period suggest that thermal cracking reactions occur. Similar thermal cracking kinetic phenomena observed by others with pitch, oil shale, etc. indicate the same kind of components exist in the cyclone fouling deposits.

3. In the long time isothermal aging process, the kinetics can be divided into two different periods. In the initial period, the dimensionless release rate of volatiles, which declines dramatically with reaction time, was described by a 2\textsuperscript{nd} order exponential decay equation. A zero
order reaction model can be used to describe the subsequent slow aging reaction period, in which the apparent activation energy is 9.61 kJ/mol.

4. The aged laboratory deposits and industrial deposit samples have similar but not identical volatile release characteristics. In the heating period, thermal cracking reactions take place for industrial samples, but not for the pre-aged laboratory deposits. In the isothermal aging period, as would occur in industrial operation, one zero order reaction model is sufficient to describe the total slow reaction aging kinetics, without a fast initial period.

5. The structural evolution of aging of cyclone fouling deposits is proposed as follows. The fresh deposit has a structure similar to the conglomerate structure of Marsh and Griffiths, consisting of a fused aromatics with much longer aliphatic chains. After the heating period and initial isothermal aging process, more condensed polyaromatic structures are formed. As aging proceeds, dehydrogenation and carbon skeleton re-arrangement occur and lead to more ordered graphitic structures. This process can be illustrated as Fig. 8-1.

![Fig. 8-1 Structure Evolution Model for Cyclone Fouling Deposits in Aging Process following Marsh-Griffiths Model [151]]
8.3 Droplet Mass Transfer Deposition Model

Depending on temperature, pressure, and composition, cyclone exit vapours can contain some liquid droplets. A deposit formation equation which is based on the droplet transport mechanism is used to predict the deposition rate in both laboratory and industrial conditions. Based on the simulation results, the following conclusions were drawn:

1. The droplet mass transfer model simulation results were compared with the laboratory experimental data and the results of a physical condensation model. The comparison results indicate that the deposition caused by droplet mass transfer mechanism in the cyclone exit line fouling is very minor compared with experimental rates and predictions based on physical condensation on the surface under laboratory conditions.

2. In the laminar flow ranges, for the assumed composition, deposition of fine droplets is very slow. The smaller droplet size will enhance the droplet deposition. The deposits distribute uniformly along the tube length in this case. The temperature effect on deposition is weak. At constant flowrate, the tube diameter effects on the mass deposition rate are not significant. The larger diameter exit tube diameter only slightly alleviates the deposition caused by liquid droplet transport mechanism.

3. In the turbulent flow range, mass transport of droplets can occur via diffusion, inertia, and impaction. As the droplet size is increased, the deposition mechanism shifts from diffusion ranges to impact ranges, which will accelerate the droplet deposition rate dramatically and cause much more deposits in the tube entrance region. In this case, small droplet size and large diameter exit tube will mitigate the deposition problem in fluid cyclone coker operation. Temperature effects are minimal.

4. With the consideration of deposit-buildup effects, the changes of linear velocity of bulk fluid, transport coefficient, and deposit thickness with running time are simulated for the
different size droplets, which indicate that the mass transfer also can cause serious deposition and blockage of tube line in industrial operation conditions, especially for the larger size droplets (i.e., >1 μm).
Chapter 9 Recommendations

9.1 Quantitative Solid-state $^{13}$C NMR Analysis

As discussed in Chapter 3 and 4, all carbons except graphite in the carbonaceous deposits contribute equally to the intensity of $^{13}$C NMR spectra. Paramagnetic species, e.g., graphitic-like carbon, are invisible to NMR. Therefore, the proportion of aromatic and aliphatic carbons in the deposits observed by NMR can then be calculated by the integrals of different coke spectra through a calibration line of a reference sample, and the fractions of aliphatic ($f_p$), aromatic ($f_a$) and graphitic carbons ($f_G$) can be calculated from equation (3-3) to (3-5), respectively. To obtain quantitative spectra (i.e. correct line intensity and corresponding good integrals), a flat baseline is required. In this study, efforts were made to find $f_p$, $f_a$ and $f_G$ in different samples by using cholesterol as a reference standard, however, it was found that the carbon contents are always over estimated compared with bulk elemental analysis results. The reason is perhaps that the signals of carbons from aromatics and aliphatics are partly overlapped with each other in the deposit samples. This leads to a non-flat baseline and more errors in integrals.

Thus, it was assumed that either there is zero or 40 wt% graphitic carbon in the fresh laboratory deposits in this study, which means either 100 wt% or 60 wt% carbons in the fresh deposits are visible to $^{13}$C NMR, and the fresh lab deposits were used as a reference standard to calculate $f_a$, $f_p$ and $f_G$, rather than using a standard compounds, such as cholesterol. Therefore, the calculated $f_a$, $f_p$ and $f_G$, are approximate values. In further study, efforts can be continued to get more accurate fractions of different type carbons by $^{13}$C NMR analysis.

9.2 Hot Wire and Cold Finger Probe

A hot wire probe was constructed to incorporate in the laboratory fluid coker cyclone fouling rig to test the deposition in a mixing chamber between the cyclone, exit tube and 90 cm
vertical test sections. This permits a point value of a thermal deposition measurement on a heated surface, and isothermal condition. A cold finger probe was also incorporated into the unit for testing deposition with a cold surface, and isothermal condition. Details are provided in Appendix 9. Initial tests showed some stability issues. Further work should be done to provide a direct indication of the relative roles of physical condensation and chemical reaction at prevailing conditions.

9.3 The Effects of Velocity or Flow Regime on Deposit Morphology

For laboratory deposits, there are additional amorphous features produced during aging. Based on the literature, the differences in morphology which remain after aging with industrial deposits appear to be due to the differences in hydrodynamic conditions during deposit laydown. However, there was no experimental explanation for the morphology differences of the industrial samples with the aged lab samples. The effects of velocity or flow regime on deposit morphology should be established.

9.4 Other Applications

As outlined in the thesis, somewhat similar problems of carbonaceous deposition occur in several other processes, for example, transfer line heat exchangers of ethane crackers. The approaches developed here to characterize deposits, and their aging, as well as the modeling of deposition could be applied in future work to such situations.
## Nomenclature

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATB</td>
<td>Atmospheric Topped Bitumen</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>CML</td>
<td>Cross-polarized Light Microscopy</td>
</tr>
<tr>
<td>CP</td>
<td>Cross Polarization</td>
</tr>
<tr>
<td>DRIFT</td>
<td>Diffuse-reflectance Infrared Fourier Transform Spectrometer</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential Thermogravimetric Analysis</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analyzer</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy Dispersive X-ray Analyzer</td>
</tr>
<tr>
<td>ESP</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid Catalytic Cracking</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HTC</td>
<td>High Temperature Coke</td>
</tr>
<tr>
<td>HTT</td>
<td>Heat Treatment Temperature</td>
</tr>
<tr>
<td>HWP</td>
<td>Hot Wire Probe</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Spectrometer</td>
</tr>
<tr>
<td>LGO</td>
<td>Light Gas Oil</td>
</tr>
<tr>
<td>LTC</td>
<td>Low Temperature Coke</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic Angle Spinning</td>
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<tr>
<td>MCR</td>
<td>Microcarbon Residue</td>
</tr>
<tr>
<td>MPD</td>
<td>1-methyl-2-pyrolidone</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectroscopy</td>
</tr>
</tbody>
</table>
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SFE</td>
<td>Supercritical Fluid Extraction</td>
</tr>
<tr>
<td>SPE</td>
<td>Single Pulse Excitation</td>
</tr>
<tr>
<td>TC</td>
<td>Thermocouple</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TLE</td>
<td>Transfer Line Exchanger</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature Programmed Oxidation</td>
</tr>
<tr>
<td>UV–Vis</td>
<td>Ultraviolet and Visible Spectroscopy</td>
</tr>
<tr>
<td>VGO</td>
<td>Vacuum Gas Oil</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ssb</td>
<td>spinning side band</td>
</tr>
</tbody>
</table>

### Nomenclature

- $A_{wire}$: surface area of wire, m$^2$
- $C$: concentration, mol/L
- $C_b$: bulk concentration of droplets, mol/L
- $C_s$: droplet concentration adjacent to deposition surface, mol/L
- $C^*$: concentration of coke precursor, mol/L
- $C^*_w$: concentration of coke precursor near the tube wall, mol/L
- $\hat{C}_p$: constant pressure heat capacity, J/mol·K
- $\hat{C}_v$: constant volume heat capacity, J/mol·K
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{C}$</td>
<td>the average concentration, mol/L</td>
</tr>
<tr>
<td>$D$</td>
<td>diameter, m</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Brownian diffusivity of droplets in suspension, m$^2$/s</td>
</tr>
<tr>
<td>$D_z$</td>
<td>circumference length at the location $z$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy, J/mol or kJ/mol</td>
</tr>
<tr>
<td>$E_{a0}$</td>
<td>mean activation energy in Anthony-Howard model</td>
</tr>
<tr>
<td>$F$</td>
<td>molar flow rate, mol/s</td>
</tr>
<tr>
<td>$F_j$</td>
<td>molar flow rate of jth component, mol/s</td>
</tr>
<tr>
<td>$Fr$</td>
<td>friction factor, dimensionless</td>
</tr>
<tr>
<td>$G$</td>
<td>total mass flow rate, g/ m$^2$.s</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>heat of reaction, J/mol</td>
</tr>
<tr>
<td>$\Delta H_{VB}$</td>
<td>Enthalpy of vapourization, J/mol</td>
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<tr>
<td>$I$</td>
<td>current, A</td>
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<tr>
<td>$K$</td>
<td>Watson characterization factor for the carbon mixture</td>
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<tr>
<td>$L$</td>
<td>tube length, m</td>
</tr>
<tr>
<td>$M_c$</td>
<td>coke molecular weight, g/mol</td>
</tr>
<tr>
<td>$M_m$</td>
<td>mean molecular weight, g/mol</td>
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<tr>
<td>$N_B$</td>
<td>molar flux of component B</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number, dimensionless</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure, Pa</td>
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<tr>
<td>$Pe$</td>
<td>Peclet number, dimensionless</td>
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<tr>
<td>$P^*_{B,w}$</td>
<td>saturation pressure of species B at $T_{wi}$, kPa</td>
</tr>
<tr>
<td>$P_{B,\text{bulk}}$</td>
<td>partial pressure of species B in the bulk, kPa</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl Number, dimensionless</td>
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<tr>
<td>$R$</td>
<td>gas constant, J/mol·K</td>
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<tr>
<td>$R_{d}$</td>
<td>droplet deposition rate, mol/m²·s</td>
</tr>
<tr>
<td>$R_{ext}$</td>
<td>electrical resistance of circuit external to wire, $\Omega$</td>
</tr>
<tr>
<td>$R_0$</td>
<td>electrical resistance at 0°C, $\Omega$</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number, dimensionless</td>
</tr>
<tr>
<td>$S$</td>
<td>cross section area, m²</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number, dimensionless</td>
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<td>$T$</td>
<td>temperature, K</td>
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<td>fluid bulk temperature, K</td>
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<tr>
<td>$T_B$</td>
<td>boiling point, K</td>
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<tr>
<td>$T_g$</td>
<td>temperature of gas, K</td>
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<tr>
<td>$T_w$</td>
<td>wall or wire temperature, K</td>
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<tr>
<td>$T_{w0}$</td>
<td>value of $T_w$ under clean condition, K</td>
</tr>
<tr>
<td>$U$</td>
<td>overall heat transfer coefficient, W/m²·K</td>
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<tr>
<td>$V$</td>
<td>volatile components, wt%</td>
</tr>
<tr>
<td>$V^*$</td>
<td>maximum volatile components, wt%</td>
</tr>
<tr>
<td>$W_0$</td>
<td>sample initial weight, mg</td>
</tr>
<tr>
<td>$W_t$</td>
<td>sample weight at time $t$, mg</td>
</tr>
<tr>
<td>$W_f$</td>
<td>Sample weight at the final time, mg</td>
</tr>
<tr>
<td>$d$</td>
<td>equivalent diameter</td>
</tr>
<tr>
<td>$d_p$</td>
<td>droplet diameter, m or $\mu$m</td>
</tr>
</tbody>
</table>
\( d_t \)  
- tube diameter, m

\( f \)  
- Fanning friction factor, dimensionless

\( f_a \)  
- the fraction of aromatic carbons in the deposits, wt%

\( f_G \)  
- the fraction of graphitic carbons in the deposits, wt%

\( f_p \)  
- the fraction of aliphatic carbons in the deposits, wt%

\( f_a^* \)  
- the fraction of aromatic carbons in the deposits detected by \(^{13}\)C NMR, wt%

\( f_p^* \)  
- the fraction of aliphatic carbons in the deposits detected by \(^{13}\)C NMR, wt%

\( ff \)  
- fouling factor, m\(^2\)-K/W

\( h \)  
- convection heat transfer coefficient, W/m\(^2\)-K

\( i \)  
- reaction number,

\( j \)  
- species

\( k \)  
- thermal conductivity, W/m-K

\( k_w \)  
- tube wall conductivity, W/m-K

\( k_i \)  
- tube wall conductivity, W/m-K

\( k \)  
- specific reaction rate coefficient

\( k_0 \)  
- Arrhenius frequency factor

\( k_B \)  
- Boltzmann constant = 1.38x10\(^{-23}\) J/K

\( k_c \)  
- specific reaction rate coefficient of coke formation

\( k_d \)  
- deposition coefficient, m/s

\( k_m \)  
- mass transfer coefficient, m/s

\( k_t \)  
- transport coefficient, m/s

\( m \)  
- mass flow rate, kg/s

\( p_t \)  
- total pressure, Pa
Nomenclature

\( p_s^* \)  partial pressure of coke precursors in the bulk, Pa

\( p_w^* \)  partial pressure of coke precursors near the wall, Pa

\( p_s \)  severity of cracking

\( q \)  heat flux, J/m\(^2\).s or W/m\(^2\)

\( r \)  reaction rate, mol/L.s

\( r_m \)  mass transfer rate, mol/m\(^2\).s

\( r_w \)  chemical reaction rate at the wall, mol/m\(^2\).s

\( r_c \)  deposit formation rate, mol/m\(^2\).s or g/m\(^2\).s

\( r_c^* \)  formation rate of coke precursors, mol/m\(^2\).s

\( s_{ij} \)  the stoichiometric coefficient

\( t_p^* \)  droplet relaxation time, dimensionless

\( v \)  volumetric flowrate of fluid, m\(^3\)/s

\( x_w \)  tube wall thickness, m

\( x \)  fraction conversion , %

\( y_i \)  molar fraction of species \( i \) in the gas

\( z \)  reactor length coordinate, m

Greek symbols

\( \Gamma \)  dimensionless volatile release rate

\( \alpha \)  constant in pressure drop equation

\( \delta \)  dilution factor (moles of N\(_2\)/moles of feed)

\( \delta_c \)  deposit thickness, m

\( \delta_t \)  tube thickness, m
Nomenclature

\( v \) linear fluid velocity, m/s

\( \overline{v} \) average linear fluid velocity, m/s

\( v_z \) linear fluid velocity in z direction, m/s

\( v^* \) friction velocity, m/s

\( \varepsilon \) expansion factor (moles produced/moles of feed cracked)

\( \mu \) viscosity, kg/m-s

\( \Theta \) dimensionless reaction time

\( \rho \) gas density, kg/m\(^3\)

\( \rho_c \) the density of the coke, g/cm\(^3\) or kg/m\(^3\)

\( \rho_p \) droplet density, kg/m\(^3\)

\( \sigma \) standard deviation

\( \tau \) residence time, s

\( \nu \) kinetic viscosity, m\(^2\)/s

\( \omega \) dimensionless volatile components
References


## Appendix 1 Detailed Temperature of Different Test Positions in Individual Runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>BHT2 wall of lower coker</th>
<th>T4 vapour of lower coker</th>
<th>T5 vapour of upper coker</th>
<th>T6 vapour btw reactor and cyclone</th>
<th>T7 vapour in cyclone</th>
<th>T8 vapour in exit tube lower</th>
<th>T9 wall of exit tube upper</th>
<th>T10 wall of exit tube</th>
<th>T11 vapour btw cyclone and long tube</th>
<th>T13 vapour in long tube</th>
<th>BHT5 wall of 1st test zone</th>
<th>BHT6 wall of 2nd test zone</th>
<th>BHT7 wall of 3rd test zone</th>
<th>T14 vapour in long test tube outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>521</td>
<td>535</td>
<td>536</td>
<td>535</td>
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<td>553</td>
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<td>550</td>
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<th>Liquid (oil+water,) collection (ml)</th>
<th>Liquid recovery (%)</th>
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</tr>
<tr>
<td>B21</td>
<td>5.5</td>
<td>1.88</td>
<td>1.55</td>
<td>0.122</td>
<td>1.060</td>
<td>2700</td>
<td>78.7</td>
<td>350.0</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B22</td>
<td>6</td>
<td>2.24</td>
<td>1.75</td>
<td>0.013</td>
<td>0.390</td>
<td>4830</td>
<td>87.0</td>
<td>109.0</td>
<td>2ndary steam 1.6kg</td>
</tr>
<tr>
<td>B23</td>
<td>3</td>
<td>1.17</td>
<td>0.88</td>
<td>0.043</td>
<td>0.496</td>
<td>1700</td>
<td>82.9</td>
<td>112.0</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B24</td>
<td>6</td>
<td>2.26</td>
<td>1.76</td>
<td>0.043</td>
<td>0.473</td>
<td>3200</td>
<td>80.0</td>
<td>374.0</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B25</td>
<td>6</td>
<td>2.22</td>
<td>1.75</td>
<td>0.013</td>
<td>0.252</td>
<td>7200</td>
<td>97.0</td>
<td>116.0</td>
<td>2ndary steam 3.3kg</td>
</tr>
<tr>
<td>B26</td>
<td>4.5</td>
<td>1.60</td>
<td>1.26</td>
<td>0.650</td>
<td>1.587</td>
<td>2225</td>
<td>78.6</td>
<td>12.0</td>
<td>Coker temp. 570°C</td>
</tr>
<tr>
<td>B27</td>
<td>6</td>
<td>2.24</td>
<td>1.74</td>
<td>0.009</td>
<td>0.112</td>
<td>3350</td>
<td>84.0</td>
<td>300.0</td>
<td>Coker temp. 500°C</td>
</tr>
<tr>
<td>B28</td>
<td>6</td>
<td>2.21</td>
<td>1.73</td>
<td>0.025</td>
<td>0.410</td>
<td>2850</td>
<td>72.0</td>
<td>149.0</td>
<td>With secondary N₂</td>
</tr>
<tr>
<td>B29</td>
<td>6</td>
<td>2.10</td>
<td>1.58</td>
<td>0.057</td>
<td>0.540</td>
<td>3000</td>
<td>81.6</td>
<td>173.0</td>
<td>⅝&quot; long test tube</td>
</tr>
<tr>
<td>B30</td>
<td>6</td>
<td>2.21</td>
<td>1.71</td>
<td>0.181</td>
<td>1.120</td>
<td>3200</td>
<td>81.4</td>
<td>328.0</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B31</td>
<td>6</td>
<td>2.14</td>
<td>1.72</td>
<td>0.038</td>
<td>0.228</td>
<td>3000</td>
<td>77.7</td>
<td>170.0</td>
<td>⅜&quot; long test tube</td>
</tr>
<tr>
<td>B32</td>
<td>5.5</td>
<td>1.96</td>
<td>1.70</td>
<td>0.051</td>
<td>0.450</td>
<td>3000</td>
<td>82.0</td>
<td>115.0</td>
<td>⅝&quot; long test tube</td>
</tr>
</tbody>
</table>
**Appendix 2 Summary of Operation Conditions and Experimental Results (continued)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Run time (hrs)</th>
<th>Total bitumen feed (kg)</th>
<th>Total steam feed (kg)</th>
<th>Deposition rate (cyclone+exit tube) (g/kg bitumen)</th>
<th>Deposition rate (long test tube) (g/kg bitumen)</th>
<th>Liquid (oil+water,) collection (ml)</th>
<th>Liquid recovery (%)</th>
<th>Deposit in reactor (g)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B33</td>
<td>6</td>
<td>2.12</td>
<td>0</td>
<td>0.028</td>
<td>0.330</td>
<td>850</td>
<td>40.0</td>
<td>455</td>
<td>No steam in reactor</td>
</tr>
<tr>
<td>B34</td>
<td>3</td>
<td>1.03</td>
<td>0.86</td>
<td>0.053</td>
<td>0.570</td>
<td>1300</td>
<td>68.7</td>
<td>51</td>
<td>¼&quot; long test tube</td>
</tr>
<tr>
<td>B35</td>
<td>3</td>
<td>0.93</td>
<td>0.86</td>
<td>0.058</td>
<td>0.600</td>
<td>1400</td>
<td>78.2</td>
<td>44</td>
<td>¼&quot; long test tube</td>
</tr>
<tr>
<td>B36</td>
<td>6</td>
<td>2.02</td>
<td>1.80</td>
<td>/</td>
<td>1.880</td>
<td>3300</td>
<td>86.0</td>
<td>113.0</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B37</td>
<td>4</td>
<td>1.05</td>
<td>1.15</td>
<td>0.124</td>
<td>1.580</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B38</td>
<td>3.7</td>
<td>1.34</td>
<td>1.06</td>
<td>1.740</td>
<td>1.937</td>
<td>1800</td>
<td>75.0</td>
<td>129.8</td>
<td>Cooling vapour</td>
</tr>
<tr>
<td>B39</td>
<td>1.7</td>
<td>0.61</td>
<td>0.49</td>
<td>0.475</td>
<td>2.508</td>
<td>800</td>
<td>72.7</td>
<td>57</td>
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<tr>
<td>B40</td>
<td>6</td>
<td>2.20</td>
<td>1.76</td>
<td>0.311</td>
<td>2.389</td>
<td>3100</td>
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<td>144</td>
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<tr>
<td>B41</td>
<td>6</td>
<td>2.20</td>
<td>1.78</td>
<td>0.311</td>
<td>2.782</td>
<td>2800</td>
<td>70.3</td>
<td>82.8</td>
<td>Cooling vapour</td>
</tr>
</tbody>
</table>
Appendix 3 SEM of Deposits in Exit Tube at Lower Temperature Conditions

Fig. A-1 SEM of Amorphous Deposits in Exit Tube (Run B20, T\textsubscript{wall}=443\degree C)

Fig. A-2 SEM of Amorphous Deposits in Exit Tube (Run B40, T\textsubscript{wall}=425\degree C)
Appendix 3 SEM of Deposits in Exit Tube at Lower Temperature Conditions

Fig. A-3 SEM of Platelet Deposits in Exit Tube (Run B19, $T_{wall}=428^\circ C$)

Fig. A-4 SEM of Platelet Deposits in Exit Tube (Run B40, $T_{wall}=425^\circ C$)
Appendix 4 SEM of Deposits in Exit Tube at Higher Temperature Conditions

Fig. A-5 SEM of Platelet Deposits in Exit Tube (Run B25, $T_{\text{wall}}=500^\circ\text{C}$)

Fig. A-6 SEM of Platelet Deposits in Exit Tube (Run B30, $T_{\text{wall}}=500^\circ\text{C}$)
Appendix 4 SEM of Deposits in Exit Tube at Higher Temperature Conditions

Fig. A-7 SEM of Platelet Deposits in Exit Tube (Run B11, $T_{wall}$=618°C)

Fig. A-8 SEM of Platelet Deposits in Exit Tube (Run B16, $T_{wall}$=603°C)
Appendix 4 SEM of Deposits in Exit Tube at Higher Temperature Conditions

Fig. A-9 SEM of Platelet and Amorphous Deposits in Exit Tube (Run B17, $T_{\text{wall}}$=633°C)

Fig. A-10 SEM of Amorphous Deposits in Exit Tube (Run B30, $T_{\text{wall}}$=500°C)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-11 SEM of One Day Aged Deposits (Run B20)

Fig. A-12 SEM of 10 Days Aged Deposits (Run B20)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-13 SEM of 20 Days Aged Deposits (Run B20)

Fig. A-14 SEM of 2 Days Aged Deposits (Run B40)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-15 SEM of 11 Days Aged Deposits (Run B40)

Fig. A-16 Magnified SEM of 1-day-aged Deposits (Run B19)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-17 Magnified SEM of 1-day-aged Deposits (Run B20)

Fig. A-18 Magnified SEM of 10-day-aged Deposits (Run B20)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-19 Magnified SEM of 18-day-aged Deposits (Run B20)

Fig. A-20 Magnified SEM of 2-day-aged Deposits (Run B40)
Appendix 5 SEM of Aged Deposit Collected in Different Runs

Fig. A-21 Magnified SEM of 11-day-aged Deposits (Run B40)

Fig. A-22 Magnified SEM of 11-day-aged Deposits (Run B40)
Appendix 6 Summary of Analysis Methods Used in Constant Heating Rate Pyrolysis

1. Integral Method

The Integral method [135,136] uses the integration of equation (6-5), with the initial temperature \( T_0 \) chosen at 0 K, at which the rate, as well as the total volatile yield, is negligible. Integration equation (6-5), with \( T_0 \) assumed to be 0 K, gives:

\[
-\ln\left(\frac{V^* - V}{V^*}\right) = \frac{k_0}{C}[T \exp\left(-\frac{E_a}{RT}\right) + \frac{E_a}{R}E\left(-\frac{E_a}{RT}\right)]
\]  \hspace{1cm} (A-1)

The exponential integral \( E\left(-\frac{E_a}{RT}\right) \) can be approximated by:

\[
E\left(-\frac{E_a}{RT}\right) = \exp\left(-\frac{E_a}{RT}\right) \left(\frac{1}{E_a/RT} - \frac{1}{E_a/RT} + \frac{2}{(E_a/RT)^2} - \ldots\right)
\]  \hspace{1cm} (A-2)

If the first three terms of the approximation are used, equation (A-1) become:

\[
-\ln\left(\frac{V^* - V}{V^*}\right) \approx \frac{k_0RT^2}{CE_a}(1 - 2RT/E_a)\exp\left(-\frac{E_a}{RT}\right)
\]  \hspace{1cm} (A-3)

Dividing both sides of equation (A-3) by \( RT^2(1 - 2RT/E_a)/C \) and taking logarithm, gives:

\[
Y = \ln\left(\frac{RT}{V^* - V}\right) - \ln\left(1 - \frac{2RT}{E_a}\right) \approx \ln\left(\frac{k_0}{E_a} - \frac{E_a}{RT}\right)
\]  \hspace{1cm} (A-4)

2. Coats-Redfern Methods

When the activation energy \( E_a >> 2RT \), the term of \( 2RT/E_a \) on the left hand side can be ignored in above equation. Then, the Coats-Redfern method [137] can be expressed as follows,

\[
Y = \ln\left(\frac{RT}{V^* - V}\right) \approx \ln\left(\frac{k_0}{E_a} - \frac{E_a}{RT}\right)
\]  \hspace{1cm} (A-5)

3. Friedman Method

The Friedman method [138] determines the values of \( E_a \) and \( k \), from the ratio \( dV/dT \) versus temperature, taking the logarithm of equation (6-5):
\[ Y = \ln\left(\frac{C}{V^*} \frac{dV}{dT}\right) - \ln\left(1 - \frac{V}{V^*}\right) = \ln k_0 - \frac{E_a}{RT} \]  

(A-6)

However, the Friedman method is usually handicapped by the necessity of differentiating the raw TGA data, which is prone to cause errors. Application of this method for the analysis of nonisothermal TGA data for pyrolysis would therefore lead to incomplete, even wrong, information on the kinetic parameters.

4. Chen-Nuttall Method

The Chen-Nuttall method [139] assumed \( V = 0 \), at an initial temperature of 0 K, in the integration of equation (6-5). Integration of equation (6-5), and multiplying both sides of the equation by \( -\frac{C(E_a + 2RT)}{RT^2} \) and taking logarithms, gives:

\[ Y = \ln\left(-\frac{C(E_a + 2RT)}{RT^2}\ln\left(1 - \frac{V}{V^*}\right)\right) = \ln k_0 - \frac{E_a}{RT} \]  

(A-7)

The values of \( E_a \) and \( k_0 \) of above models can be obtained by nonlinear multiple regression of experimental data.

5. Anthony-Howard Method

All the above four methods assumed that a single activation energy and a single pre-exponential factor can adequately describe the evolution of the pyrolysis products. However, for most pyrolysis process, it is physically realistic to expect evolution of products from a wide range of chemically nonequivalent sources. Hence, more than one rate constant should be required to describe the pyrolysis process. Anthony and Howard [140] proposed a model which describes the evolution of products by a number of parallel, first order rate processes, each represent a rate constant \( k \). Each rate constant has the same pre-exponential factor, and differs only in activation energy. The number of parallel reactions is assumed to be sufficiently large for the activation energies to be described by a Gaussian distribution function, with mean activation \( E_{a0} \) and standard deviation \( \sigma \). Integration of equation (6-5) in the activation rage of 0 to \( \infty \) gives:
\[ V = V^* (1 - \frac{1}{\sigma (2\pi)^{0.5}} \int \exp \left( \frac{k_0 RT^2}{CE_a} (\exp(-\frac{E_a}{RT}))(1 - \frac{2RT}{E_a}) \right) \exp(-0.5(\frac{E_a - E_{a0}}{\sigma})^2) dE_a \) \quad (A-8) \]

A more complex nonlinear multiple regression method to fit the experimental data as described by Yue [133] must be used to find the values of \( E_{a0}, k_0 \) and \( \sigma \).

**Appendix 7 Example of Non-linear Multiple Regression MATLAB Program**

```matlab
% Powerfit.m
% powerfit.m is an example script file that fits the nonlinear power expression of Integral or Chen-Nuttal model. Initial estimate of the two parameters, \( a_1 \) and \( a_2 \) are based on the empirical data from the literature. The augmented Jacobian matrix of the nonlinear fit is calculated in the function 'coeff1.m' which uses two additional functions as arguments, namely 'ffit.m', which defines the nonlinear fitting equations, and 'diff.m', which defines the its derivatives w.r.t. \( a_1 \) and \( a_2 \).

% x = the temperature in the TGA program, K
% y = ln(-C*ln(1-V/V*)) in the integral or Chen-Nuttal Model
% a1 = pre-exponential factor k0
% a2 = activation energy

% Specify the \( (x,y) \) data, which are from the TGA data of Run B20 in the first stage (<440C).

global n

x=[395.07, 410.02, 427.2, 444.33, 461.61, 478.13, 495.07, 511.9, 528.94,...
   545.66, 562.47, 579.37, 596.23, 613.19, 629.93, 646.87, 663.66, 680.57,...
   697.38, 713.97];
y=[-2.3273, -1.6292, -1.2188, -0.9261, -0.6979, -0.3512, -0.2125, 0.02107,...
   0.1217, 0.2995, 0.3791, 0.5237, 0.6527, 0.7125, 0.8242, 0.9270, 1.0225,...
   1.1545, 1.2755, 1.4236];

% Assign variables required by the fitting procedure

tol=1e-5; maxit=50; relax=1; n=length(x);

% Initial estimate of \( a_1 \) and \( a_2 \)

a(1)=0.5; a(2)=17000;

%Use Newton's method to carry out the nonlinear fit

maxda=1e10; iter=0;
while maxda>tol
   alpha=coeff1(x,y,a);
   da=gauss(alpha);
   a=a+relax*da;
   maxda=max(abs(da));
   iter=iter+1;
   if iter>maxit
      fprintf('\n maxit exceeded - maxda= \%8.3e\n',maxda)
```
return
end
end

% Output results including variance of fit
m=length(a);
yfit=fffit(x,a); % read data from 'fffit.m'
var=sum((y-yfit).^2)/(n-m);
fprintf('
 Fitted parameters: 
')
fprintf(' a(\%1.0f) = %8.6f 
',[1:m; a])
fprintf(' x y yfit
')
fprintf(' %6.2f %10.2f %10.2f 
', [x;y;yfit])
fprintf('
 Variance = %8.3e 
', var)

% Plot results
plot(x,y,'o',x,yfit)
xlabel('x'), ylabel('y')

***********************************************************************
function alpha=coeff1(x,y,a)

% 'coeffl.m' is a function m-file that calculates the augmented Jacobian
% matrix required by Newton's method for nonlinear curve fitting.

% Input arguments
% x=matrix of x values
% y=Vector of y values
% a=Vector of initial parameter estimates

% Output argument
% alpha=augmented Jacobian matrix

% determine matrix of differences and partial differentials
n=length(x); m=length(a); mp=m+1;
for k=1:n
    diff(k)=y(k)-ffit(x(k),a);
    for i=1:m
        dfda(i,k)=dffit(i,x(k),a);
    end
end

% Calculate elements of the augmented Jacobian matrix
alpha=zeros(m,mp);
for i=1:m
    for j=i:m
        for k=1:n
            alpha(i,j)=alpha(i,j)+dfda(i,k)*dfda(j,k);
        end
        if j~=i
            alpha(j,i)=alpha(i,j);
        end
    end
end
for k=1:n
    alpha(i,mp)=alpha(i,mp)+diff(k)*dfda(i,k);
end
end

function x=gauss(A)

% gauss.m is a function m-file that uses gauss elimination
% to solve linear equations

% Input argument: % A= Matrix

% Output argument: % x=solution values

n=size(A,1); nm=n-1; np=n+1;
% Carry out elimination process n-1 times
for k=1:nm
    kp=k+1;
    maxAik=abs(A(k,k)); pivot=k;
    for i=kp:n
        absAik=abs(A(i, k));
        if absAik>maxAik
            maxAik=absAik; pivot=i;
        end
    end

    % Change rows k and pivot if pivot ~=k
    if pivot~=k
        for j=k:np
            temp=A(pivot, j);
            A(pivot, j)=A(k, j);
            A(k, j)=temp;
        end
    end

    % Check to see if pivot coefficient is zero
    if A(k,k)==0
        error('Zero pivot coefficient encountered!')
    end

    %Elimination coefficient of x(k) from rows k+1 through n
    for i=kp:n
        quot=A(i,k)/A(k,k);
        for j=kp:np
            A(i,j)=A(i,j)-quot*A(k,j);
        end
    end
end
% Check to see if last pivot coefficient is zero
if A(n,n)==0
    error('Zero pivot coefficient encountered in last row!')
end

% Back substitution
x(n)=A(n,np)/A(n,n);
for i=n:-1:1
    sum=0;
    for j=i+1:n
        sum=sum+A(i,j)*x(j);
    end
    x(i)=(A(i,np)-sum)/A(i,i);
end

******************************************************************************

function dy=dffit(i,x,a)
% 'dffit.m' is a function m-file that defines the partial
derivatives of the power law curve fitting relationship
w.r.t. the fitting parameters a1 and a2.
% Input arguments
% i = index indicating p. d. w.r.t. a1 or a2
% x = independent x values
% a = vector of fitting parameters
% Output argument:
% y = partial derivative values
R=8.314;
if i==1
    dy=1/a(1);
    %dy=-2/a(2)+1/(a(2)-2*R*x)-1/(R*x); %for integral model;
else
    dy=-1/(a(2)+2*R*x)-1/(R*x); % for Chen-Nuttal model
end

******************************************************************************

function y=fffit(x,a)
% 'ffit.m' is a function m-file that output the date to "powerfit.m"
% Input arguments
% x = independent x values
% a = vector of fitting parameters
% Output argument:
% y = fitted y values
global n
R=8.314;
%for Integral model
%y=log(R*a(1)*x(i).^2/a(2))+(log(1-2*R*x(i)/a(2)))-a(2)/(R*x(i));
% for Chen-Nuttal model
for i=1:n
    y(i)=log(a(1)*R*x(i).^2/(a(2)+2*R*x(i)))-a(2)/(R*x(i));
end
Appendix 8 MATLAB Program for Solution of Ordinary Differential Equations

% labfouling.m

% 'labfouling.m' is a script m-file that uses Runge-Kutta Cash-Karp method to solve laboratory coker cyclone fouling problems.

global T0 cp0 KB u dp vb l d

a=0; b=0.9; ya=[813.16;0]; tol=1e-10; n=25;
d=input('
 tube diameter= ');
dp=input('
 droplet size= ');

% Calculate initial constants

nm=n-1; dx=(b-a)/nm; dtol=tol/nm;
hstart=dx; hmin=1e-3*dx; hmax=dx;
x(1)=a; y(:,1)=ya; nfuntot=0;

% Generate x(i) and y(i) solution vectors

for i=1:n
    ip=i+1;
    x(ip)=x(i)+dx;
    [y(:,ip),nfun,hstart]=odesolve('rhsf',x(i),x(ip),y(:,i),...
        dtol,hstart,hmin,hmax);
    nfuntot=nfuntot+nfun;
    cp(i)=cp0*(1-y(2,i))*T0/y(1,i); % droplet concentration mol/L
    D(i)=KB*(y(l,i)/(3*pi*u*dp)); % Diffusivity of droplet
    Pe(i)=d*vb/D(i); % Peclet number
    Sh(i)=1.62*(Pe(i)*d/l)^(1/3); % Sherwood Number
    km(i)=Sh(i)*(D(i)/d); % transport coefficient, m/s
    r(i)=1907*km(i)*cp(i)*10^(-3); % deposition rate, g/m2 s
    t=6; % reaction time hrs
    dc=1.27; % density of deposits
    delta(i)=3.6*r(i)*t/dc; % deposit thickness
end

% print results

fprintf('
 x T(K) x cp(mol/L) km(m/s) rc(g/m2s) thickness(mm) \n \n')
for i=1:n
    fprintf('%5.2f %10.2f %7.4f %7.4f %14.3e %10.3e %12.3e \n',x(i),y(l,i),y(2,i),cp(i),km(i), r(i),delta(i))
end
fprintf('
 Number of function evaluations = %4.Of \n
',nfuntot)

*************************************************

function Z=rhsf(x,y)

global T0 cp0 KB u dp vb l d

% 'rhsf.m' is a function m-file that is used to define the energy balance and molar balance in the fluid coker cyclone exit tube
% input argument
% x=temperature along the exit tube
% y=reaction conversion fraction of droplets along the exit tube

Fv=6.666*10^-3; % molar flowrate of vapour, mol/s
Fp0=5.947*10^-7; % molar flowrate of droplets, mol/s
Q=1157; % heat transfer, W/m^2
vol=4.442*10^-4; % bulk volumetric flowrate, m^3/s
vb=vol/(0.25*pi*d^2); % bulk linear velocity, m/s
SG1= 1.0678; % density of droplet at 15C
K1=11.63; % Watson characterization factor
SG2=0.993; % Density of bitumen at 15C
K2=11.77; % Watson factor of bitumen
CF1=((12.8/K1-1)*(10/K1-1)*100)^2; % factor of droplets
al=-0.32646+0.02678*K1-CF1*(0.084773-0.080809*SG1); % droplet
bl=-(1.3892-1.2122*K1+0.0383*K1^2-CF1*(2.1773-2.0826*SG1))*10^-4; % droplet
c1=-(1.5393+CF1*(0.78649-0.70423*SG1))*10^-7; % droplet
Cp1=0; % heat capacity of droplets J/mol K
CF2=((12.8/K2-1)*(10/K2-1)*100)^2; % factor of bitumen
a2=-0.32646+0.02678*K2-CF2*(0.084773-0.080809*SG2); % bitumen
b2=-(1.3892-1.2122*K2+0.0383*K2^2-CF2*(2.1773-2.0826*SG2))*10^-4; % bitumen
c2=-(1.5393+CF2*(0.78649-0.70423*SG2))*10^-7; % bitumen
Cp2=0.01699*Cpbitumen+0.2753*CpN2+0.7077*Cpwater;
u=3.38*10^-5; % viscosity of bulk fluid, kg/m s
rou=0.497; % density of bulk fluid, kg/m^3
Re=d*rou*vb/u; % Reynolds number
l=0.9; % tube length, m
KB=1.38*10^-23; % Bolzmann constant
D=d*Kb*y(1)/(3*pi*u*dp); % diffusity of droplets, m^2/s
Pe=d*vb/D; % Peclet number
Sh=1.62*(Pe*d/l)^(1/3); % Sherwood number
km=Sh*(D/d); % Transport coefficient, m/s
cp0=1.34; % initial droplet concentration, mol/L
T0=813.16; % initial temperature, K
T=cp0*(1-y(2))*(T0/y(1)); % local concentration of droplets, mol/L
r=km*cp*10^-3; % droplet deposition rate, mol/m^2.s
Z(1)=Q*pi*d/(Fp0*(1-y(2))*Cp1+Fv*Cp2); % Energy balance equation
Z(2)=r*pi*d/Fp0; % Molar balance equation
Z=[Z(1);Z(2)];

% labfouling1.m
% 'labfouling.m' is a script m-file that uses Runge-Kutta Cash-Karp
% method to solve laboratory coker cyclone fouling problems at constant
% wall temperature.
global T0 cp0 KB u dp vb l d

a=0; b=0.9; ya=[813.16;0]; tol=1e-10; n=25;
d=input('\n tube diameter= ');
dp=input('\n droplet size= ');

% Calculate initial constants

nm=n-1; dx=(b-a)/nm; dtol=tol/nm;
hstart=dx; hmin=1e-3*dx; hmax=dx;
x(1)=a; y(:,1)=ya; nfuntot=0;

% Generate x(i) and y(i) solution vectors
for i=1:n
    ip=i+1;
    x(ip)=x(i)+dx;
    [y(:,ip),nfun,hstart]=odesolve('rhsf3',x(i),x(ip),y(:,i), ...  
        dtol,hstart,hmin,hmax);
    nfuntot=nfuntot+nfun;
    cp(i)=cp0*(1-y(2,i))*T0/y(1,i); % droplet concentration mol/L
    D(i)=KB*(y(l,i)/(3*pi*u*dp)); % Diffusivity of droplet
    Pe(i)=d*vb/D(i); % Peclet number
    Sh(i)=1.62*(Pe(i)*d/l)^(1/3); % Sherwood Number
    km(i)=Sh(i)*D(i)/d; % Transport coefficient, m/s
    r(i)=1907*km(i)*cp(i)*10^(-3); % deposition rate, g/m² s
    t=6; % reaction time hrs
    dc=1.27; % density of deposits
    delta(i)=3.6*r(i)*t/dc; % deposit thickness
end

% print results
fprintf('\n Z T(K) x cp(mol/L) km(m/s) rc(g/m²/s) thickness(mm)\n
')
for i=1:n
    fprintf(' %5.2f %6.2f %7.2e %6.3f %10.3e %10.3e %12.3e\n',x(i),y(l,i),y(2,i),cp(i),km(i), r(i), delta(i))
end
fprintf('\n Number of function evaluations = %4.Of\n
' , nfuntot)

*********************************************
function Z=rhsf3(x,y)

global T0 cp0 KB u dp vb l d

% 'rhsf.m' is a function m-file that is used to define the energy balance
% and molar balance in the fluid coker cyclone exit tube
% input argument
% x=temperature along the exit tube
% y=reaction conversion fraction of droplets along the exit tube

Fv=6.666*10^(-3); % molar flowrate of vapour, mol/s
Fp0=5.947*10^(-7); % molar flowrate of droplets, mol/s
U=13.178; % overall heat transfer coefficient, W/m² K
vol=4.442*10^(-4); % bulk volumetric flowrate, m³/s
vb=vol/(0.25*pi*d^2); % bulk linear velocity, m/s
Tw=773; % tube wall temperature
Appendix

SG1 = 1.0678; % density of droplet at 15C
K1 = 11.63; % Watson characterization factor
SG2 = 0.993; % density of bitumen at 15C
K2 = 11.77; % Watson factor of bitumen

\[ CF1 = \left( \frac{12.8}{K1-1} \right) \left( \frac{10}{K1-1} \right) \times 100 \] % factor of droplets
\[ a1 = -0.32646 + 0.02678 \cdot K1 - CF1 \left( 0.084773 - 0.080809 \cdot SG1 \right) \] % droplet

\[ b1 = -1.3892 - 1.2122 \cdot K1 + 0.0383 \cdot K1^2 - CF1 \left( 2.1773 - 2.0826 \cdot SG1 \right) \times 10^{-4} \] % droplet
\[ c1 = -1.5393 + CF1 \left( 0.78649 - 0.70423 \cdot SG1 \right) \times 10^{-7} \] % droplet

Cp1 = 0; % heat capacity of droplets J/mol K

\[ CF2 = \left( \frac{12.8}{K2-1} \right) \left( \frac{10}{K2-1} \right) \times 100 \] % factor of bitumen
\[ a2 = -0.32646 + 0.02678 \cdot K2 - CF2 \left( 0.084773 - 0.080809 \cdot SG2 \right) \] % bitumen

\[ b2 = -1.3892 - 1.2122 \cdot K2 + 0.0383 \cdot K2^2 - CF2 \left( 2.1773 - 2.0826 \cdot SG2 \right) \times 10^{-4} \] % bitumen
\[ c2 = -1.5393 + CF2 \left( 0.78649 - 0.70423 \cdot SG2 \right) \times 10^{-7} \] % bitumen

Cpbitumen = a2 + b2 \cdot y(1) + c2 \cdot y(1)^2 \times 750 \times 4.184; % heat capacity of bitumen, J/mol K

Cpwater = 29.16 + 14.49 \cdot y(1) \times 10^{-3} - 2.022 \cdot y(1)^2 \times 10^{-6}; % heat capacity of steam, J/mol K

CpN2 = 27.32 + 6.226 \cdot y(1) \times 10^{-3} - 0.9502 \cdot y(1)^2 \times 10^{-6}; % heat capacity of nitrogen, J/mol K

Cp2 = 0.01699 \cdot Cpbitumen + 0.2753 \cdot CpN2 + 0.7077 \cdot Cpwater; % heat capacity of fluid, J/mol K

u = 3.38 \times 10^{-5}; % viscosity of bulk fluid, kg/m s

\[ \text{Re} = \frac{d \cdot \rho \cdot v}{\mu}; \quad \text{Reyolds number} \]

l = 0.9; % tube length, m

KB = 1.38 \times 10^{-23}; % Boltzmann constant

D = KB \cdot y(1) / \left( 3 \cdot \pi \cdot u \cdot dp \right); % diffusivity of droplets, m^2/s

Sh = D^2 \cdot \left( Pe^2 \right) / (3 \cdot \pi) \left( Pe \right) \left( 1 / 3 \right); % Sherwood number

km = Sh \cdot D / dp; % Transport coefficient, m/s

cp0 = 1.34; % initial droplet concentration, mol/L

T0 = 813.16; % initial temperature, K

\[ cp = cp0 \cdot (1 - y(2)) \cdot (T0 / y(1)); \] % local concentration of droplets, mol/L

r = km \cdot cp \times 10^{-3}; % droplet deposition rate, mol/m^2.s

Z(1) = -U \cdot (y(1) - Tw) \cdot \pi \cdot d / (Fp0 \cdot (1 - y(2)) \cdot Cp1 + Fv \cdot Cp2); % Energy balance equation

Z(2) = r \cdot (pi * d) / Fp0; % Molar balance equation

Z = [Z(1); Z(2)];

% indfouling.m

% 'indfouling.m' is a script m-file that uses Runge-Kutta Cash-Karp method to solve industrial coker cyclone fouling problems.

global T0 cp0 KB u dp vb l d tp vstar rou

dp = input('\n droplet size = ');
x(ip)=x(i)+dx;
y(:,ip),nfuntot,hstart=odesolve('rhsf2',x(i),x(ip),y(:,i),...
dtol,hstart,hmin,hmax);
nfuntot=nfuntot+nfun;
cp(i)=cp0*(1-y(2,i))*T0/y(1,i); % droplet concentration mol/L
D(i)=KB*(y(1,i)/(3*pi*u*dp)); % Diffusivity of droplet
Sc(i)=u/(rou*D(i)); % Schmidt number
% transport coefficient in diffusion regime, m/s
if tp<0.1
    km(i)=0.0847*vstar/Sc(i)^{(2/3)};
% transport coefficient in inertia regime, m/s
elseif (0.1<tp & tp<10)
    km(i)=0.00035*tp^2;
% transport coefficient in impact regime, m/s
else
    km(i)=0.18*vstar;
end
r(i)=1227*km(i)*cp(i)*10^(-3); % deposition rate, g/m2 s
% reation time hrs
dc=1.1; % density of deposits
delta(i)=3.6*r(i)*t/dc; % deposit thickness
end
% print results
fprintf('
 %5.2f %10.2f %7.4f %10.4f %14.3e %10.3e %12.3e
',x(i),y(1,i),y(2,i),cp(i),km(i), r(i), delta(i))
end
fprintf('
 Number of function evaluations = %4.0f

',nfuntot)
function Z=rhsf2(x,y)
global T0 cp0 KB u dp vb l d tp vstar rou
% 'rhsf2.m' is a function m-file that is used to define the energy balance
% and molar balance in the fluid coker cyclone exit tube under industrial
% conditions.
% input argument
% x = reaction conversion fraction of droplets along the exit tube
% y = temperature along the exit tube
Fv=418.70; % molar flowrate of vapour, mol/s
Fp0=0.612; % molar flowrate of droplets, mol/s
d=0.67; % tube diameter, m
Q=4934; % heat transfer, W/m^2
vol=14.31; % bulk volumetric flowrate, m^3/s
vb=vol/(0.25*pi*d^2); % bulk linear velocity, m/s
SG1= 1.0678; % density of droplet at 15C
K1=11.63; % Watson characterization factor
SG2=0.993; % Density of bitumen at 15C
K2=11.77; % Watson factor of bitumen
CF1=((12.8/K1-1)*(10/K1-1)*100)^{(2/3)}; % factor of droplets
a1=-0.32646+0.02678*K1-CF1*(0.084773-0.080809*SG1); % droplet
b1=-(1.3892-1.2122*K1+0.0383*K1^2-CF1*(2.1773-2.0826*SG1))*10^(-4); % droplet
c1=-(1.5393+CF1*(0.78649-0.70423*SG1))*10^(-7); % droplet
% heat capacity of droplets J/mol K
Cp1=(a1+1.8*b1*y(1)+3.24*c1*y(1)^2)*1227*4.18;

CF2=1*(12.8/K2-1)*(10/K2-1)*100)^2; % factor of bitumen
a2=-0.32646+0.02678*K2-CF2*(0.084773-0.080809*SG2); % bitumen
b2=-1.3892-1.2122*K2+0.0383*K2-2-CF2*(2.1773-2.0826*SG2)))*10^(-4); % bitumen
c2=-1.5393+CF2*(0.78649-0.70423*SG2)))*10^(-7); % bitumen

% heat capacity of bitumen, J/mol K
Cpbitumen=(a2+1.8*b2*y(1)+3.24*c2*y(1)^2)*750*4.184;
% heat capacity of steam, J/mol K
Cpwater=29.16+14.49*y(1)*10^(-3)-2.022*y(1)^2*10^(-6);
% heat capacity of nitrogen, J/mol K
CpN2=27.32+6.226*y(1)*10^(-3)-0.9502*y(1)^2*10^(-6);
% heat capacity of fluid, J/mol K
Cp2=0.01699*Cpbitumen+0.2753*CpN2+0.7077*Cpwater;

u=3.11*10^(-5); % viscosity of bulk fluid, kg/m s
rou=1.715; % density of bulk fluid, kg/m^3
Re=d*rou*vb/u; % Reynolds number
l=5.2; % tube length, m
KB=1.38*10^(-23); % Bolzmann constant
D=KB*y(1)/(3*pi*u*dp); % diffusity of droplets, m^2/s
f=0.0791/(Re^0.25); % friction factor
Pe=d*vb/D; % Peclet number
Sc=u/(rou*D); % Schmidt number
vk=u/rou; % kinematic viscosity m^2/s
vstar=vb*(f/2)^0.5; % friction velocity
roup=760; % density of droplet, kg/m^3

% droplet relaxation time, dimesionless
tp=(roup*dp^2*vstar^2)/(18*u*vk);

% transport coefficient in diffusion regime, m/s
if tp<0.1
    km=0.0847*vstar/Sc^(2/3);
% transport coefficient in inertia regime, m/s
elseif (0.1<tp & tp<10)
    km=0.00035*tp^2;
% transport coefficient in impact regime, m/s
else
    km=0.18*vstar;
end

% initial droplet concentration, mol/L
T0=813.16; % initial temperature, K
Cp0=42.8; % initial droplet concentration, mol/L
T0=813.16; % initial temperature, K
Cp=Cp0*(1-y(2)^2)*T0/y(1)); % local concentration of droplets
r=km*Cp*10^(-3); % droplet deposition rate, mol/m^2.s
Z(1)=Q*pi*d/(FpO*(1-y(2)))*Cp1+Fv*Cp2; % Energy balance equation
Z(2)=r*(pi*d)/Fp0; % Molar balance equation
Z=[Z(1);Z(2)];
function [yb,nfun,hstart]=odesolve(f,a,b,ya,tol,hstart,hmin,hmax)

% 'odesolve.m' is a function m-file that uses Runge-Kutta Cash-Karp
% method to solve n simultaneous first order initial problems to a
% user-prescribed accuracy. Accuracy is checked by adaptively
% adjusting the step-size of the solution subinterval to ensure
% that a global tolerance is met.

% Input arguments
% f = dummy name rhs functions
% a = start of solution interval
% b = end of solution interval
% ya = values of y at x=a
% tol = global accuracy required at x=b
% hstart = initial step size
% hmin = minimum step size
% hmax = maximum step size
% j = index of rhs equation and y

% Output arguments
% yb = values of y at x=b
% nfun = number of rhs function evaluation needed
% hstart = last successful value of hnew before return

% Initial variables
hold=hstart; xold=a; yold=ya; nfun=0; success=0;

% Loop until yb is determined to required tolerance
while success==0
    nfun=nfun+6;
    [ynew,ydiff]=rkck(f,xold,yold,hold);
    gamma=(tol*hold/(ydiff*(b-a)))^0.25;
    hnew=0.8*gamma*hold;

    if gamma<1
        if hnew<hold/10
            hnew=hold/10;
        end
        if hnew<hmin
            fprintf('
 odesolve failed at x= %8.3e 

', xold)
            error
        end
        hold=hnew;
    % If gamma>=1, accept ynew and add hold to xold
    else
        if hnew>5*hold
            hnew=5*hold;
        end
        if hnew>hmax
            hnew=hmax;
        end
        if xold+hold<b
            xold=xold+hold; hold=hnew; yold=ynew;

% xold+hold>=b, calculate yb and return
else
    success=1; hstart=hnew; hold=b-xold; nfun=nfun+6;
    [yb,ydiff]=rkck(f,xold,yold,hold);
end
done
end

******************************************************************************

function [y2,ydiff]=rkck(f,xl,yl,h)

% 'rkck' is a function m-file that evaluates the Runge-Kutta Cash-Karp
% formula to solve n simultaneous first-order initial value problems.
% The solution is advanced using the 5-th order formula, while the
% difference between the 4-th and 5-th order methods, is determined to
% help update the step-size in 'odesolve.m'

% Input arguments
% f = dummy name of rhs functions
% xl = value of start of solution interval
% yl = values of y at start of solution interval
% h = solution interval stepsize
% j = Index of rhs equations and y

% Output arguments
% y2 = Values of y at solution interval
% ydiff = rhs function evaluations needed

kl=h*feval(f,xl,yl);
k2=h*feval(f,xl+h/5,yl+kl/5);
k3=h*feval(f,xl+3*h/10,yl+3*kl/40+9*k2/40);
k4=h*feval(f,xl+3*h/5,yl+3*kl/10-9*k2/10+6*k3/5);
k5=h*feval(f,xl+h,yl-ll*kl/54+5*k2/2-70*k3/27+...
            35*k4/27);
k6=h*feval(f,xl+7*h/8,yl+1631*kl/55296+175*k2/512+...
            575*k3/13824+44275*k4/110592+253*k5/4096);
y2=yl+37*kl/378+250*k3/621+125*k4/594+...
    512*k6/1771;
ydiff=abs((37/378-2825/27648)*kl+(250/621-18575/48384)*k3+...
    (125/594-13525/55296)*k4-277*k5/14336+(512/1771-1/4)*k6);
ydiff=max(ydiff);
% 'fouling.m' is a script m-file that calculated the changes of fluid 
% velocity, transport coefficient, deposition thickness and pressure 
% drop with running time in industrial coker cyclone fouling.

t=input('
  time interval='); % time interval, day
dp=input('  droplet size, m');
d=0.67; % initial tube diameter, m
deltal=0; % initial deposit thickness
T=813.16; % reaction temperature
vol=14.31; % bulk volumetric flowrate, m^3/s
u=3.11*10^(-5); % viscosity of bulk fluid, kg/m s
rou=1.715; % density of bulk fluid, kg/m^3

KB=1.38*10^(-23); % Boltzmann constant
dc=1.1; % density of deposit
cp0=42.8; % initial droplet concentration, mol/L
T0=813.16; % initial temperature, K
roup=760; % density of droplet, kg/m^3
D=KB*T/(3*pi*u*dp); % diffusivity of droplets, m^2/s
Sc=u/(rou*D); % Schmidt number
vk=u/rou;
deltap=l; % initial value of pressure drop
n=1; % count the running time, days

fprintf('time(d)  vb  km(m/s)  rc(g/m^2s)  thickness(mm)  deltap  tp

')
while (d>0 & deltap<400)
  vb=vol/(0.25*pi*d^2); % bulk linear velocity, m/s
  Re=d*rou*vb/u; % Reynolds number
  f=0.0791/(Re^0.25); % friction factor
  vstar=vb*(f/2)^0.5; % friction velocity

  % droplet relaxation time, dimensionless
  tp=(roup*dp^2*vstar^2)/(18*u*vk);
  if tp<0.1 % transport coefficient in diffusion regime, m/s
      km=0.0847*vstar/Sc^(2/3);
  elseif (0.1<tp & tp<10) % transport coefficient in inertia regime, m/s
      km=0.00035*tp^2;
  else % transport coefficient in impact regime, m/s
      km=0.18*vstar;
  end
  r=1227*km*cp0*10^(-3); % droplet deposition rate, g/m^2.s
  delta=t*86.4*r*10^(-3)/dc; % deposit thickness accumulation in one day
  deltal=deltal+delta; % update deposit thickness
  d=0.67-2*deltal;
  deltap=(0.67/d)^5; % pressure drop
  thick=deltal*10^3;
  T=n*t;
  fprintf('  %5.1f  %7.3f  %10.3e  %10.3e  %8.3f  %8.3f  %8.4f  
    T, vb, km, r, thick, deltap, tp)
Appendix 9 Hot Wire Probe and Cold Finger Probe

Fig. A-23 shows the proposed set-up of hot wire probe and cold finger probe, and Fig. A-24 are pictures of hot wire and cold finger probes used in several test runs. These measurements could provide a direct indication of the relative roles of physical condensation and chemical reaction at prevailing conditions.

Side View

End View

Fig. A-23 Hot Wire Probe and Cold Finger Probe for Testing Deposition
Fig. A-24 Pictures of Hot Wire Probe and Cold Finger Probe
The detail connections of cold finger probe are shown in Fig. A-25. Two different diameter tubes are used in the cold finger probe: the outside tube diameter is 3/8”, and inside tube diameter ¼”. One 3/8” union tee and two ¼” female tee were used for connection of different diameter tubes and thermocouples. One 1/16” thermocouple is inserted into the probe wall to measure the wall surface temperature, and another 0.01” thermocouple is employed to measure the air temperature near the wall.

![Diagram of Cold Finger Probe Connections](image)

**Fig. A-25 The Detailed Connection of Cold Finger Probe**

The bulk temperature of vapour phase is assumed to be at constant temperature $T_b$ and ignore the heat conductivity of the tube wall. Thus

$$Q = UA(T_b - T_{air})$$  \hspace{1cm} (A-9)

under clean surface conditions,

$$\frac{1}{U_0} = \frac{\Delta T_0}{Q/A}$$  \hspace{1cm} (A-10)

and assuming the heat transfer area does not change much under fouled conditions, then

$$\frac{1}{U} = \frac{\Delta T_f}{Q/A}$$  \hspace{1cm} (A-11)

where $Q = C_{p,air} m_{air} (T_{out} - T_{in})$, and the thermal fouling resistance is given by:

$$R_f = \frac{1}{U} - \frac{1}{U_0}$$  \hspace{1cm} (A-12)

This thermal fouling resistance is plotted against time to determine the thermal fouling profile.
The hot wire probe has been used successfully for liquid fouling research [160]. It consists of a fine (0.125 mm dia.) wire, wrapped into a coil of 1.2 mm dia., place normal to the flow direction, and heated electrically by passage of a DC current through the wire. The thermal fouling resistance [160] can be given by:

\[ R_f = \frac{T_w - T_{w0}}{Q/A} \]  

(A-13)

and the power input \( Q = I^2(V/I - R_{ext}) \), \( T_w = \frac{[(R - R_{ext})/R_0] - 1}{\alpha} \), where \( \alpha \) is temperature coefficient of electrical resistance of wire, \( A \) is wire surface area, \( R \) is the electrical resistance, \( R_{ext} \) is the electrical resistance of circuit external to wire, and \( V \) the current voltage. The detailed test procedure for the hot wire probe is as follows:

1. Cut a 10cm length of stainless 302 wire (Fe/Cr18/Ni 8, 0.125mm diameter). Coil the wire tightly around the top part of a 0.043 in. diameter drill bit, weigh the wire on an analytical balance (ca. 0.01g), and connect it to the copper lead in the probe chamber.

2. Energizing the wire with about 1A for a few minutes to anneal out the bulk of the defects in the wire so that \( R_0 \) will be stable during the running process, and then measure the wire resistance with a precise multimeter at ambient temperature, and at bulk temperature (ca. 550°C), respectively. Calculate \( R_0 \) of wire by the equation \( R = R_0(1 + \alpha T) \), where \( \alpha \) is 0.00094/°C based on the literature [161], and \( T \) is equal to ambient temperature and bulk temperature, respectively. Assume \( R_0 \) does not change with the running time.

3. As fouling progresses, the power to the HWP decreases due to increasing wire temperature and thus increasing wire resistance. The power supply output must be adjusted to keep it stable during test run.

4. Weight the wire on an analytical balance and examine the deposit after test.
(5) The thermal fouling resistance can be given by equation (A-13). $R_{\text{ext}}$ is very small ($10^{-2}$ $\Omega$) compared with $R$ and can be neglected. This thermal fouling resistance is plotted against time to determine the thermal fouling profile.