

KINETICS AND STRUCTURAL EVOLUTION DURING AGING OF COKER VAPOUR DEPOSITS

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ABSTRACT

Unwanted deposition of carbonaceous material from the vapour phase is a chronic problem in piping and equipment downstream of coking units and may be a limitation to achieving longer run length. The laboratory deposits were found to exhibit major differences from those in industry. An aging study was conducted to rationalize these differences. After days to weeks of aging at elevated temperature, the lab deposits become very similar to those of the graphitic industrial deposits. The differences in morphology which remain after aging, were attributed to differences in hydrodynamic conditions during the deposit laydown. During aging, the composition and structure of deposits change with the time. This process includes complex chemical reactions, and finally leads to more condensed polyaromatic and graphitic structures. Deposit aging kinetics was also studied through thermogravimetric analysis. Deposit characterization and kinetic studies yielded a consistent picture of the evolution from the heavy fluid phase components which initially deposit from the vapour due to physical condensation, to the final massive, graphitic, coke-like solids found in industrial units. This structural evolution is described following the Marsh-Griffiths model.

INTRODUCTION

Unwanted deposition of carbonaceous material from the vapour phase is a chronic problem in piping and equipment downstream of coking units and may be a limitation to achieving longer run length. Fluid coker cyclone exit line fouling has been a subject of detailed studies (Watkinson et al., 2002; Zhang and Watkinson, 2005a,b; Fan and Watkinson, 2006a,b), and it was found that under laboratory conditions fouling was primarily caused by physical condensation of heavy hydrocarbon vapours, although carryover from bitumen feed droplets also contribute to the deposition. The deposition caused by physical condensation mechanism has also been implicated in transfer line fouling in naphtha crackers for olefins production (Zou et al., 1992; Kopinke et al., 1993). Characterization of the laboratory deposits has shown major differences from those of an industrial coker cyclone exit

line (Fan and Watkinson 2006a). The laboratory deposits were collected after six hours running in the bench-scale fluid coker unit, whereas the industrial samples had been aging in place in the presence of hydrocarbons at temperatures around 500°C for an undetermined time period of many months.

In order to interpret behaviour in industrial units, and to relate short-term laboratory results to long term industrial operation, it is important to understand the aging process as fresh deposits undergo reaction over long periods at elevated temperature. During aging of fouling deposits from fluid coker cyclone exit lines, the composition and structure of deposits change with the time. This process includes complex chemical reactions, and finally leads to more condensed polyaromatic and graphitic structures. In this work, the deposit aging kinetics were also studied through thermo-gravimetric analysis, and a model of deposit structural evolution during the aging process was proposed, based on kinetics of the deposit aging process and characterization results. The overall aims of this work are to examine the evolution of deposit composition and structure over time, and to rationalize the differences between the laboratory deposits and industrial samples.

EXPERIMENTAL METHODS

Materials Fresh deposit samples (B19, B20, B30 and B40) from the test exit tube were collected from the bench-scale fluid coker cyclone fouling unit after running six hours. The four deposits were collected under the vapour temperature between ca. 450~520°C, and tube wall temperature between ca. 430~500°C. 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 operating conditions of each run, and the properties of bitumen feed were given in Fan and Watkinson (2006a). Deposit B and D are industrial samples, in which sample B was collected from the cyclone snout outlet, and sample D from gas outlet tube.

Aging of Fresh Deposits As described in Fan and Watkinson 2006b, in closed-system batch aging studies, samples are placed in a 10 mm dia. glass liner inserted into

a capped stainless steel tube, purged with nitrogen, and placed in a muffle oven at 550°C. Individual samples were removed, cooled and weighed after different aging times of the order of days. Techniques and conditions for sample characterization were given in the same paper. In the present work, an aging study was carried out using a TGA (Shimadzu) on 5~10 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 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.

RESULTS and DISCUSSION

1. Closed-System Aging Studies

1.1 H/C atomic ratio versus time Elemental composition of different deposits was analyzed by Canadian Microanalytical Service Ltd. The H/C atomic ratios of four fresh and aged deposits for different batch aging times at 550 °C are shown in Fig. 1. The H/C atomic ratio of fresh deposits is around 0.57. The H/C atomic ratio of the typical fresh samples 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. Scatter is expected at low H/C ratios because of analytical difficulties at low hydrogen values. By using non-linear regression, as shown in Fig. 1, the drop of H/C ratio with the aging time can be approximately expressed by a first order exponential decay equation, where t is the aging time (days):

$$H/C = 0.26 + 0.31\exp(-\frac{t}{0.18}) \quad (1)$$

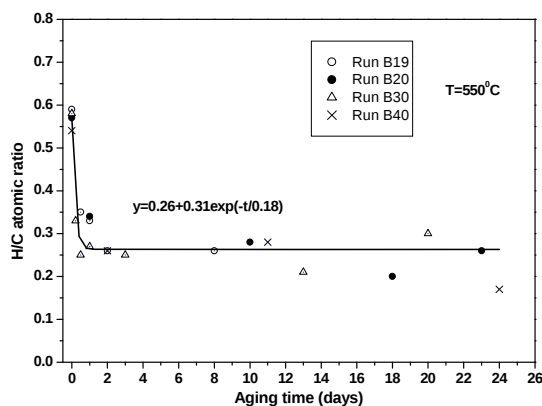


Fig. 1 Changes of H/C atomic ratio with the aging time for different laboratory deposits

Industrial deposits have much lower H/C atomic ratio (0.16~0.21) compared with fresh laboratory deposits. For deposits aged over 2 days, the H/C atomic ratios approach those of the industrial samples. The reduced H/C atomic ratio of the aged deposits is attributed to the preferential

release of paraffinic volatile components of high H/C atomic ratio, which occurs predominantly in the first one or two days. In this period, thermal cracking reactions of long aliphatic chains which either exist as side chains in poly-aromatic rings or are initially present in the deposits, take place leading to release of lower molecular weight volatile products, which causes the dramatic weight loss. In the subsequent long isothermal aging period at 550°C, weight loss continues to occur, but at a low rate. The chemical reactions leading to more condensed structures, such as cracking of short side chains in the poly-aromatic rings, dehydrogenation, cyclization, skeleton re-arrangement, etc., would occur in this latter period.

1.2 DRIFTS of Fresh and Closed-System Aged Deposits

Typical DRIFT spectra of fresh, and aged deposits (aged 2, 24 days) are given in Fig. 2. For two-day-aged deposits, paraffinic bands 2800-3000cm⁻¹ almost cannot be noticed. The coke band remains strong, but shifts from 1598 cm⁻¹ to a lower wave-number of 1594 cm⁻¹, which indicates that more poly-aromatic structures are formed during the aging process at high temperatures. All these observations indicate that most volatile components, mainly paraffinics which have a high H/C ratio, are thermally cracked and released during the first day of aging at high temperature. As well, it can be further noticed that, for one-day-aged deposits, the changes of the fingerprint region suggest that dehydrogenation reactions took place in the aging process. More detailed explanation of DRIFT spectra are given in the reference (Fan and Watkinson, 2006b).

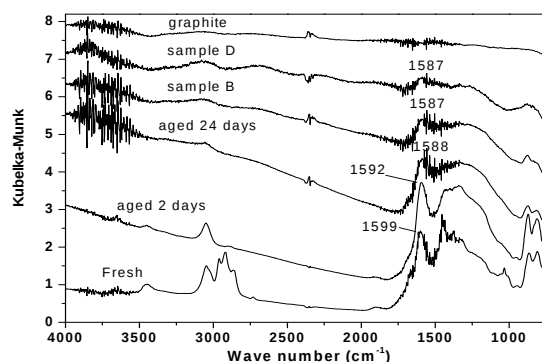


Fig. 2 DRIFT spectra of fresh, aged laboratory deposits (B40, $T_w=425^\circ\text{C}$) and industrial samples (Fan and Watkinson, 2006b)

For the DRIFT spectra of 24-day aged deposit, no absorption can be observed in paraffinic bands in the region of 2800-3000cm⁻¹, and the coke band shift to a further lower wave number, which indicate 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 as the aging time proceeds. The DRIFT spectra of industrial samples are much different from fresh laboratory deposits, and indicate more coke-like characteristics and graphitic structures which are approached by those of long-time (> 20 days) aged laboratory deposits. The structure of the 24-day aged

laboratory deposits appears very similar to that of Sample B. For both, the coke band shifts to a much lower frequency (1587cm^{-1}) and has much lower intensity, which indicated more condensed poly-aromatic structures; the stretching vibration of C-H for aromatics are all very weak and almost cannot be noticed; the weak absorptions in fingerprint region indicate dehydrogenation reactions take place in the aging process. The DRIFT spectra of Sample D is very similar to that of pure graphite (Fig. 2); both are almost featureless. Thus the evolution of deposits from heavy hydrocarbon components to graphitic structures can be clearly observed.

1.3 Solid-state ^{13}C NMR Spectra of the Aged Deposits

The comparison of fresh, aged, and industrial quantitative ^{13}C NMR spectra are given Fig. 3 (Fan and Watkinson 2006b). For the fresh lab deposit, the NMR spectra exhibit both paraffinic and aromatic characteristics. However, the NMR spectra of aged deposits (both 2-day and 24-day) only exhibit aromatic peak centered at 128 ppm. It 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) and close to that of industrial sample B (9.04×10^7), which indicates that there is more NMR-invisible graphite in the 24-day aged deposits. Sample D exhibits more NMR-invisible graphitic structures (integral intensity 9.29×10^5). 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 is similar to industrial samples: graphitic structures dominate in both. This is consistent with the results of elemental, and DRIFTS analysis.

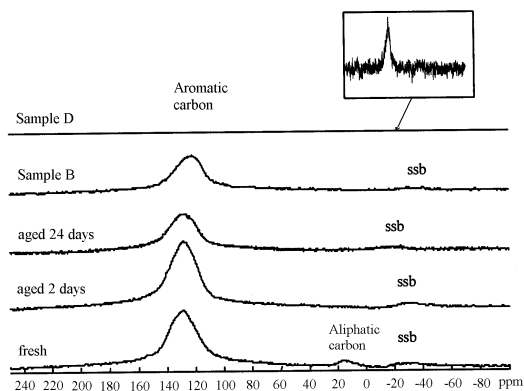


Fig. 3 Comparison of quantitative ^{13}C NMR of fresh, aged and industrial deposits (Fan and Watkinson, 2006b)

1.4 The Morphology of Fresh and Aged Deposits The SEM micrographs of fresh deposits show platelet features predominant at high temperature conditions ($>500^\circ\text{C}$), amorphous features predominant at lower temperatures ($<500^\circ\text{C}$), and mixtures of platelet and amorphous features are found for deposits collected around 500°C (Fan and Watkinson, 2006b). Additional amorphous features appeared as aging times increased from 1 to 20 days. This suggests that the part of the volatile components released

from the deposits during the aging process, re-condensed or adsorbed on the deposit surface. The low wettability of the surface of the glass tube wall, and the stagnant gas atmosphere in the sealed reactor appear to result in the surface of the aged deposits being mainly amorphous. Visually the fresh lab deposits appear as black powder or tiny flakes whereas both the industrial samples are massive black bulk rock-like material, without any loose powder or flakes. Platelet or amorphous deposits are not found in the industrial samples. The reason for this is perhaps that the condensed tar droplets are readily spread on the wall under the shear force of the high vapour velocity characteristic of industrial conditions. Song et al. (2009) have linked deposit apparent density of deposits in fluid catalytic cracking units to velocity. The differences in morphology between lab deposits and industrial samples which remain after aging, are attributed to the difference in hydrodynamic conditions during the deposit laydown and aging, and the duration of aging.

1.5 Thermogravimetric Study of Deposits As most changes in deposit chemical properties appeared during the initial day or so, the kinetics of deposit aging was investigated using thermogravimetric analysis. Thermogravimetry was employed to monitor the weight loss on line during the first 12 hours aging time to investigate how the release of volatiles proceeds in the initial aging periods, and the typical aging results of fresh lab deposits are indicated by Fig. 4. For the fresh deposits, the weight loss curves show a sharp drop within the first two hours, and then subsequently decrease gradually. There is very little weight loss below 300°C ($<15\text{ wt\%}$ or less of the total); extensive weight loss (ca. $40\sim 65\%$ of the total) occurs between 300 and 550°C . During the isothermal aging period at 550°C , the weight loss mainly happens in the initial two hours period, and then subsequently drops gradually at a very slow rate.

The closed-system pre-aged deposits and the industrial samples were given the same TGA treatment as described above for the fresh samples. Some weight loss occurred over the first half day maintained at 550°C , for all the pre-aged and industrial deposits, although they had been aged for quite a long time. However, the final weight loss is much less ($2\sim 6\text{ wt\%}$) than that of the fresh deposits ($13\sim 14\text{ wt\%}$) for the same experimental conditions. The weight loss occurs at a very low rate ($<0.443\text{ wt\%/hr}$), with no dramatic weight loss as occurred with the fresh deposits. Chemical reactions to form condensed poly-aromatic or graphitic structures may be the main reason to cause the small weight loss. The relatively rapid weight loss in the heat-up period for the industrial samples is perhaps due to some fresh material deposited on the surface prior to sampling.

2 Kinetics of Carbonaceous Deposit Aging

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. 4, in which the final aging temperature is 550°C . For the deposits aging at other temperatures, the maximum volatile contents V^* increase as the final temperature is

raised, and this increase mainly happened in the heating periods. Only those of the final aging temperature at 550°C are discussed in detail in the paper, since the similar thermal behaviour at other final aging temperatures. In this figure, 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_i . Thus,

$$V^* = \frac{W_0 - W_f}{W_0} \times 100\% \quad (2)$$

$$V = \frac{W_0 - W_i}{W_0} \times 100\% \quad (3)$$

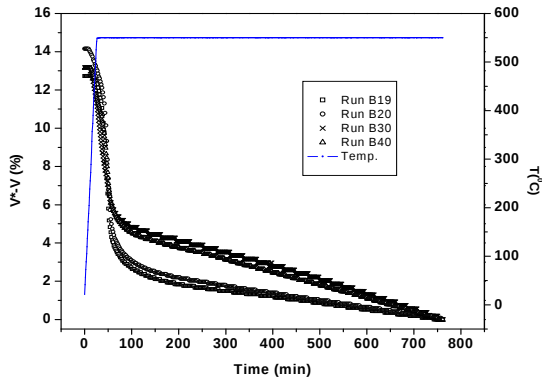


Fig. 4 Changes of volatile components in different fresh deposits with aging time in the TGA

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

Feed	MCR wt%	Sample	T_v^a (°C)	V^* heating wt%	V^* aging wt%	V^* total wt%
ATB-A	19.3	B19	448	7.55	5.18	12.73
		B20	473	8.43	5.87	14.16
ATB-B	12.5	B30	520	7.05	6.12	13.17
		B40	458	6.04	7.11	13.15

^a T_v is the vapour phase temperature at which the deposits were collected

Fig. 4 shows that 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 B19 and B20, from the heavier bitumen feed (ATB-A), exhibits similar thermal characteristics; B30 and B40, which are collected from the lighter feed ATB-B, demonstrate similar thermal characteristics but different with those of B19 and B20. Sample 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 B30 and B40. The quantitative data are given in Table 1, in which the comparison of maximum volatile components V^* (wt%) of different deposits in different periods are listed. However, from Fig.4, it can be observed that all deposit samples have some common characteristics, i.e., the shapes of all the curves are basically similar, and there is a dramatic drop for the volatile components which occurs at

the temperature around 550°C, although the drop is much sharper for the deposits of B19 and B20.

2.1 Methodology of Kinetic Models for Deposits Aging
Typical TGA aging results for fresh laboratory deposits are illustrated in Fig. 5. 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. This period may be of less importance for aging in the plant, as fresh deposits would already be at the aging temperature. In the present work, aging is taking place at temperatures above those at which the deposit was initially formed. 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.

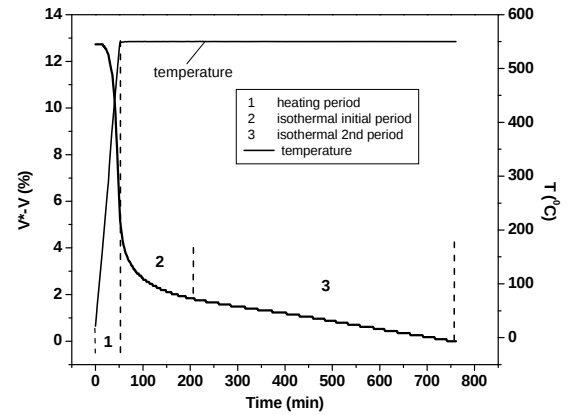


Fig. 5 Different kinetic models and their corresponding reaction time regions

2.2 Two and One Stage First Order Reaction Model

From the literature, multi-step behaviour has been clearly identified for the pyrolysis process of oil shale, pitch and heavy residuum fractions (Yue and Watkinson, 1998). Here, the pyrolysis of fresh 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 behaviour in that stage. This causes the significant change of the reaction behaviour. Based on the analysis (Fan, 2006), this critical temperature which changes the pyrolysis behaviour should be at about 440°C. Then, the two-stage pyrolysis mechanism of fresh laboratory deposits can be expressed as follows,

$$\frac{dV}{dT} = \sum_{i=1}^2 C\alpha_i k_{0,i} \exp\left(-\frac{E_{a,i}}{RT}\right)(V^* - V) \quad (4)$$

where $\alpha_1 = 1$, $\alpha_2 = 0$ when $T < 440^\circ\text{C}$, and $\alpha_1 = 0$, $\alpha_2 = 1$ when $T \geq 440^\circ\text{C}$. For a single stage reaction, $\alpha_1 = 1$ for all temperatures and $\alpha_2 = 0$. For deposits which formed at high temperatures, a single stage model was adequate, however for those deposits formed at low temperatures, the two-stage model was necessary. A number of methods have been suggested to extract values of k_0 , and E_a for the single stage version of Equation (4) from experiments in which V is measured as a function of T at a constant heating rate. Equations are given below for the integral method (Shih et al. 1978; Carraso et al., 1993) which gave similar results to the Chen-Nuttall method (Thakur and Nuttall, 1987). The term Y represents the function for each model which should give a linear plot with $1/T$ to yield the activation energy.

Integral method

$$Y = \ln\left(\frac{-C \ln(1 - \frac{V}{V^*})}{RT^2}\right) - \ln\left(1 - \frac{2RT}{E_a}\right) \approx \ln \frac{k_0}{E_a} - \frac{E_a}{RT} \quad (5)$$

In examining the Y values of samples B19, B20 and B40 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 for the integral model. Results for Chen-Nuttall model were similar with those of the integral model (Fan, 2006). Thus only the results from integral model are presented in the remaining discussion. Inflection points are observed at $1/T$ value of 0.0014 (ca. 440°C), and the same point was also observed by Yue and Watkinson (1998). Therefore, first order single step reaction models fail to apply over the whole temperature range of the above samples. However, the Y values of sample B30 and $1/T$ have a good linear relationship, as shown in Fig. 6. This suggests that both the single-stage integral and Chen-Nuttall methods can predict the volatile contents of high temperature laboratory deposits very well. The calculated pre-exponential factor and activation energy for sample B30 are 13.1 min^{-1} and 28.51 kJ/mol , respectively. This data is in 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., $E_a = 30 \sim 35 \text{ kJ/mol}$, $k_0 = 35 \sim 150 \text{ min}^{-1}$ for pitch pyrolysis, Coats et al., 1964; Thakur et al., 1987).

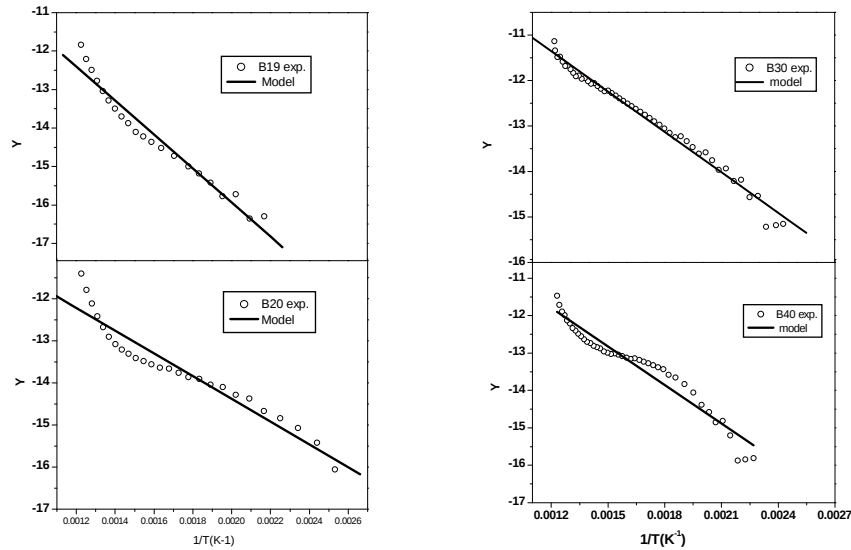


Fig. 6 Comparison of model-predicted and experimental Y results of fresh deposits with a final temperature of 550°C by single-stage first order reaction model

For the low-temperature deposits, the TGA data were therefore divided into two stages: Data from each stage were fitted to the model by integral and Chen-Nuttall method, respectively. The calculated kinetic parameters by integral method are listed in Table 2 for the each sample. 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 (thus only the results of integral method are presented). Table 2 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 higher than those of the

first stage. The kinetic compensation effects, low activation energy associating with low exponential factor, are also observed in Table 2.

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. 7. Both of the methods have good prediction of the volatile content over the whole range of temperatures for samples B19 and B20, which suggests that both the two-stage integral and Chen-Nuttall models adequately describe the reactions in the above samples during the heating period. The Y values of the above samples for each two-

stage reaction model and $1/T$ have a good linear relationship for sample B19 and B20 aging at a final temperature of 550°C, (Fig. 8), however, the Y values and $1/T$ have a good linear relationship only in the high temperature range for B40. The discontinuity arises at the temperature of about 440°C where first stage ends and the second stage begins.

Table 2 Kinetic Parameters of Two-Stage 1st Order Reaction for Different Deposits Aging in Heating Period

Sample	$k_{0,1}$ min ⁻¹	$E_{a,1}$ kJ/mol	σ	$k_{0,2} \times 10^4$ min ⁻¹	$E_{a,2}$ kJ/mol	σ
B19, 550°C	7.43	30.88	0.011	6.81	81.40	0.0031
B20, 550°C	1.23	19.17	0.023	5.43	80.27	0.0057
B40, 550°C	9.73	26.96	0.068	1.38	56.24	0.0076
B20, 500°C	3.16	22.03	0.020	3.43	99.63	0.0044
B20, 600°C	1.24	20.89	0.026	5.78	68.52	0.0028
B40, 500°C	9.24	25.01	0.037	6.88	75.75	0.0089
B40, 600°C	6.47	27.13	0.061	0.021	48.01	0.011

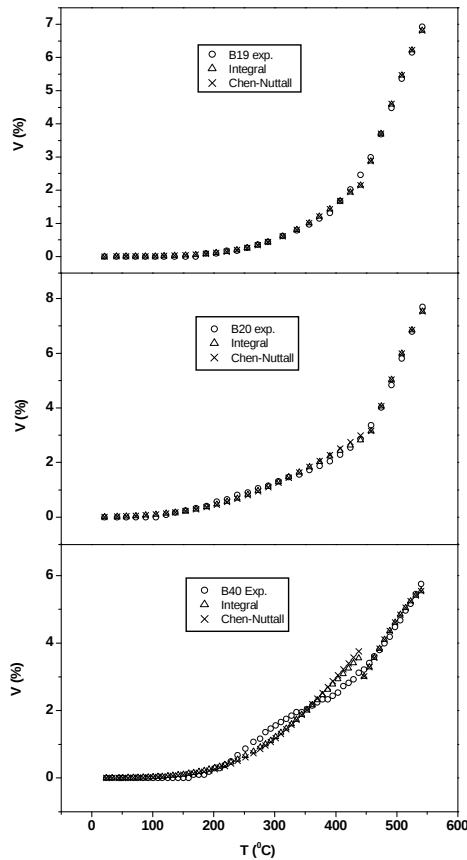


Fig. 7 Comparison of model prediction and experimental volatiles for samples with a final temperature of 550°C with two-stage first order reaction model

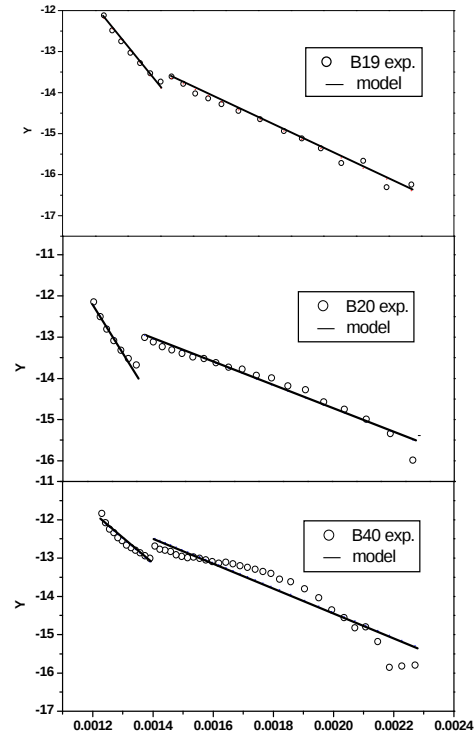


Fig. 8 Comparison of model-predicted and experimental Y results of samples with a final temperature of 550°C with two-stage first order integral reaction model

Discussion of Heating Period Results For the laboratory deposits collected at high temperatures ($>500^\circ\text{C}$), in which only small amounts volatile components exist, a single stage first order kinetic model of low activation energy barrier and low pre-exponential factor can describe their thermal properties very well. This model was developed for relatively low volatile content materials and processes such as coal pyrolysis (Haddadin et al, 1974, 1980; Braun et al., 1975; Yue and Watkinson, 1998). For the laboratory fresh deposits collected at low temperatures ($<500^\circ\text{C}$), 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. The calculated apparent activation energies (17~100 kJ/mol) in this study are of the same magnitude with thermal cracking of hydrocarbon mixtures (ca. 50 kJ/mol) (Liang, 1995), pitch pyrolysis (18~100 kJ/mol) (Yue and Watkinson, 1998) and oil shale decomposition (38~62 kJ/mol) (Thakur, 1987), etc., especially similar with those of the Athabasca pitch (+524°C fraction) pyrolysis reported by Yue and Watkinson

(1998). This suggests that thermal cracking reactions taking place during the process of deposit aging. The close thermal cracking kinetic phenomena with pitch, oil shale, etc. indicate the similar components exist in the deposits of fluid coker cyclone exit lines.

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 the 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 energy, e.g., cracking of short chains of polyaromaic rings, dehydrogenation, skeleton rearrange-ment of polyaromatics, etc. will dominate the aging process, and a higher apparent activation energy is observed. For 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 freshest deposits condensed on the surface of “old” deposit can be cracked, and exhibits a low apparent activation energy.

2.3 Kinetic Models in Isothermal Period Initially, irreversible reactions were assumed to take place in the deposit during the isothermal aging process, according to a power law equation. However, 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, which is widely used for complex kinetic phenomena, such as gasification of coal char, etc. (Agarwal et al., 1978; Mahajan et al., 1978; Chin et al, 1983; Yang 1991), is introduced in present study. Following the approach of Mahajan (1978), it can be assumed that:

$$\omega = \frac{V^* - V}{V^*} \times 100\% \quad (6)$$

and

$$\theta = \frac{t_i - t_0}{t_{1/2}} \quad (7)$$

where ω is the dimensionless volatile content, θ the dimensionless reaction time, and $t_{1/2}$ the time needed when the ω reaches 50%. Assuming an irreversible reaction in the deposits isothermal aging process, the overall dimensionless reaction rate can be expressed as:

$$-\Gamma = -\frac{d\omega}{d\theta} = f(k_i, \omega) \quad (8)$$

2.3.1 Kinetic Models for the Initial Isothermal Aging Stage The relationship of dimensionless volatile content ω and dimensionless time θ for all the samples are given in Fig. 9. The V^* and $t_{1/2}$ of different samples are given in Table 3. All curves appear to collapse to a unique curve which appears similar to an exponential decay curve, only one sample (B40 aging at 500°C) has a little variation.

The volatile component changes of all samples with reaction time approximately follow the same 2nd order exponential decay equation as follows,

$$\omega = A \exp\left(-\frac{\theta}{a_1}\right) + B \exp\left(-\frac{\theta}{a_2}\right) \quad (9)$$

where $A = 32.28$, $B = 65.32$, $a_1 = 0.39$ and $a_2 = 3.00$. From the slope of every θ point, the dimensionless volatile components release rate can be determined, correspondingly. Thus,

$$-\Gamma = -\frac{d\omega}{d\theta} = k_1 \exp\left(-\frac{\theta}{a_1}\right) + k_2 \exp\left(-\frac{\theta}{a_2}\right) \quad (10)$$

where k_1 and k_2 are rate constant, and $k_1 = A/a_1 = 82.77$ and $k_2 = B/a_2 = 21.74$, respectively. Therefore, the reaction rate changes with the dimensionless time θ also follows a 2nd order exponential decay equation but with a much faster decay rate as given in equation (10). The dimensionless volatile components release rate drops dramatically at the very beginning, and gradually slows down to a very low rate, i.e., from ca. 104 to ca. 0.40.

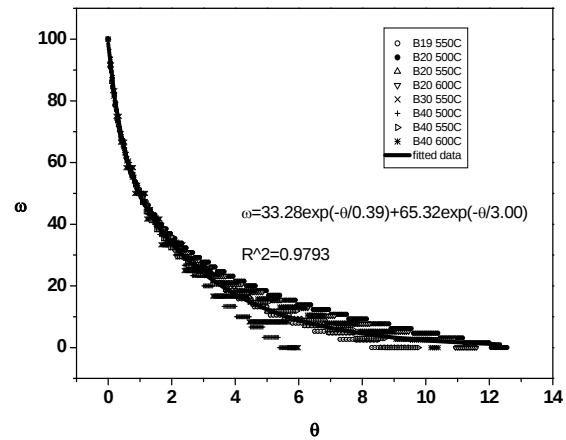


Fig. 9 Dimensionless kinetic curves of all deposit samples in initial isothermal period

Table 3 Values of V^* and $T_{1/2}$ for Different Samples in Isothermal Aging Period

Sample	V^* (%)	$t_{1/2}$ (min)
B19, 550°C	3.61	16.8
B20, 500°C	4.43	12.0
B20, 550°C	3.84	15.5
B20, 600°C	3.08	13.0
B30, 550°C	2.39	24.5
B40, 500°C	2.48	26.1
B40, 550°C	3.52	15.3
B40, 600°C	3.29	14.5

Based on the above analysis, one reaction rate equation describes 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.

2.3.2 Kinetic Models in The Second Isothermal Period

The second isothermal period, exhibited a near zero order reaction with respect to volatile components. This was a very slow reaction, and only ca. 1.5~4.0 wt% volatile components were released in about 10 hours. The relationship of dimensionless volatile content ω and dimensionless time θ ($t > 200$ min) at the temperature of 550°C for B19, B20, B30 and B40 are given in Fig. 10. 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,

$$-\Gamma = -\frac{d\omega}{d\theta} = 47.72 \quad (11)$$

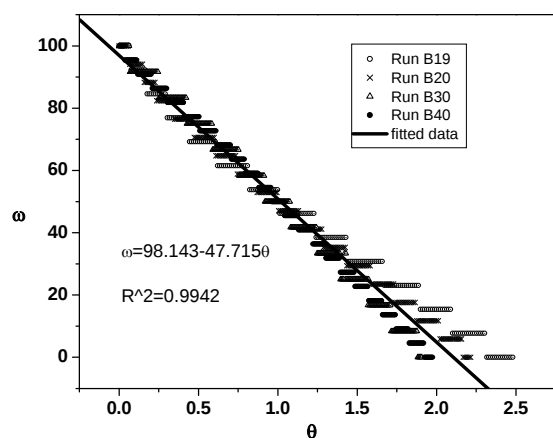


Fig. 10 Dimensionless kinetic curve of all deposit samples at 550 °C in the second isothermal period

3 Structure Evolution of Laboratory Fresh Deposits in the Aging Process

According to characterization results, the fresh laboratory deposits are composed of mostly polyaromatic structures with some aliphatic chains; for the closed reactor pre-aged laboratory deposits, it is mainly the condensed polyaromatic structures. The results of characterization of different aging deposits and TGA kinetic study indicate there are mostly thermal cracking reactions of aliphatic chains taking place in the heating period at initial isothermal period. In the following long aging period, more complex slow reactions take place to produce more condensed polyaromatic structures, and finally lead to graphitic structures. The industrial samples which have been aging in plant for months demonstrate mostly graphitic structures. Marsh and Griffiths (1982) proposed a model of the structural evolution in carbonization/graphitization process based on their XRD and TEM experimental results. Although this generally applies at much higher temperature, it appears to provide a useful approach in the current work as illustrated in Fig. 11. Compared with the heat treatment of pitch coke, aging of cyclone fouling deposits occurs at

much lower temperatures but over longer reaction times. 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 take place and produce more condensed polyaromatic structures with or without short aliphatic groups. As aging proceeds, dehydrogenation and carbon skeleton re-arrangement happen and lead 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 laboratory 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 deposition 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.

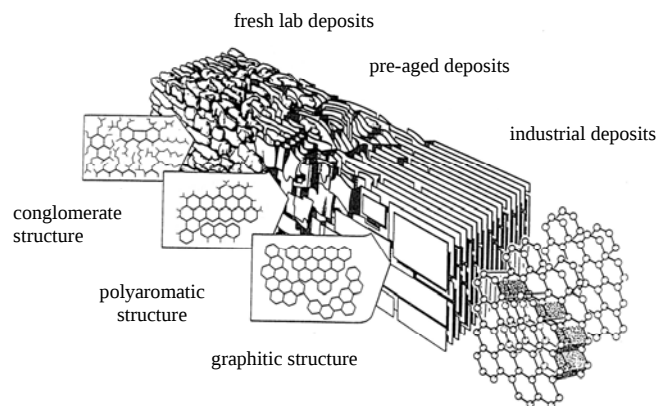


Fig. 11 Structure evolution model for cyclone fouling deposits in aging process following Marsh-Griffiths model

CONCLUSIONS

1. Characterization results indicate that industrial samples are much different than the fresh laboratory deposits. After days to weeks of aging at elevated temperature, the composition and structure of lab deposits could 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 when initially deposit from the vapour to the final massive graphitic coke-like deposit formed in the industrial coker cyclone exit tube.

2. Kinetic models were developed to describe reactions in different aging periods based on thermal behaviour of fresh lab deposits. It was not possible to construct a single mathematical model to describe the weight loss behaviour of all deposits during the entire thermogravimetric heating process. 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. With dimensionless manipulation, isothermal kinetic models were used to characterize the weight loss phenomena with time at different final temperatures. The values of apparent activation energies in the heating period suggest that thermal cracking reactions are taking place.

3. A structural evolution model of 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 rearrangement occur and lead to more ordered graphitic structures. The structure of closed reactor pre-aged deposits represents a transition state between the polyaromatic and graphitic structures.

Acknowledgement

The authors are grateful to the financial support of Natural Science and Engineering Research Council of Canada (NSERC) and Syncrude Canada Ltd.

NOMENCLATURE

C	heating rate ($^{\circ}\text{C}/\text{min}$)
E_a	activation energy (J/mol)
$E_{a,i}$	activation energy of i th stage of reaction (J/mol)
E_{a0}	mean activation energy in Anthony-Howard model (J/mol)
k	reaction rate constant
k_i	dimensionless reaction constant
k_0	pre-exponential factor (min^{-1})
$k_{0,i}$	pre-exponential factor of i th stage of reaction (min^{-1})
MCR	Microcarbon residue (wt%)
n	total number of data point
R	gas constant, $8.314 \text{ J}/\text{mol}\cdot\text{K}$
T	temperature (K or $^{\circ}\text{C}$)
t	reaction time (min)
t_0	initial time (min)
t_i	any given time (min)
$t_{1/2}$	time needed when dimensionless volatile content reaches to 50% conversion (min)
V	volatile components released at temperature T , wt%
V^*	maximum volatile components at the final time, wt%
$V_{i,\text{exp}}$	experimental volatile contents (wt%)

$V_{i,\text{fit}}$	model predicted volatile contents (wt%)
W_0	sample initial weight, mg
W_i	sample weight at time t_i , mg
W_f	sample weight at the final given time, mg

Greek letters

α_1	constant used to characterize the change of chemical natures in the deposit residue
Γ	dimensionless reaction rate
θ	dimensionless reaction time
σ	standard deviation
ω	dimensionless volatile components

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