Residua coke formation predictability maps☆

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Abstract

The dispersed particle solution model of petroleum residua structure was used to develop predictors for pyrolytic coke formation. Coking Indexes were developed in prior years that measure how near a pyrolysis system is to coke formation during the coke formation induction period. These have been demonstrated to be universally applicable for residua regardless of the source of the material. Coking onset is coincidental with the destruction of the ordered structure and the formation of a multi-phase system. The amount of coke initially formed appears to be a function of the free solvent volume of the original residua. In the current work, three-dimensional coke make predictability maps were developed at 400, 450 and 500 °C for four residua with nominal H/C atomic ratios of 1.4. The maps relate residence time and free solvent volume to the amount of coke formed at a particular pyrolysis temperature. Coke formation reactions can be modeled with zero-order kinetics which occur in two stages. The first stage produces 22.5–27.0 wt% coke with activation energies ranging from 22,000 to 38,000 cal/mol. The second stage continues the reaction to completion, producing 58.1–63.6 wt% coke with activation energies ranging from 54,000 to 83,000 cal/mol. The activation energies correlate with the original residua free solvent volumes. The results provide a new tool for ranking residua, gauging proximity to coke formation, and predicting initial coke make tendencies. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Residua; Pyrolysis; Coke

1. Introduction

1.1. Coking Indexes

Petroleum residua can be modeled as ordered systems of polar asphaltenes dispersed in a lower polarity solvent phase, held together by intermediate polarity resins. Vacuum distillation processes and coking of the vacuum residua require significant heat input. When a residuum is heated above the temperature at which pyrolysis begins (350 °C), there is typically an induction period before coke formation begins [1–3]. To minimize fouling of heat exchangers due to undesired coking, distillation heating is stopped sooner than need be, resulting in less than maximum product yield. In prior work, two new Coking Indexes were developed for measuring the proximity to the coke formation onset in thermal treatment [4]. These are based on asphaltene flocculation titration data and the solubility of heptane asphaltenes in cyclohexane. Coking onset appears to coincide with the depletion of resin-type, asphaltene-solubilizing components in residua, resulting in a multi-phase system. This is consistent with observations of the formation of a neophase at the onset of coke formation [5]. Pyrolysis reactions involve the cleavage of carbon bonds with carbon, hydrogen, and heteroatoms resulting in the formation of free radicals which continue scission reactions or condense into carbon-rich material [6,7]. Use of the Coking Indexes can allow distillation to proceed to the verge, but not beyond the onset of coke formation, resulting in significant increases in distillate yield while minimizing the risk of fouling.

1.2. Free solvent volume considerations

A possible predictive tool is the free solvent volume of the original residuum. This is based on the Pal and Rhodes model, which has been discussed in detail elsewhere [8,9]. This has been related to the amount of heat-induced deposition below pyrolysis temperatures and the amount of coke make in the early stages of a pyrolytic process [9, 10]. The free solvent volume, ϕ_{FS}, can be calculated using

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the equation below:

$$\phi_{FS} = 1 - K_S K_F \phi_a = 1 - 1.6 \left(\frac{1}{1 - p_a} \right) \left(\frac{\chi_a}{1.2} \right)$$

In the equation, χ_a is the mass fraction of heptane asphaltenes divided by an assumed density of 1.2 g/cm^3 to yield the volume fraction of asphaltenes, ϕ_a. The term p_a represents the fraction of bound solvent phase obtained from the asphaltene flocculation titration [9]. The volume fraction of asphaltenes is increased by the K_S and K_F terms. In the current study, initial coke make values were obtained for four residua at 400, 450 and 500 °C at various residence times. Correlations of coke make vs. ϕ_{FS} were evaluated at both temperatures.

2. Experimental

Four residua materials were used for the coke map development work. These were Boscan, Lloydminster, and Redwater, B.C. from prior non-proprietary work at Western Research Institute (WRI). The MaxCL2 was provided by Conoco.

Heptane asphaltenes were isolated using a 40:1 (v/w) mixture of reagent-grade *n*-heptane and residuum. The mixture was heated to 70 °C for about 1/2 h while stirring, followed by stirring overnight at room temperature. For the determination of the amount of heptane asphaltenes soluble in cyclohexane, a portion of *n*-heptane asphaltenes was ground to a fine powder using a mortar and pestle and stirred with cyclohexane at a 200:1 (v/w) ratio.

Automated asphaltene flocculation titrations were performed with a WRI computer-controlled Automated Flocculation Titrimeter (AFT) unit at 25.0 ± 0.1 °C with 5–20 wt% residua solutions in toluene using 2,2,4-trimethyl-pentane (isooctane) as titrant at an average titrant delivery rate of 0.35 ml/min [10]. The procedures used are described in detail elsewhere [11].

Pyrolysis experiments were performed with 5 g residua samples weighed into 0.75 in. × 7 in. tube reactors constructed from 316 stainless steel. Atmospheric air was evacuated using a vacuum pump. The tube reactors were pressurized to 100 psig with nitrogen and leak-checked in water. The reactors were evacuated again and pressurized with 10 psig of nitrogen prior to pyrolysis. A total of four tube reactors were attached to a rack that contained a fifth tube reactor fitted with an internal thermocouple. Each tube

weighed about 750 g and had significant thermal capacity. In order to maintain uniform and repeatable heating profiles, the pyrolysis experiments were always run with five tubes on the rack. The rack was placed into a Techne, 4000-watt, fluidized sand bath set at the appropriate temperature for the experiment. The time to achieve the reaction temperature was typically under 10 min. Pyrolysis reactions do not occur until the temperature is > 350 °C, and occur at a relatively slow rate until about 400 °C. Conditions were kept constant for experiments performed at a particular temperature to allow for subsequent data comparison. The pyrolysis time frame was started when the thermocouple in the reactor tube indicated that the desired temperature had been reached. After the tube reactors were in the sand bath for the desired time, they were removed and cooled by immersing them in another fluidized sand bath at room temperature. The reaction products were collected in toluene and vacuum filtered using Ace, 140 ml, 10–20 μm, sintered glass filters to obtain toluene insolubles (coke). All of the coke was weighed. Liquid and gaseous products were not measured separately since the primary interest was the amount of coke formed.

Conradson Carbon determinations were performed by Core Laboratories, Houston, Texas, using ASTM D-189. Elemental determinations (C, H, N, S) were performed by Huffman Laboratories, Golden, CO.

3. Results

3.1. Residua characteristics

The residua used in the current study are Boscan, MaxCL2 (Conoco), Lloydminster, and Redwater, B.C. These are not the same lots of residua that we used in prior work [11,12]. Their thermal histories, asphaltene contents, and Heithaus titration parameters were not identical to similar residua used in the past. Also, the asphaltene isolation procedure was modified from prior work as described in the next section. Elemental analysis data (C, H, N, S) and H/C atomic ratios for the four residua are provided in Table 1. All four of the H/C ratios are very similar, near a value of 1.4 when rounded to two significant figures. Therefore, the H/C atomic ratio was not a variable in the current work.

The weight percent of the heptane asphaltenes, weight percent of the cyclohexane-soluble heptane asphaltenes, and

Table 1
Elemental analysis data and H/C atomic ratios

Residuum	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Total (wt%)	H/C atomic ratio
Boscan	83.3	9.5	0.8	5.7	99.3	1.4
MaxCL2	84.6	9.9	0.6	4.9	100.0	1.4
Lloydminster	83.4	9.8	0.5	5.5	99.2	1.4
Redwater, B.C.	86.8	9.9	0.7	2.1	99.5	1.4

Table 2
Asphaltene contents and Heithaus parameters

Residuum	X: wt% n-C7 asphaltenes	Y: wt% cyclohexane soluble asphaltenes	Heithaus parameters	
			p_a	C_{min}
Boscan	17.6, 17.6, 17.7	30.5, 31.7	0.698	0.466
MaxCL2	17.0	29.7, 30.6	0.664	0.447
Lloydminster	16.9	34.2	0.621	0.340
Redwater, B.C.	8.9	34.0	0.655	0.301

the Heithaus parameters, p_a and C_{min}, are provided in Table 2. The asphaltene contents of Boscan, MaxCL2, and Lloydminster are virtually identical, ranging from 16.9 to 17.6 wt%. The asphaltene content of the Redwater, B.C. is significantly lower at 8.9 wt%.

The WRI Coking Indexes, Y/X (ratio of weight percent cyclohexane-soluble material in heptane asphaltenes to the weight percent heptane asphaltenes in residua), and p_a/C_{min} (ratio of Heithaus parameters) are provided in Table 3. For the four residua, these values are all above unity, indicating that the residua are far from producing coke on the coke formation induction timeline [12]. The free solvent volumes of these four residua are also provided in Table 3. These range from 0.22 for Boscan to 0.66 for Redwater, B.C.

3.2. Asphaltene determination

There are many differences in the various procedures used to obtain asphaltenes including choice of solvent and the ratio of solvent to oil, which must be in significant excess [12]. Temperature is an important variable. Heptane asphaltene values varied from 20.2 wt% at 24 °C to 16.6 wt% at 50 °C and 14.7 wt% at 80 °C [13]. ASTM D-3279 [14] and ASTM D-4124 [15] recommend heating, while the Strategic Highway Research Program (SHRP) procedure is performed at room temperature [16]. A comparison of results between the heated mixture method used for the current work and the room temperature SHRP procedure is provided in Table 4 for Boscan, MaxCL2, and Lloydminster residua.

3.3. Pyrolysis experiments

Pyrolysis results, especially at the lower temperatures employed in the current study(400 and 450 °C) require very

careful time and temperature control. This is because the coke formation reactions are being quenched as they are proceeding at a rapid rate and the reactions are extremely dependent on the heat input to the reactor tubes. Slight variations in time or temperature variables can result in large differences in the amount of coke formed. Very careful and repeatable operation of the equipment is required.

Results from pyrolysis experiments at 400 °C at 30, 45, 60, 75, 90, 100, 120, and 150 min are presented in Table 5. The data show increased coke yield with increased residence time. The Boscan residuum produced coke at all the residence times above 30 min. The MaxCL2 and Lloydminster residua began producing coke by 90 min residence time, and the Redwater, B.C. produced coke at the 150 min residence time.

Results from pyrolysis experiments at 450 °C at 5, 15, 30, 60, 90, and 120 min are presented in Table 6. The data show increased coke yield with increased residence time. The Boscan and MaxCL2 residua produced coke at all the residence times. The Lloydminster and Redwater, B.C. residua began producing coke by 15 min residence time.

Results from pyrolysis experiments at 500 °C at 15, 30, 45, and 60 min are shown in Table 7. All four residua produced significant coke at all four residence times.

4. Discussion

4.1. Coke formation map at 400 °C

At 400 °C, the amount of coke formed for a particular residuum increases with increasing residence time (Table 5). At a residence time of 150 min, the amount of coke formed is greatest for the Boscan residuum, which has the smallest free solvent volume of the four residua (0.22). The amount of coke formed is least for the Redwater, B.C. residuum,

Table 3
WRI residua Coking Indexes and free solvent volumes

Residuum	WRI Coking Indexes		ϕ_{FS}
	Y/X	p_a/C_{min}	
Boscan	1.8	1.5	0.22
MaxCL2	1.8	1.5	0.32
Lloydminster	2.0	1.8	0.40
Redwater, B.C.	3.8	2.2	0.66

Table 4
Comparison of room temperature and heated (70 °C) asphaltene yields

Residuum	Weight percent n-heptane asphaltenes	
	Room temperature	Heated (70 °C)
Boscan	19.8	17.6, 17.6
MacCL2	19.2	17.0
Redwater, B.C.	11.7	8.9

Table 5
Coke yields at 400 °C (wt% coke)

Residuum	Residence time (min)							
	30	45	60	75	90	100	120	150
Boscan	<0.3	3.1	4.2	7.9	9.1,8.8	11.1	12.1	14.8
MaxCL2	–	–	–	–	<0.3	6.4	9.9	12.0
Lloydminster	–	–	–	–	<0.3	2.2	5.4	8.9
Redwater, B.C.	–	–	–	–	<0.3	<0.5	<0.5	6.2

which has the largest free solvent volume of the four residua (0.66). To build the three-dimensional map, the intercepts for the x, y, and z axes must be determined, as well as several points along the contour. The Boscan residuum yielded coke at residence times from 45 to 150 min. A plot of wt% coke vs. residence time for the Boscan residuum shows a linear relationship (Fig. 1). Plots of wt% coke vs. free solvent volume at various residence times for the four residua are provided in Fig. 2. Lines for 150, 120, and 100 min can be drawn using data for three or four of the residua. Only the Boscan residuum yielded coke at the shorter timeframes. To estimate the free solvent volume intercepts of the lines at $y = 0$, a plot of slope of wt% coke vs. free solvent volume lines was made (Fig. 3). The plot appears to be linear in the range of 60–160 min residence times, and approaches a negative vertical asymptote at a time of zero minutes. From this plot, the slopes of the plots at residence times of 45, 60, and 90 min can be estimated. The actual and extrapolated slope and intercept data for the lines are provided in Table 8. The mean value of intercept of wt% coke formed at 400 °C at $\phi_{FS} = 0$ at 150 min is 20.9 wt% ($n = 7$, $s = 1.4$). The extrapolated lines are included in Fig. 2.

From the above data plots and extrapolations, a three-dimensional map (time, coke yield, free solvent volume) was constructed (Fig. 4). The data used for the ϕ_{FS} calculations and the ϕ_{FS} values for the four residua are provided in Tables 2 and 3, respectively. In the current study, correlations of free solvent volume with initial coke make were made by holding K_S constant at 1.6. Thus, the only measurements required for calculation of ϕ_{FS} were the weight percent heptane asphaltenes and the Heithaus p_a value.

4.2. Coke formation map at 450 °C

At 450 °C, the amount of coke formed for a particular

Table 6
Coke yields at 450 °C (wt% coke)

Residuum	Residence time (min)					
	5	15	30	60	90	120
Boscan	7.4	18.5	27.8	31.0	33.3	39.4
MaxCL2	0.8	13.7	22.1	30.8	33.4	36.5
Lloydminster	<0.5	9.3	17.2	27.7	31.3	35.8
Redwater, B.C.	<0.5	9.2	16.5	25.3	29.8	34.4

Table 7
Coke yields at 500 °C (wt% coke)

Residuum	Residence time (min)			
	15	30	45	60
Boscan	36.5	36.8	45.6	46.6,46.4
MaxCL2	37.1	38.0	41.4	44.8
Lloydminster	34.6	33.7	40.4	39.1,39.2
Redwater, B.C.	34.3	33.9	39.0	38.2

residuum increases with increasing residence time (Table 6). At a residence time of 120 min, the amount of coke formed is greatest for the Boscan residuum, which has the smallest free solvent volume of the four residua (0.22). The amount of coke formed is least for the Redwater, B.C. residuum, which has the largest free solvent volume of the four residua (0.66). To build the three-dimensional map, the intercepts for the x, y, and z axes must be determined, as well as several points along the contour. The Boscan residuum yielded coke at residence times from 5 to 120 min. Plots of wt% coke vs. free solvent volume at various residence times for the four residua are provided in Fig. 5. To minimize experimental error in estimating the free solvent volume intercepts of the lines at $\phi_{FS} = 0$, a plot of slope of wt% coke vs. free solvent volume lines was made for Boscan, MaxCL2, and Lloydminster residua (Fig. 6). The original experimental slopes and intercepts are provided in Table 9, and the smoothed interpolated values are provided in Table 10. The extrapolated lines are included in Fig. 5. In Fig. 5, extrapolated lines for the Lloydminster and Redwater, B.C. residua can be drawn from two points each to determine the coke formation intercept at $\phi_{FS} = 1$ (Table 11).

From the above data plots and extrapolations, a three-dimensional map (time, coke yield, free solvent volume) was constructed (Fig. 7). The data used for the ϕ_{FS} calculations and the ϕ_{FS} values for the four residua are provided in Tables 3, 10 and 11.

Table 8
Weight percent coke vs. ϕ_{FS} line slopes and intercepts at 400 °C

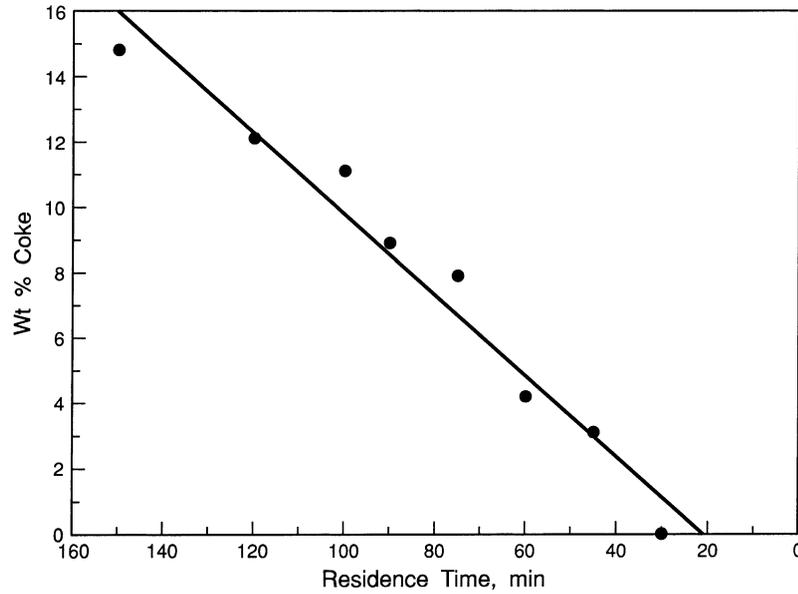| Time (min)	$y = mx + b$			ϕ_{FS} at $y = 0$
	m	b	r	
Actual				
150	−18.9	18.0	0.954	0.95
120	−36.5	20.6	0.966	0.56
100	−49.3	22.0	1.000	0.45
Extrapolated				
90	−55.5	21.1	–	0.38
75	−64.7	22.1	–	0.34
60	−73.9	20.4	–	0.28
45	−86.0	22.0	–	0.26

Fig. 1. Coke formed with Boscan residuum at various times at 400 °C.

4.3. Coke formation map at 500 °C

At 500 °C, coke formation rapidly proceeds to completion (Table 12). Coke make vs. free solvent volume plots for the various residence times are provided in Fig. 8. The amount of coke formed at 60 min was essentially the same as the amount of coke formed at 45 min for each particular residuum, and this probably represents the completion of coke formation. Coke yields were somewhat less at shorter residence times. A plot of wt% coke vs. residence time for Boscan residuum is provided in Fig. 9.

The amount of coke formed at completion is related to the atomic H/C ratio. All four residua studied have H/C ratio values of 1.4 (Table 1), so they would be expected to have similar amounts of coke at completion. Indeed, this was the case; the amount of coke for all four residua at 45 and 60 min ranged from 38.2 to 46.4 wt%. The average wt% coke formed at 45 and 60 min for the four residua was 42.0 wt% with a standard deviation of 3.5 wt% (Table 8). If this number is divided by 1.6, which is the empirical ratio of delayed coker yield to Conradson carbon residue (CCR) or microcarbon residue (MCR) as reported by Gary and Handwerk [17] for a particular set of refinery coker conditions, a value of 26.2 wt% as MCR emerges with a
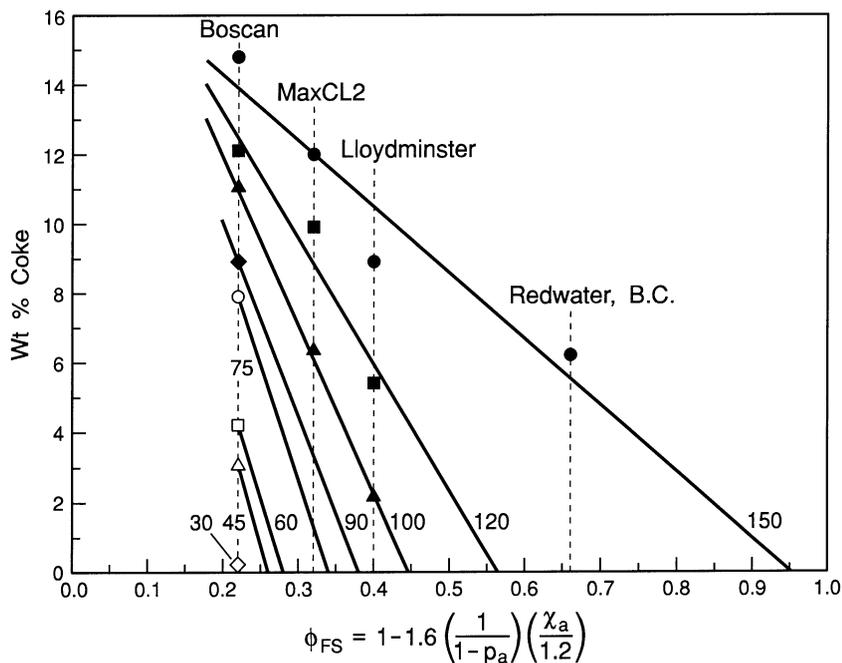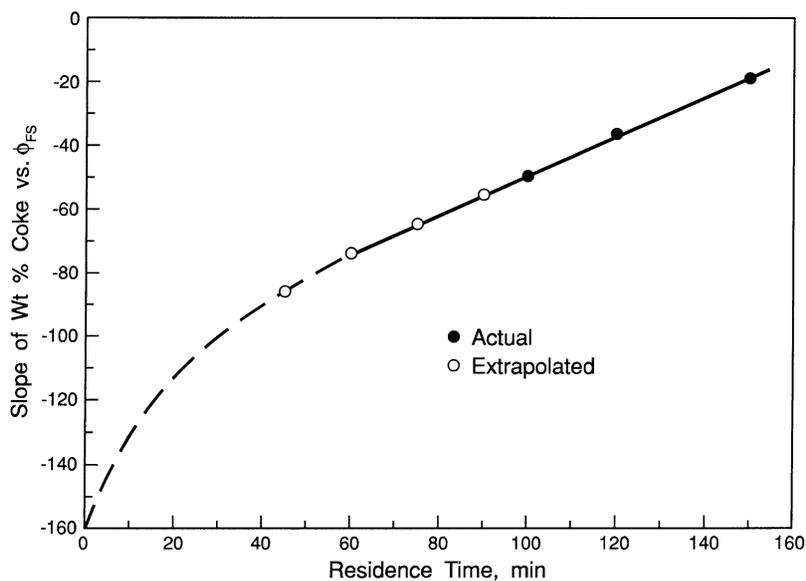

Fig. 2. Wt% Coke vs. free solvent volume at 400 °C.

Fig. 3. Slope of coke formation lines vs. residence times at 400 °C.

standard deviation of 2.2 wt%. The Conradson carbon values for all four residua ranged from 16.4 to 22.3 wt%, with an average value of 19.0 wt% and a standard deviation of 2.5 wt%. The ratio of the average coke yield in the sealed reactor at 45 and 60 min to the average CCR value is 2.2. Both values of 26.2 or 19.0 wt% fall within rounding to two significant figures and experimental error for elemental analysis near the MCR vs. atomic H/C ratio line for an H/C ratio of 1.4 [18–20]. The three-dimensional coke formation

predictability map for 500 °C (932 °F) is shown in Fig. 10. At this temperature, coke formation is rapid and fairly independent of the free solvent volume. Completion of coking appears to have occurred at a residence time of 45 min.

4.4. Activation energies

Plots of wt% coke vs. time for Boscan, MaxCL2,
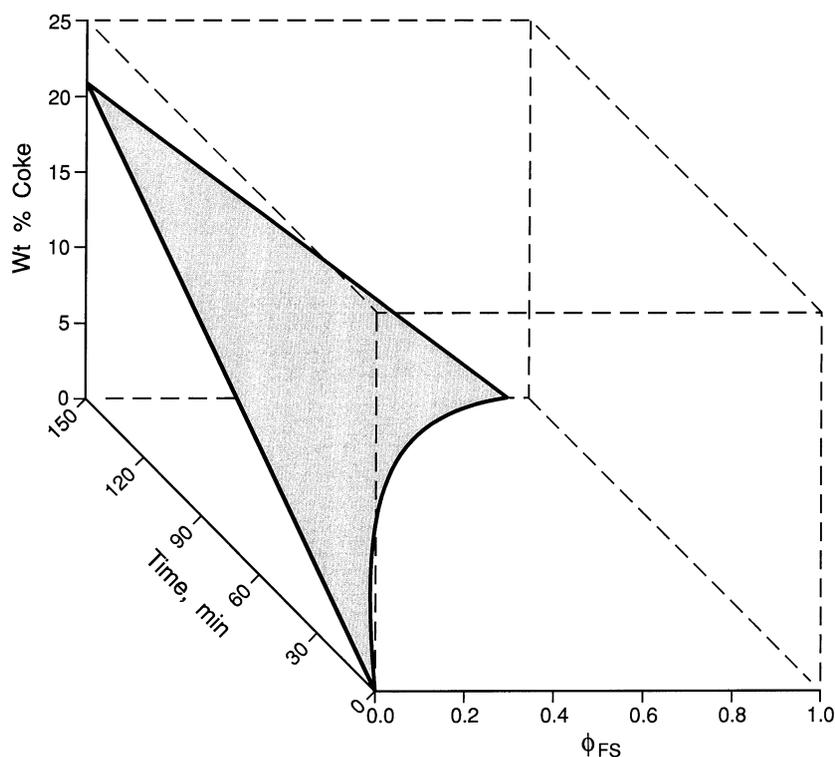
Fig. 4. Three-dimensional coke formation predictability map at 400 °C.
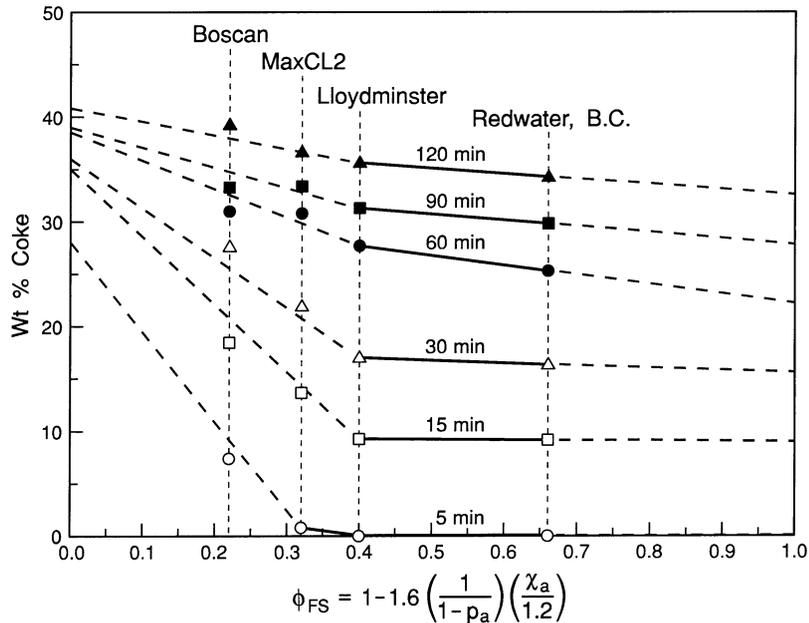
Fig. 5. Wt% coke vs. free solvent volume at 450 °C.

Lloydminster, and Redwater, B.C. residua at 400, 450, and 500 °C are provided in Figs. 11–14, respectively. The plots for the four residua are all qualitatively similar. These are mostly linear in nature, indicating zero-order (decomposition) kinetics. Several attempts were made to plot the data in terms of half-order (square root of wt% coke), first-order (log wt% coke), or second-order ((wt% coke)$^{-1}$). These gave smaller linear correlation coefficients than zero-order (wt% coke) plots, with the exception of the MacCL2 line at 400 °C, which has some first-order characteristics. Zero-order kinetics suggests bulk decomposition reaction mechanisms.

Phillips et al. [2] calculated a coke formation activation energy of 42,000 cal/mol for Athabaska bitumen assuming first-order kinetics. Del Bianco et al. [7] also assumed first-

order kinetics in coke formation from Athabaska bitumen, however the data show linear coke formation with time at 400 °C, suggesting that this process proceeds with zero-order kinetics. In a study of the kinetics of pyrolysis of Cold Lake residuum, Wiehe [3] provided data showing first-order kinetics at 400 °C for coke formation from asphaltenes. Zero-order kinetics were evident from the data provided for coke formation from pyrolysis of the maltenes. Coke formation data for pyrolysis of the whole Cold Lake residuum suggested first-order kinetics. Coke formation most likely involves a complex suite of reactions which on the whole fall somewhere between zero-order and first-order kinetic mechanisms.

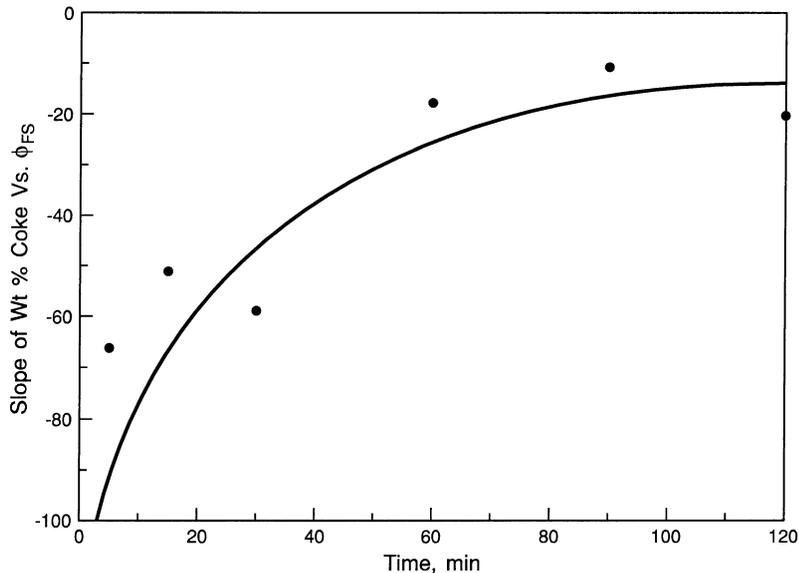If zero-order kinetics are used to interpret the data in the

Fig. 6. Slope of coke formation lines vs. residence times for Boscan, MaxCL, and Lloydminster residua at 450 °C.

Table 9
Weight percent coke vs. ϕ_{FS} line slopes and intercepts for Boscan, MaxCL2, and Lloydminster residua at 450 °C

Time (min)	$y = mx + b$		
	m	$b(\phi_{FS} = 0)$	r
120	−20.2	43.7	0.982
90	−10.6	36.0	0.808
60	−17.7	35.4	0.861
30	−58.8	40.8	1.000
15	−51.0	29.8	0.999
5	−66.0	21.9	1.000

Table 11
Weight percent coke vs. ϕ_{FS} line slopes for Lloydminster and Redwater, B.C. residua at 450 °C

Time (min)	$y = mx + b$		
	m	$b(\phi_{FS} = 0)$	y at $\phi_{FS} = 1$
120	−5.38	38.0	32.6
90	−5.77	33.6	27.8
60	−9.23	31.4	22.2
30	−2.69	18.3	15.6
15	−0.38	9.4	9.0
5	0	0	0

current study, two different coke formation mechanisms or processes are evident from the change in slope in the 450 °C line. The first is represented by the line at 400 °C and the lower line at 450 °C. The second is represented by the upper line at 450 °C. The coke formation process at 500 °C is very rapid up to the limiting amount of coke (determined by the H/C ratio) which is evidenced by the break in the slope of the upper portion of the 500 °C plot. The change in slope at the top of the 500 °C is most likely due to the upper limit of coke formation having been reached. Slopes were not determined for these. To estimate the activation energies of the initial or primary coke formation process, the slopes of the least-square wt% vs. time line at 400 °C and the slope of the lower line at 450 °C was calculated. Activation energy E* was determined from the equation:

$$E^* = -\ln\left(\frac{k_1}{k_2}\right)R(T_2 T_1)/(T_2 - T_1)$$

where T_1 and T_2 are the lower and higher temperatures, respectively, k_1 and k_2 are the slopes of the respective lines, and R is the gas constant. Once the activation energies were determined, the slope of the lower portion of the 500 °C line was calculated from the initial coke formation activation energy and the slope of the lower line at 450 °C. Using the calculated 500 °C slope and the upper secondary coke formation line slope at 450 °C, the activation energy of the secondary coke formation process was estimated. The

slopes of the lines and the correlation coefficients are provided in Table 13.

The results of the calculations are listed in Table 14. The activation energies for the initial coke formation reactions are estimated to be 38,000, 30,000, 30,000, and 22,000 cal/mol for Boscan, MaxCL2, Lloydminster, and Redwater, B.C. residua, respectively. The activation energies for the secondary coke formation reactions are 2.2–2.6 times higher than for the initial coke formation. Some of the secondary coke formation reactions could also involve wall effects in the reactor tubes. The initial coke formation represents 58.1–63.6% of the final coke yield for the four residua. This is consistent with the observations of Sanford [21] in studies with Athabaska bitumen in which the first 40–50% of conversion reactions involve the cleavage of side chains followed by coke-producing reactions. Del Bianco et al. [7] derived activation energies for cracking and coke formation reactions of 41,000 and 64,000 cal/mol, respectively, assuming first-order kinetics using a Belaym vacuum residuum. These results suggest that heat and time are not fully interchangeable variables in thermal conversion. To maximize conversion yield, the feed should be kept at a temperature low enough to maximize the bond cleavage reactions and minimize the coke formation reactions [7].

There also appears to be a correlation between the activation energies for both the primary and secondary coke formation reactions and the residuum free solvent volume (Fig. 15). A residuum with a lower free solvent volume which is indicative of the presence of a more highly ordered system has higher activation energies than a residuum with a higher free solvent volume.

Table 10
Weight percent coke vs. ϕ_{FS} interpolated line slopes and intercepts for Boscan, MaxCL2, and Lloydminster residua at 450 °C

Time (min)	$y = mx + b$	
	m	$b(\phi_{FS} = 0)^a$
120	−14	41
90	−16	38
60	−26	38
30	−48	36
15	−65	35
5	−90	28[b]

[a] Calculated from slope and coke yield at $\phi_{FS} = 0.40$.
[b] Calculated from slope and coke yield at $\phi_{FS} = 0.32$.

Table 12
Coke formed at 45 and 60 min at 500 °C and Conradson carbon values

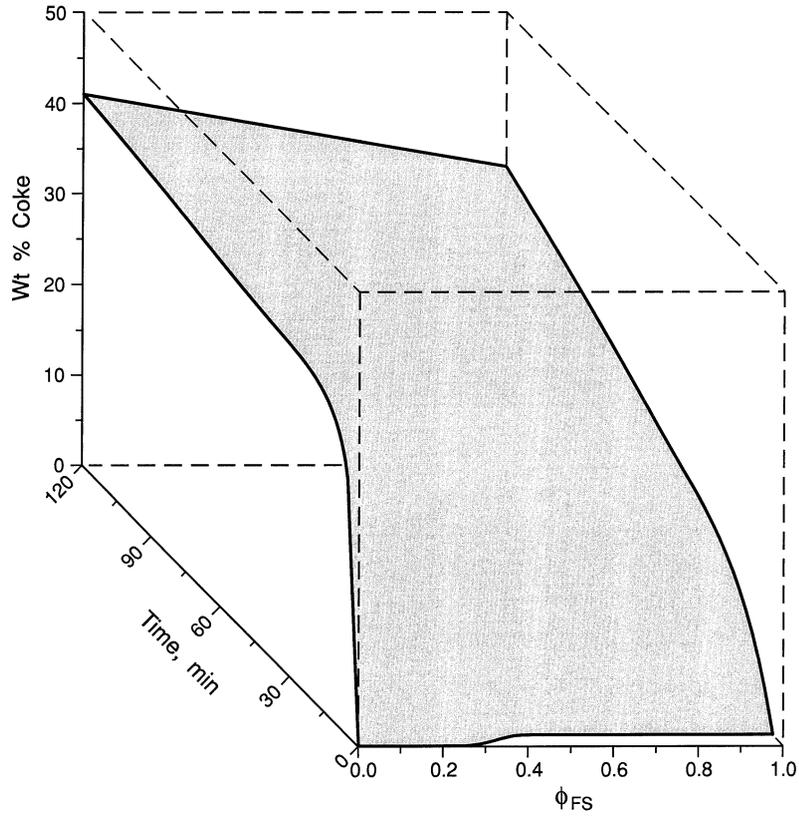| Residuum	Average wt% coke	÷ 1.6	CCR (wt%)
Boscan	46.2 (45.6, 46.6, 46.4)	28.9	18.9
MaxCL2	43.1 (41.4, 44.8)	26.9	22.3 (21.4, 23.2)
Lloydminster	39.6 (40.4, 39.1, 39.2)	24.8	16.4 (16.2, 16.5)
Redwater, B.C.	38.6 (39.0, 38.2)	24.1	18.2 (17.7, 18.7)
Average	41.9 ($s = 3.5$)	26.2 ($s = 2.2$)	19.0 ($s = 2.5$)

Fig. 7. Three-dimensional coke formation predictability map at 450 °C.

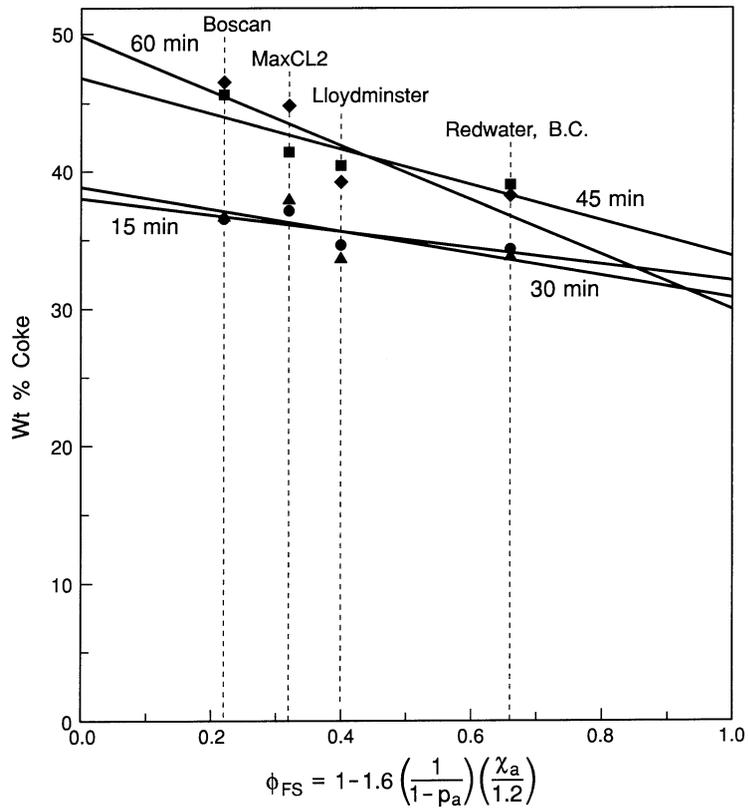$$\phi_{FS} = 1 - 1.6 \left(\frac{1}{1-p_a}\right)\left(\frac{\chi_a}{1.2}\right)$$

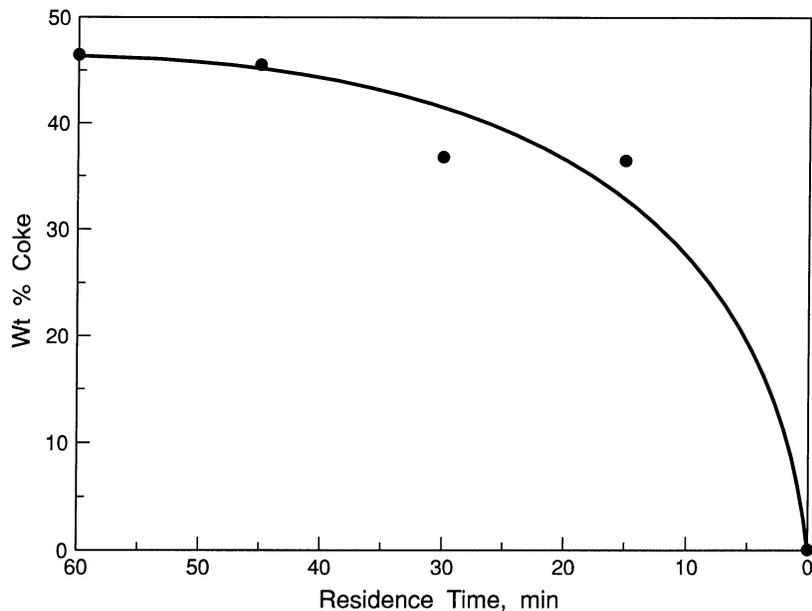Fig. 8. Wt% coke vs. free solvent volume at 500 °C.

Fig. 9. Coke formed with Boscan residuum at various times at 500 °C.

The physical difference between the primary and secondary coke is that the primary, or initial coke made is mostly in the form of a suspension in the liquid product oil. Once the secondary coke begins to form at 450 °C, the coke takes the form of a hard, solid cross-linked mass which adheres to the reactor tube walls. At 500 °C, all of the coke is of the latter variety. In future experiments, sufficient coke material from both primary and secondary reactions will be collected and analyzed to further define the differences between these materials.

5. Conclusions

Pyrolysis experiments were conducted with four residua with H/C atomic ratios of 1.4 at 400, 450, and 500 °C at
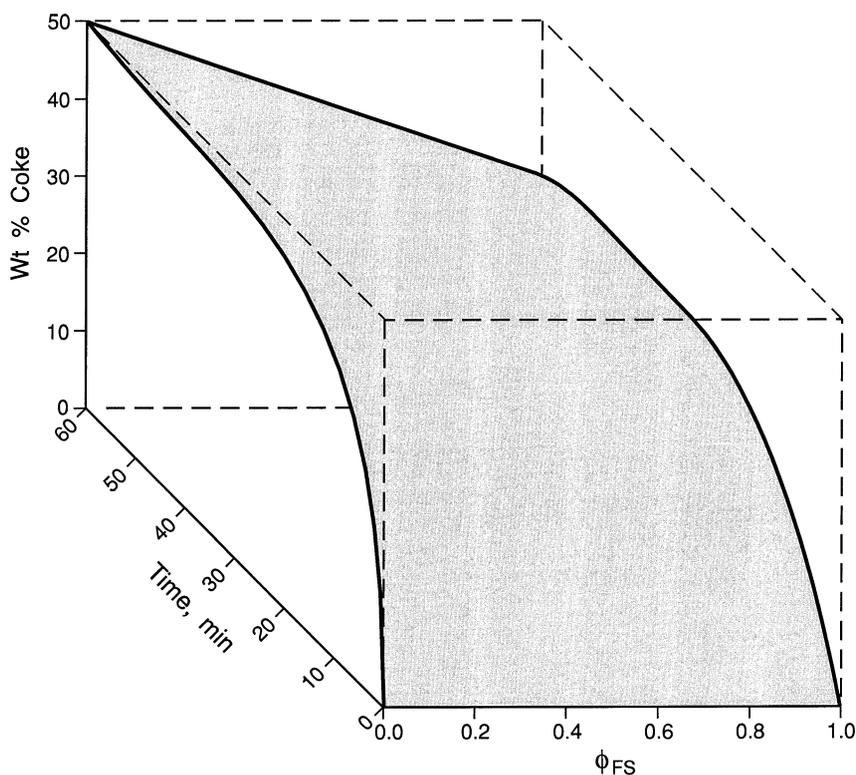
Fig. 10. Three-dimensional coke formation predictability map at 500 °C.
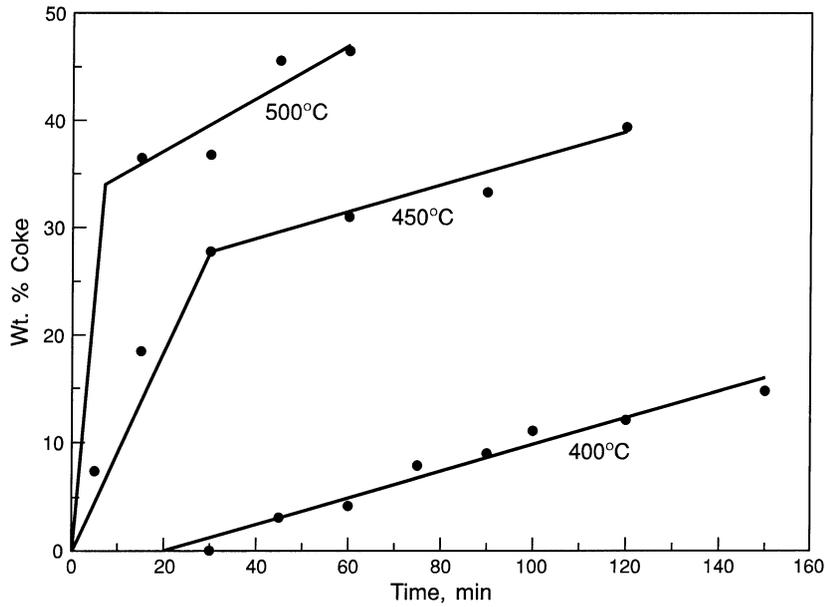
Fig. 11. Coke formation lines for Boscan residuum.

various residence times. Three-dimensional coke make predictability maps were developed. The initial amount of coke formed correlates with residence time and free solvent volume at 400 and 450 °C. At 500 °C, coke formation is very rapid. The amount of coke initially formed at 400 °C appears to be a function of the free solvent volume of the original residua. The appearance of coke can be modeled in terms of two stages of zero-order (decomposition) reactions. The first stage appears to be dominated by bond cleavage reactions with activation energies ranging from 22,000 to 38,000 cal/mol. The second stage is probably dominated by coke formation reactions and has activation energies ranging from 54,000 to 83,000 cal/mol. The activation energies appear to correlate with the initial residua free solvent volume. When carried to completion, the amount of coke formed is related to the atomic H/C ratio. The results provide a new tool for ranking residua and predicting initial coke make tendencies. Additional materials with higher and lower H/C ratios should be studied to determine if the maps can be applied to a wide variety of residua in a universal manner, or if the correlations need to be modified.

6. Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agencies
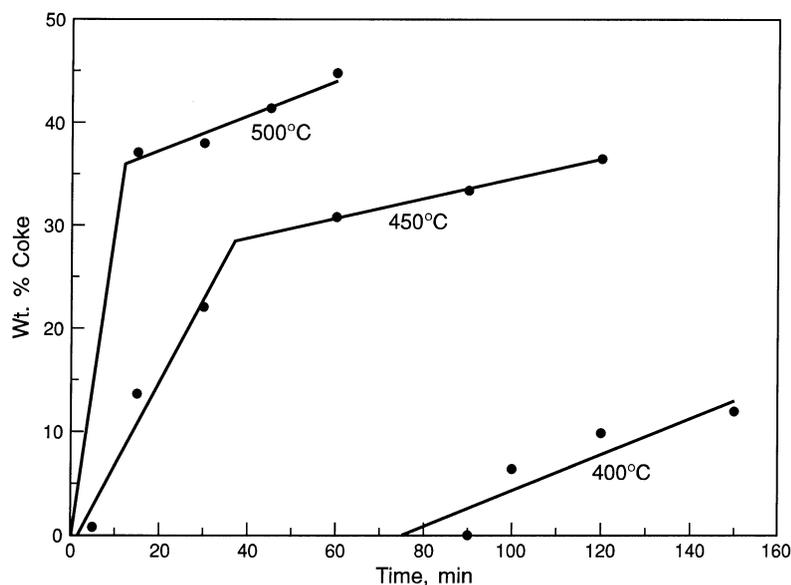

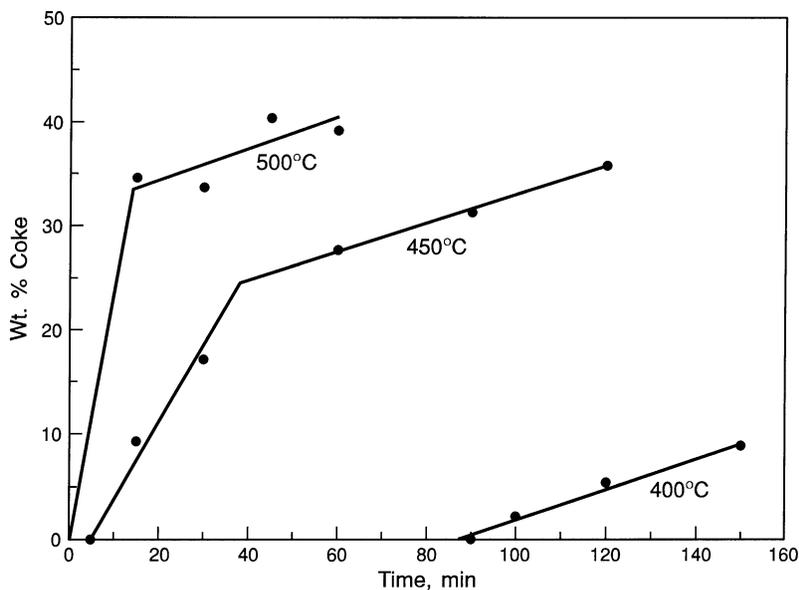Fig. 12. Coke formation lines for MaxCL residuum.

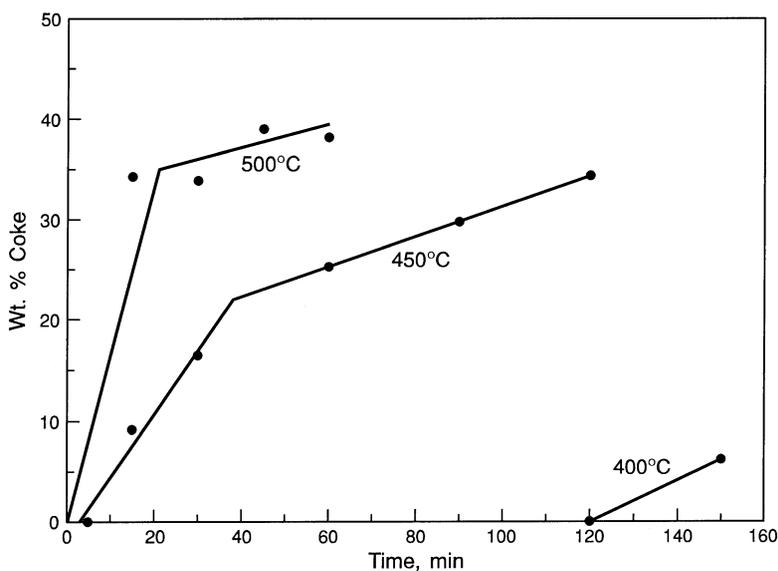Fig. 13. Coke formation lines for Lloydminster residuum.

Fig. 14. Coke formation lines for Redwater, B.C. residuum.

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Table 13
Slopes of wt% coke vs. time lines (wt%/min) and correlation coefficients

Residuum	400 °C		450 °C				500 °C
	Slope	r	Lower slope	r	Upper slope	r	Slope
Boscan	0.124	0.9814	0.909	0.9831	0.124	0.9775	5.14
MaxCL2	0.178	0.8960	0.829	0.9722	0.0950	0.9987	3.17
Lloydminster	0.146	0.9922	0.675	0.9869	0.135	0.9979	2.58
Redwater, B.C.	0.207	1.000	0.646	0.9836	0.152	1.000	1.74

Table 14
Estimated activation energies of coke formation

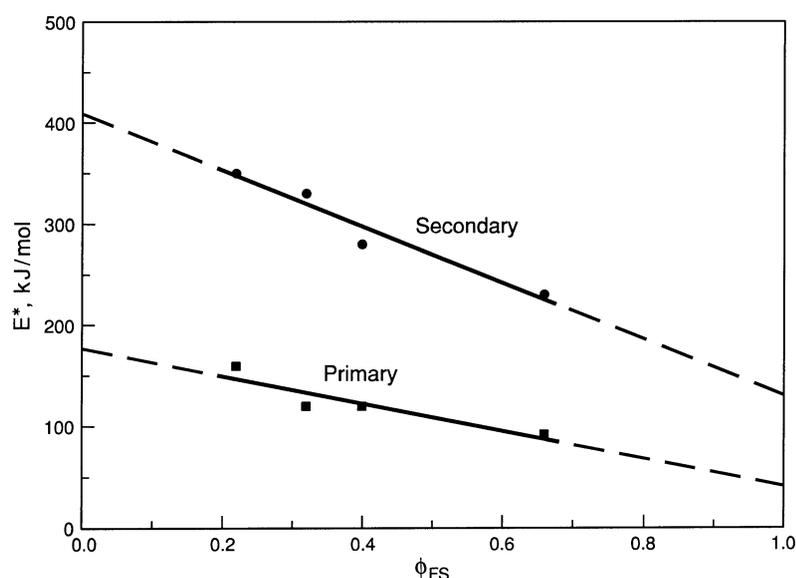| Residuum	Activation energy E^* (cal/mol)			
	Primary coke formation	Primary wt% (450 °C)	Secondary coke formation	Total wt% (500 °C)
Boscan	38,000	27.0	83,000	58.1
MaxCL2	30,000	28.5	78,000	63.6
Lloydminster	30,000	24.5	66,000	62.5
Redwater, B.C.	22,000	22.5	54,000	59.9

Fig. 15. Activation energy and free solvent volume correlation.

or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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