WRI-02-R012

RESIDUA UPGRADING EFFICIENCY IMPROVEMENT MODELS: COKE FORMATION PREDICTABILITY MAPS

Topical Report

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May 2002

Work Performed Under Cooperative Agreement
DE-FC26-98FT40322 Task 1.8

For
U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Morgantown, West Virginia

And
BetzDearborn
Division of Hercules
The Woodlands, Texas

Chevron Lummus Global LLC
Richmond, California

Conoco, Inc.
Ponca City, Oklahoma

ExxonMobil Research and Engineering Co.
Annandale, New Jersey

By
Western Research Institute
Laramie, Wyoming

ACKNOWLEDGMENTS

Funding for this study was provided by the U.S. Department of Energy under Cooperative Agreement DE-FC26-98FT40322, and by BetzDearborn Division of Hercules, Inc., Chevron Lummus Global LLC, Conoco, Inc., and ExxonMobil Research and Engineering Co. The authors would like to acknowledge Tony Munari for preparing the figures.

DISCLAIMER

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 multiphase 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 EC, 450 °C, and 500 EC (752 EF, 842 EF, and 932 EF). These relate residence time and free solvent volume to the amount of coke formed at a particular pyrolysis temperature. Activation energies for two apparent types of zero-order coke formation reactions were estimated. The results provide a new tool for ranking residua, gauging proximity to coke formation, and predicting initial coke make tendencies.

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EXECUTIVE SUMMARY

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 multiphase 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 °C, 450 °C, and 500 °C (752 °F, 842 °F, and 932 °F) 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 to follow zero-order kinetics, and these appear to 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 results provide a new tool for ranking residua, gauging proximity to coke formation, and predicting initial coke make tendencies.

OBJECTIVES

The objectives of this work are to further develop diagnostic tools to study the changes that occur during residua pyrolysis and develop predictive models of coke formation based on the dispersed particle solution model. Ideally, the model should apply to different residua processed at a given time and temperature, based on the state of their initial ordered structure. Correlations can be developed using the results from relatively simple measurements such as the asphaltene flocculation titration and asphaltene content. The goal of the current effort is to take four residua and subject them to pyrolysis at three temperatures, 400 EC, 450 EC, and 500 EC (752 EF, 842 EF, and 932 EF), at residence times up to and past the point of coke formation. Data for the original residua will be combined as appropriate into a model that a refiner can use to preselect optimal conditions for thermal processing of any residuum. The ultimate goal is to develop predictive tools so that residua can be ranked in terms of their coke formation propensity. With such tools it should be possible to preselect conditions for optimized distillation or thermal conversion based on parameters determined anywhere in the world where the residuum is purchased. This should result in significant efficiency improvement, reductions in downtime, and less heat wasted in refinery operations.

INTRODUCTION

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 EC, 662 EF), there is typically an induction period before coke formation begins (Magaril and Aksenova 1968, Phillips et al. 1985, Wiehe 1993). 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 (Schabron et al. 1999, 2000, 2001a). 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 multiphase system. This is consistent with observations of the formation of a neophase at coke formation onset (Shenghua et al. 1999). Pyrolysis reactions involve the cleavage of carbon bonds with carbon, hydrogen, and heteroatoms resulting in the formation of free radicals that continue scission reactions or condense into carbon-rich material (Singh et al. 1990, Del Bianco et al. 1993). 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.

Asphaltene Flocculation Titration

The titration is performed only with the toluene-soluble components of residua. Three toluene solutions at different concentrations of residuum are titrated with a weak solvent, such as isooctane. The weight of residuum or asphalt (W), the volume of toluene (V_s), and volume of isooctane titrant (V_t) are recorded for each solution at the flocculation point when asphaltenes begin to precipitate. The flocculation ratio and dilution concentration are calculated as follows (Heithaus 1962):

$$FR = \text{Flocculation Ratio} = V_s/(V_s + V_t) \quad (1)$$

$$C = \text{Dilution Concentration} = W/(V_s + V_t) \quad (2)$$

A plot of FR vs. C is made, and the intercepts are determined (FR_{max} and C_{min}). The Heithaus parameter, FR_{max}, relates to the peptizability of asphaltenes and the solubility parameter at which asphaltenes begin to precipitate. The term, $p_a = 1 - FR_{max}$, has been shown to be numerically equivalent to ", the fraction of bound solvent phase associated with a solvated asphaltene core (Pauli and Branthaver 1998). C_{min} is a measure of the amount of isooctane, which when added to the residuum will initiate asphaltene precipitation and is thus related to the solubility parameter of the whole residuum. The term, $P = p_o/(1-p_a) = 1/C_{min} + 1$, relates to the overall compatibility of a residuum. Larger values of p_a indicate peptizable asphaltenes, and larger values of P indicate an overall compatible system.

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 (Pal and Rhodes 1989, Schabron et al. 2000). 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 (Schabron et al. 2000, 2001b, 2001c). When carried to completion, the amount of coke from pyrolysis is related to the H/C ratio and not the free solvent volume. The free solvent volume, N_{FS}, can be calculated using the equation below:

$$N_{FS} = 1 - K_S K_F N_a = 1 - 1.6\left(\frac{1}{1-p_a}\right)\left(\frac{P_a}{1.2}\right) \quad (3)$$

In the equation, P_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, N_a. The volume fraction of asphaltenes is increased by the K_S and K_F terms. Prior work measuring K_S using a variety of experimental techniques has shown that the K_S

value for unpyrolyzed residua and asphalt systems is 1.6 (Pauli and Branthaver 1998). In the current study, initial coke make values were obtained for four residua at 400 EC, 450 EC, and 500 EC (752 EF, 842 EF, and 932 EF) at various residence times. Correlations of coke make vs. N_{FS} were evaluated at both temperatures.

Free Solvent Volume Correlations

In prior work, a correlation relating free solvent volume, N_{FS}, to the amount of nonpyrolytic deposition of asphaltenic material on polar surfaces at 250 EC (482 EF) was developed (Schabron et al. 2000, 2001b). A similar correlation between free solvent volume and the amount of initial coke make at 400 EC (752 EF) at reactor residence times of 60 and 90 minutes was also developed. These results suggested the possibility of developing three-dimensional coke predictability maps that relate initial coke make to residence time and free solvent volume at a particular temperature. These are the observations upon which the current work is based.

EXPERIMENTAL DETAILS

Residua Materials

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

Asphaltene Determination

Heptane asphaltenes were isolated by heating a 40:1 (v:w) mixture of reagent-grade n-heptane and residuum to 70 EC (158 EF) for about ½ hour on a heated stir plate while stirring with a magnetic, Teflon™-coated rod. This was followed by overnight stirring at room temperature. The following morning, the stirring was stopped for 30 minutes prior to filtering the precipitated asphaltenes from the mixture. Vacuum filtration was performed using Ace, 140-mL, 10-20 micron, sintered glass filters. Residual solvent was removed from the asphaltenes contained in the filters using a vacuum oven set at 120 EC (248 EF) for 30 minutes. The asphaltenes were cooled in a desiccator prior to weighing.

Cyclohexane Soluble Asphaltenes

A portion of n-heptane asphaltenes was ground to a fine powder using a mortar and pestle. A 0.5-g portion of this was weighed into a 120-mL jar, and 100 mL of cyclohexane and a magnetic stir bar were added. The mixture was stirred overnight. Stirring was stopped and the mixture was allowed to settle for

30 minutes prior to filtration. The mixture was vacuum filtered using Ace, 140-mL, 10-20 micron, sintered glass filters. Solvent was removed from the filtrate by rotary evaporation, and traces of cyclohexane were removed in a vacuum oven at 100 EC (212 EF) for 15 minutes. The cyclohexane solubles were cooled in a desiccator prior to weighing.

Asphaltene Flocculation Titration

Automated asphaltene flocculation titrations were performed with a WRI computer-controlled Automated Flocculation Titrimeter (AFT) unit at 25.0 ± 0.1 EC with 5–20 wt % residua solutions in toluene using 2,2,4-trimethylpentane (isooctane) as titrant at an average titrant delivery rate of 0.35 mL/min (Schabron et al. 2000). The procedures used are described in detail elsewhere (Pauli 1996).

Pyrolysis

Pyrolysis experiments were performed with 5-g residua samples weighed into 0.75-inch x 7-inch 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, 4,000-watt, fluidized sand bath set at the appropriate temperature for the experiment. The time to achieve the reaction temperature was typically under ten minutes. 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 products were collected in toluene and vacuum filtered using Ace, 140-mL, 10-20 micron, sintered glass filters to obtain toluene insolubles (coke).

Conradson Carbon and Elemental Analyses

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, Colorado.

RESULTS

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 WRI used in prior work. 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 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 time line (Schabron et al. 2000, 2001c). 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.

Asphaltene Determination

There are many differences in the various procedures used to obtain asphaltenes. The most obvious is the choice of solvent, with the less polar solvent yielding higher asphaltene amounts. The ratio of solvent to residuum is important also. The solvent must be in significant excess, at a ratio of 30:1 (v:w) or higher, so that the solubility parameter of the system is essentially the same as the solubility parameter of the solvent (Speight et al. 1984). Other factors that affect the weight percent asphaltene value include heating the hydrocarbon and residuum mixture and the manner in which the solvent is removed from the filtered solids. Heptane asphaltene values that were obtained by dispersing a 30:1 (v:w) heptane residuum mixture varied from 20.2 wt % at 24 EC (75.2 EF) to 16.6 wt % at 50 EC (122 EF) and 14.7 wt % at 80 EC (176 EF) (Andersen et al. 1997). The precipitate was dried with air flow under a vacuum.

ASTM D-3279 recommends that a 100:1 (v:w) heptane/residuum mixture be refluxed for up to 30 minutes, then cooled to room temperature for one hour, then heated to 38 EC–49 EC (100.4 EF–120.2

EF) for filtering (ASTM 2000a). The precipitate is dried in an oven at 107 EC (224.6 EF) for 15 minutes, then cooled in a desiccator. ASTM D-4124 recommends mechanically stirring a 100:1 (v:w) heptane/residuum mixture while it is being heated on a steam bath for one hour (ASTM 2000b). The mixture is allowed to settle at ambient temperature overnight and then filtered. The residue is dried at 104 EC (220 EF) in an oven.

In the Strategic Highway Research Program (SHRP) procedure, the residuum is mixed with a 40:1 excess of heptane and allowed to soak for at least 16 hours at room temperature with occasional stirring with a glass rod (Petersen et al. 1994). Once the mixture is dispersed, it is filtered. The asphaltenes are air dried and then swept with nitrogen overnight.

The practice, that is occasionally reported of initially dissolving the residuum in an equal amount of toluene followed by adding an excess of heptane to precipitate asphaltenes, leads to poor repeatability in determining asphaltene values. While the solubility parameter contribution of the toluene can be rendered minimal by adding an excess of heptane, toluene has a relatively strong chromatographic effect that can influence the solubility and the nature of the asphaltene complexes that are isolated. Solubility parameters contributions are additive in proportion to volume fractions, while a small amount of a relatively strong chromatographic solvent can affect the effective size and solubility of asphaltenes (Schabron et al. 2001a).

In the current work, heptane asphaltenes were obtained by heating a 40:1 (v:w) mixture of heptane and residuum to 70 EC (158 EF) for about ½ hour on a heated stir plate while stirring with a magnetic, Teflon-coated rod until the mixture was fully dispersed. The mixture was stirred overnight at room temperature. The following morning, the stirring was stopped for 30 minutes prior to filtration. The solvent was removed in a vacuum oven set at 120 EC (248 EF) and a 22-inch Hg vacuum for 30 minutes. The asphaltenes were cooled in a desiccator prior to weighing. In all of the cases above, medium-frit filter media (10-20 micron) were used for vacuum filtration.

A comparison of results between the heated mixture method used for this work and the room-temperature SHRP procedure is provided in Table 4 for Boscan, MaxCL2, and Lloydminster residua. The significance of the above discussion is that the procedure used has a significant affect on results. In a study where properties of various residua are to be compared, it is important that the data be generated with the same procedure. In some prior work WRI used the room-temperature SHRP procedure to isolate asphaltenes. That procedure was lengthy and subject to fluctuations in room temperature during the lengthy process. In the current work the heated solvent method was used, which yields slightly lower asphaltene values, but it is rapid and provides repeatable results.

Pyrolysis Experiments

Pyrolysis results, especially at the lower temperatures employed in the current study, 400 EC (752 EF) and 450 EC (842 EF), 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 EC (752 EF) at 30, 45, 60, 75, 90, 100, 120, and 150 minutes 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 minutes. The MaxCL2 and Lloydminster residua began producing coke by 90 minutes residence time, and the Redwater, B.C. produced coke at the 150-minute residence time.

Results from pyrolysis experiments at 450 EC (842 EF) at 5, 15, 30, 60, 90, and 120 minutes 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 minutes residence time.

Results from pyrolysis experiments at 500 EC (932 EF) at 15, 30, 45, and 60 minutes are shown in Table 7. All four residua produced significant coke at all four residence times.

DISCUSSION

Coke Formation Map at 400 EC

At 400 EC (752 EF), the amount of coke formed for a particular residuum increases with increasing residence time (Table 5). At a residence time of 150 minutes, 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 45 to 150 minutes. A plot of wt % coke vs. residence time for the Boscan residuum shows a linear relationship (Figure 1). Plots of wt % coke vs. free solvent volume at various residence times for the four residua are provided in Figure 2. Lines for 150, 120, and 100 minutes can be drawn using data for three or four of the residua. Only the Boscan residuum yielded coke at the shorter time frames. 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 (Figure 3). The plot appears to be linear in the range of 60–160 minutes 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 minutes 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 (752 °F) at $N_{FS} = 0$ at 150 minutes is 20.9 wt % (n = 7, s = 1.4). The extrapolated lines are included in Figure 2.

From the above data plots and extrapolations, a three-dimensional map (time, coke yield, free solvent volume) was constructed (Figure 4). The data used for the N_{FS} calculations and the N_{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 the calculation of N_{FS} were the weight percent heptane asphaltenes and the Heithaus p_a value.

Coke Formation Map at 450 °C

At 450 °C (842 °F), the amount of coke formed for a particular residuum increases with increasing residence time (Table 6). At a residence time of 120 minutes, 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 minutes. Plots of wt % coke vs. free solvent volume at various residence times for the four residua are provided in Figure 5. To minimize experimental error in estimating the free solvent volume intercepts of the lines at $N_{FS} = 0$, a plot of slope of wt % coke vs. free solvent volume lines was made for Boscan, MaxCL2, and Lloydminster residua (Figure 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 Figure 5. In Figure 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 $N_{FS} = 1$ (Table 11).

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

Coke Formation Map at 500 °C

At 500 °C (932 °F), coke formation rapidly proceeds to completion (Table 12). Coke make vs. free solvent volume plots for the various residence times are provided in Figure 8. The amount of coke formed at 60 minutes was essentially the same as the amount of coke formed at 45 minutes 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 Figure 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 minutes and 60 minutes ranged from 38.2 to 46.4 wt %. The average wt % coke formed at 45 minutes and 60 minutes 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 ratio of delayed coker yield to Conradson carbon residue (CCR) or microcarbon residue (MCR) as reported by Gary and Handwerk (1975) for a particular set of refinery coker conditions, a value of 26.2 wt % as MCR emerges with a 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 minutes to the average CCR value is 2.2. Both values of 26.2 wt % 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 (Figure 10). The three-dimensional coke formation predictability map for 500 EC (932 EF) is shown in Figure 11. 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 minutes.

Activation Energies

Plots of wt % coke vs. time for Boscan, MaxCL2, Lloydminster, and Redwater, B.C. residua at 400 EC (752 EF), 450 EC (842 EF), and 500 EC (932 EF) are provided in Figures 12–15, respectively. The plots for the four residua are all qualitatively similar. These mostly are 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 (1/wt % coke). These gave smaller linear correlation coefficients than zero-order (wt % coke) plots, with the exception of the MacCL2 line at 400 EC (752 EF), which has some first-order characteristics. Zero-order kinetics suggest bulk decomposition reaction mechanisms.

Phillips et al. (1985) calculated a coke formation activation energy of 42,000 cal/mol for Athabaska bitumen assuming first-order kinetics. Del Bianco (1993) also assumed first-order kinetics in coke formation from Athabaska bitumen, however the data show linear coke formation with time at 400 EC (752 EF), suggesting that this process proceeds with zero-order kinetics. In a study of the kinetics of pyrolysis of Cold Lake residuum, Wiehe (1993) provided data showing first-order kinetics 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 that 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 current study, two different coke formation mechanisms or processes are evident from the change in slope in the 450 °C (842 °F) line. The first is represented by the line at 400 °C (752 °F) and the lower line at 450 °C (842 °F). The second is represented by the upper line at 450 °C (842 °F). The coke formation process at 500 °C (932 °F) 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 (932 °F) plot. The change in slope at the top of the 500 °C (932 °F) line 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 (752 °F) and the slope of the lower line at 450 °C (842 °F) was calculated. Activation energy E^* was determined from the equation:

$$E^* = -\ln\left(\frac{k_1}{k_2}\right) \cdot R \cdot (T_2 \cdot T_1) \; / \; (T_2 - T_1) \tag{4}$$

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 (932 °F) line was calculated from the initial coke formation activation energy and the slope of the lower line at 450 °C (842 °F). Using the calculated 500 °C (932 °F) slope and the upper secondary coke formation line slope at 450 °C (842 °F), 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 (1993) in studies with Athabaska bitumen in which the first 40–50% of conversion reactions involve the cleavage of side chains followed by condensation aromatic carbon radical coke-producing reactions. Del Bianco et al. (1993) 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 condensation reactions (Del Bianco et al. 1993).

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 (Figure 16). A residuum with a lower free solvent volume that is indicative of the presence of a more highly ordered system has higher activation energies than a residuum with a higher free solvent volume.

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 EC (842 EF), the coke takes the form of a hard, solid, cross-linked mass that adheres to the reactor tube walls. At 500 EC (932 EF), 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.

CONCLUSIONS

Pyrolysis experiments were conducted with four residua with H/C atomic ratios of 1.4 at 400 EC, 450 EC, and 500 EC (752 EF, 842 EF, and 932 EF) at 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 EC (752 EF) and 450 EC (842 EF). At 500 EC (932 EF), coke formation is very rapid. The amount of coke initially formed at 400 EC (752 EF) 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) coke formation 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 condensation 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.

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Table 1. Elemental Analysis Data and H/C Atomic Ratios

	Weight Percent					H/C
Residuum	C	H	N	S	Total	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

	X: Wt % n-C7	**Y**: Wt % Cyclohexane	Heithaus Parameters	
Residuum	Asphaltenes	Soluble Asphaltenes	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

Table 3. WRI Residua Coking Indexes and Free Solvent Volumes

Residuum	WRI Coking Indexes Y/X	 p_a/C_{min}	N_{FS} $(1\text{-}1.6 \bullet 1/(1\text{-}p_a) \bullet P_a/1.2)$
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 EC) Asphaltene Yields

	Weight Percent n-Heptane Asphaltenes	
Residuum	Room Temperature	Heated (70 EC)
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 EC (wt % Coke)

	Residence Time, Minutes							
Residuum	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

Table 6. Coke Yields at 450 EC (wt % Coke)

	Residence Time, Minutes					
Residuum	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 EC (wt % Coke)

	Residence Time, Minutes			
Residuum	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

Table 8. Weight Percent Coke vs. N_{FS} Line Slopes and Intercepts at 400 EC

		$y = m c x + b$		
Time, min	m	b	r	N_{FS} at y = 0
		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

Table 9. Weight Percent Coke vs. N_{FS} Line Slopes and Intercepts for Boscan, MaxCL2, and Lloydminster Residua at 450 EC

y = m c x + b

Time, min	m	b (N_{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 10. Weight Percent Coke vs. N_{FS} Interpolated Line Slopes and Intercepts for Boscan, MaxCL2, and Lloydminster Residua at 450 EC

y = m c x + b

Time, min	m	b (N_{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 N_{FS} = 0.40

[b] Calculated from slope and coke yield at N_{FS} = 0.32

Table 11. Weight Percent Coke vs. N_{FS} Line Slopes for Lloydminster and Redwater, B.C. Residua at 450 °C

$$y = m \times x + b$$

Time, min	m	b (N_{FS} = 0)[a]	y at N_{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

Table 12. Coke Formed at 45 and 60 Minutes 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)

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

	Activation Energy E^*, cal/mole			
Residuum	Primary Coke Formation	Wt % Primary (450 °C)	Secondary Coke Formation	Wt % Total (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

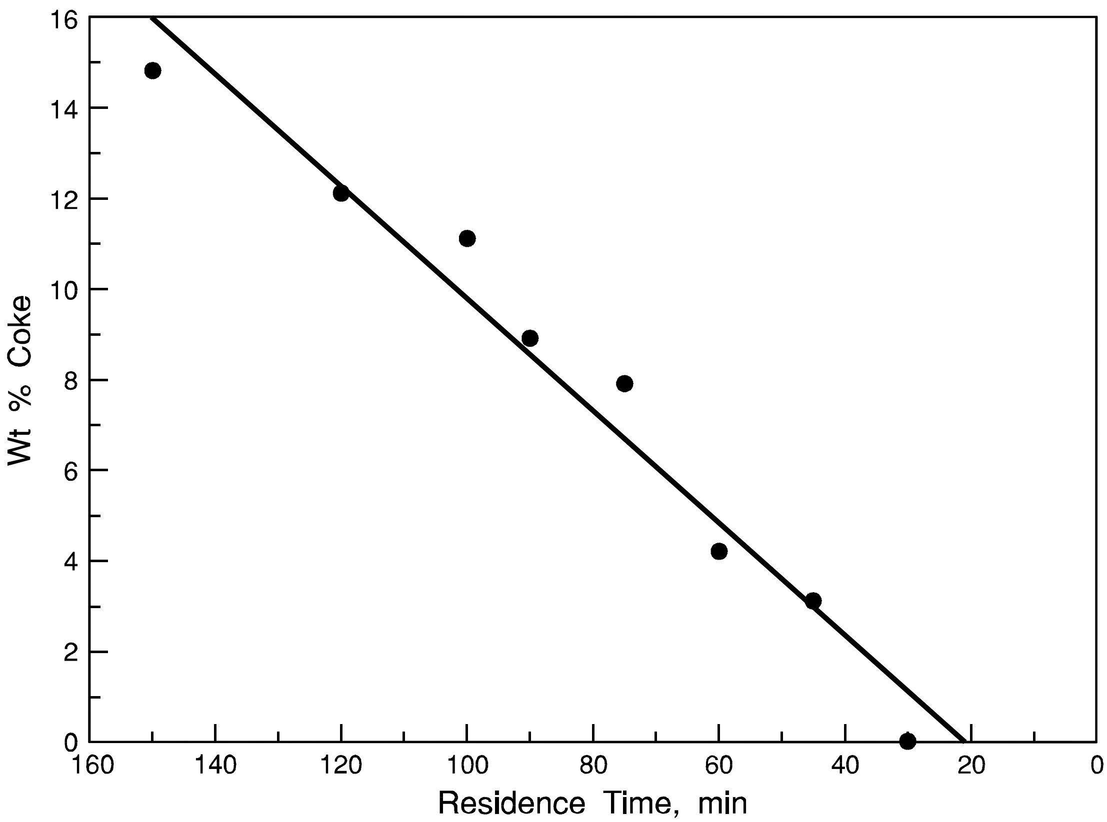

Figure 1. Coke Formed with Boscan Residuum at Various Times at 400 EC

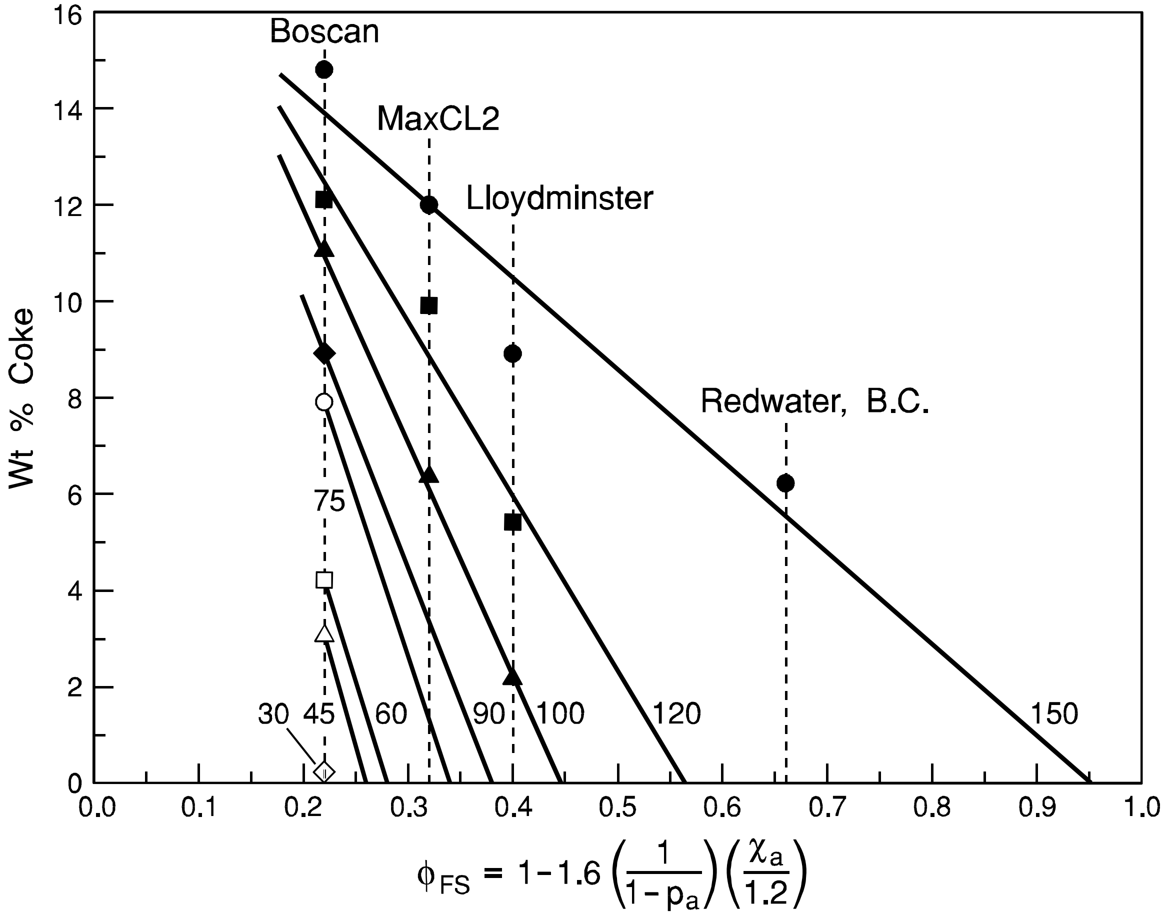

Figure 2. Wt % Coke vs. Free Solvent Volume at 400 EC

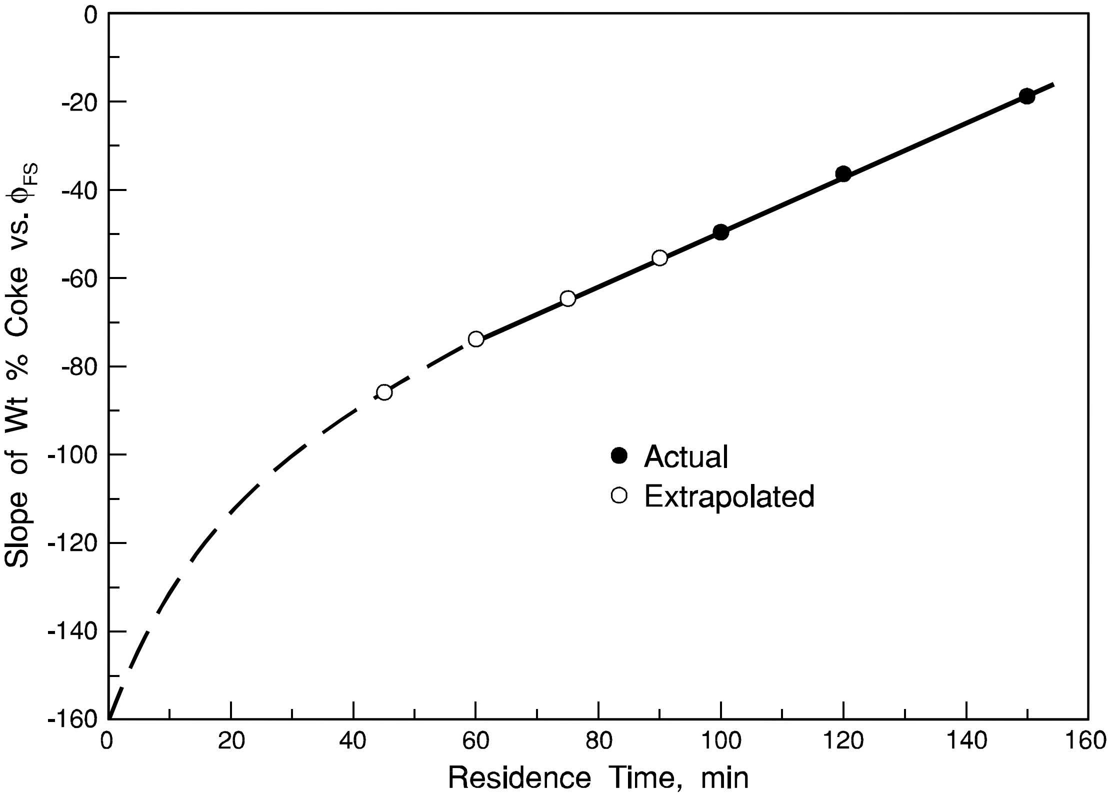

Figure 3. Slope of Coke Formation Lines vs. Residence Times at 400 EC

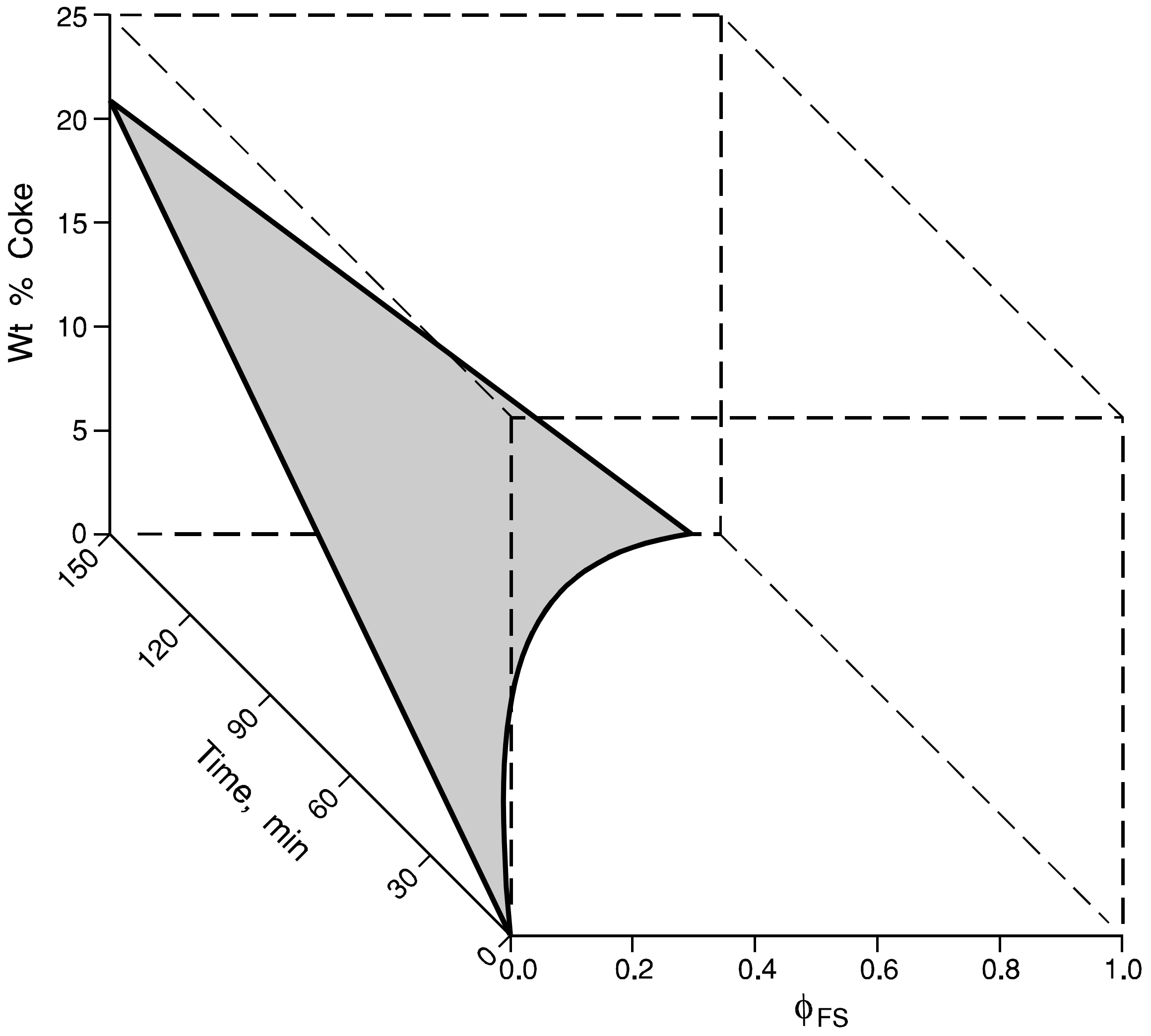

Figure 4. Three-Dimensional Coke Formation Predictability Map at 400 EC

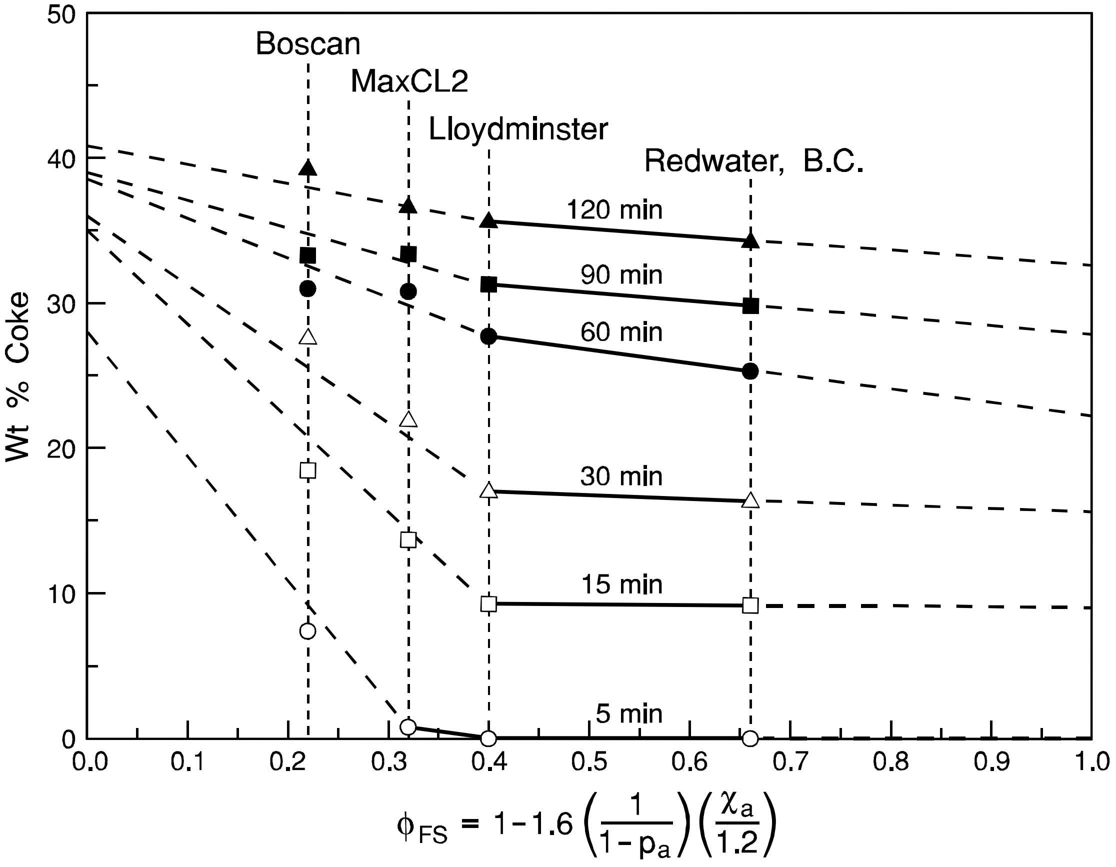

Figure 5. Wt % Coke vs. Free Solvent Volume at 450 EC

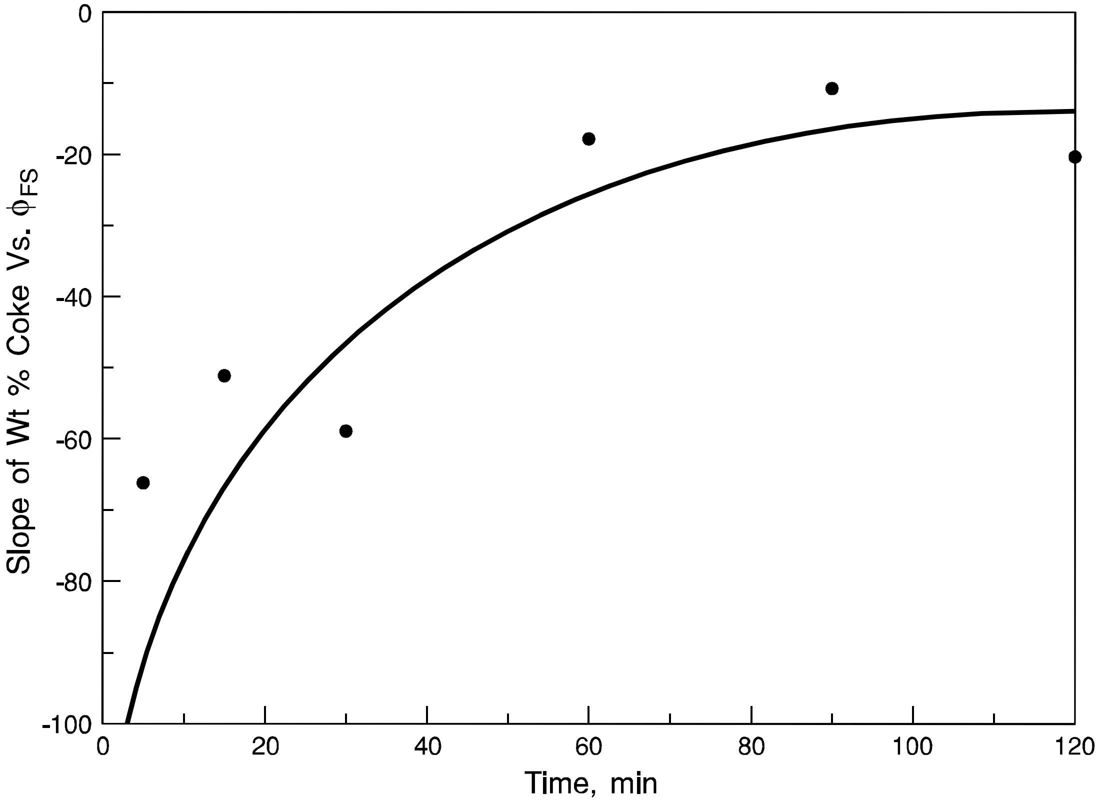

Figure 6. Slope of Coke Formation Lines vs. Residence Times for Boscan, MaxCL, and Lloydminster Residua at 450 EC

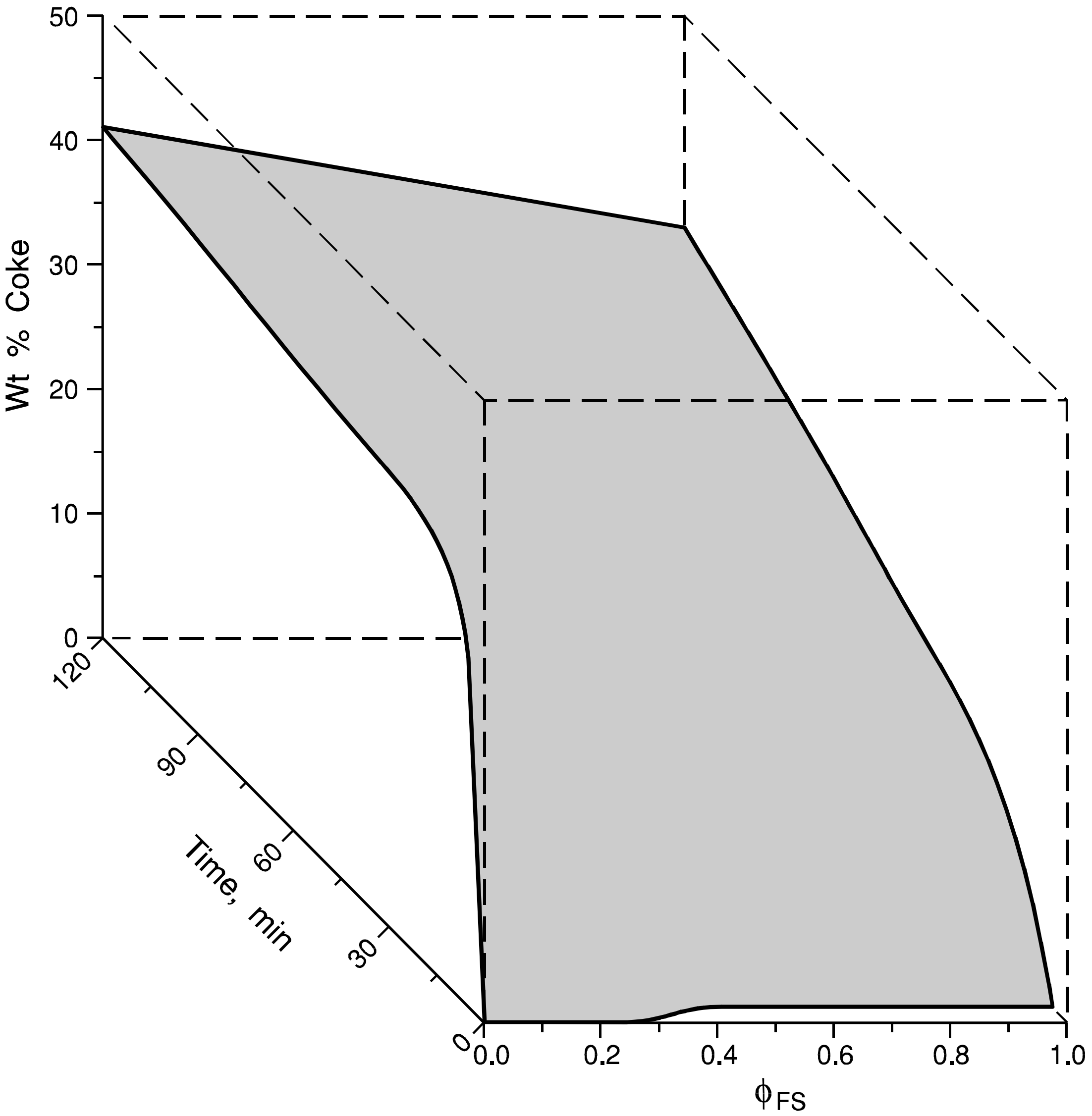

Figure 7. Three-Dimensional Coke Formation Predictability Map at 450 EC

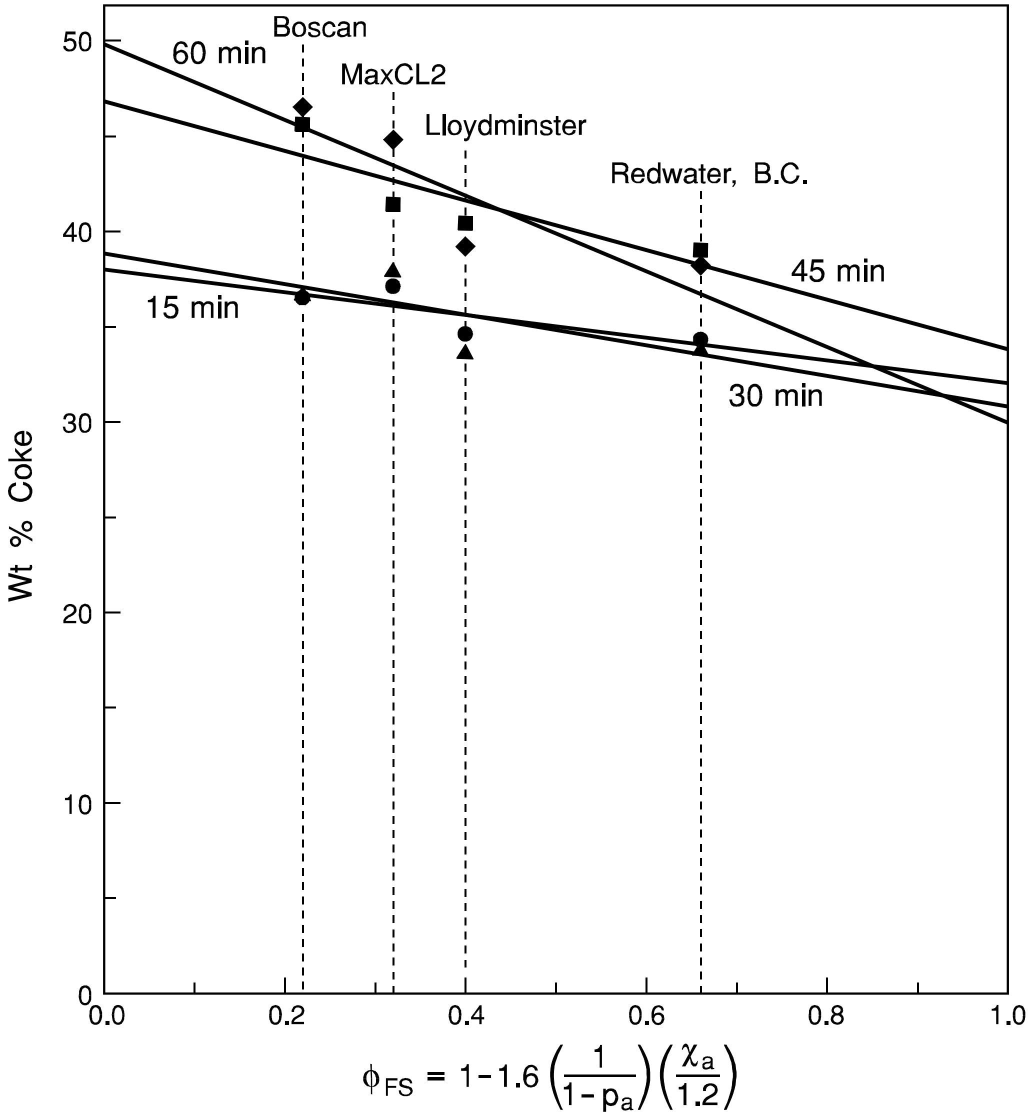

Figure 8. Wt % Coke vs. Free Solvent Volume at 500 EC

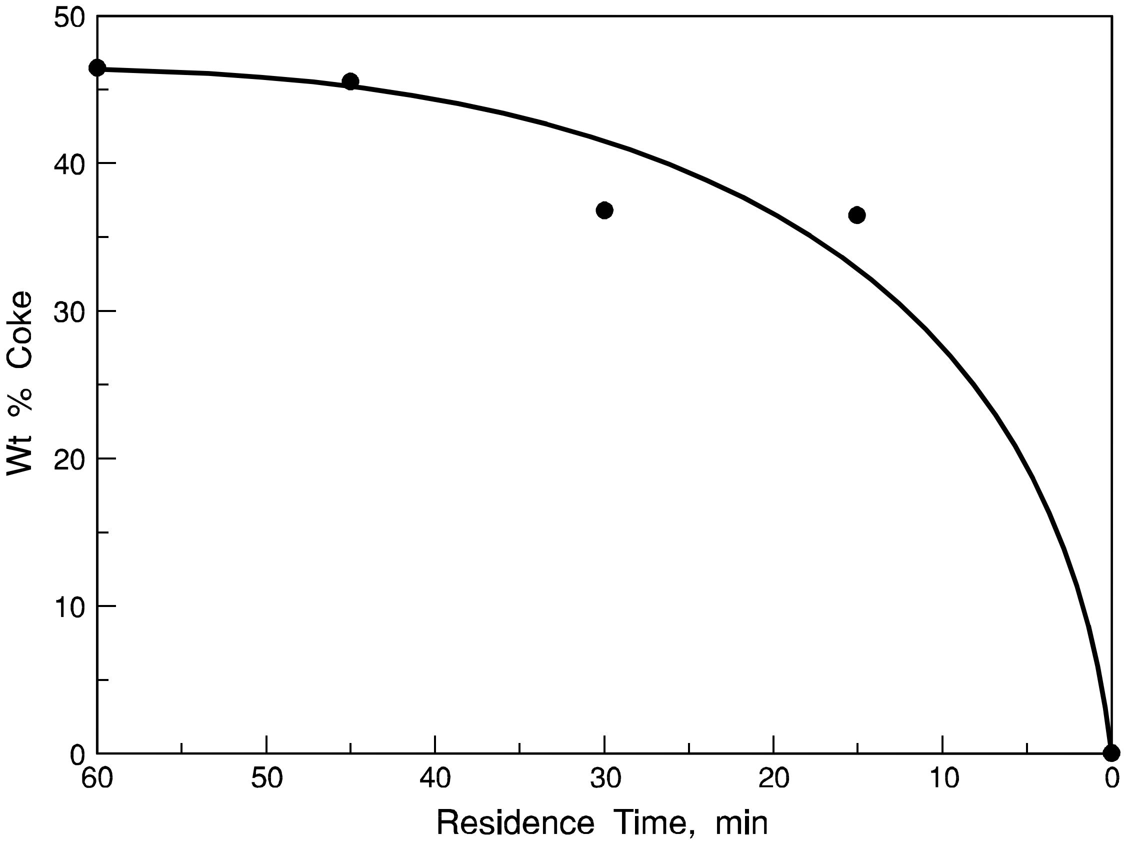

Figure 9. Coke Formed with Boscan Residuum at Various Times at 500 EC

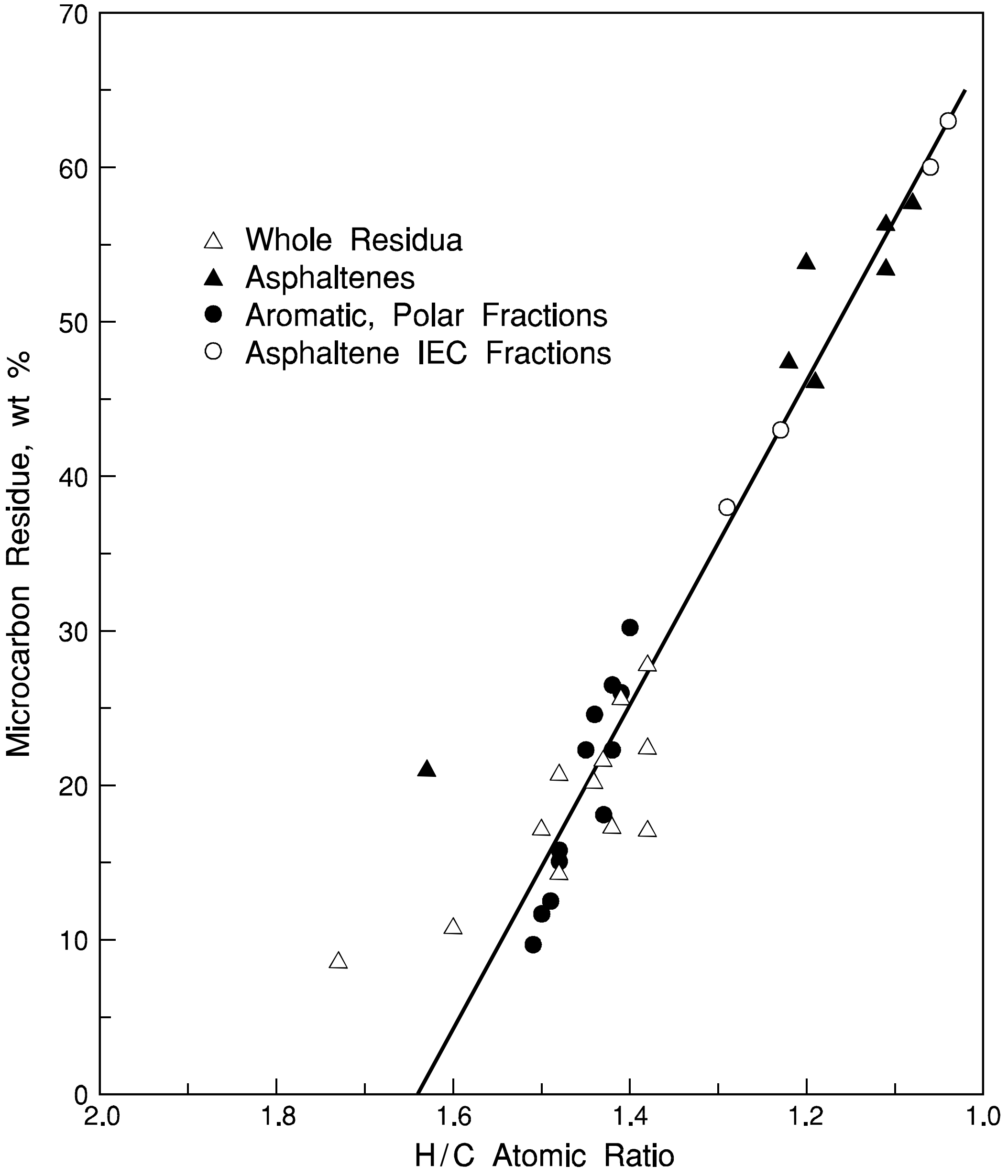

Figure 10. Carbon Residue vs. H/C Atomic Ratio Relationship

Reference: Schabron and Speight 1997

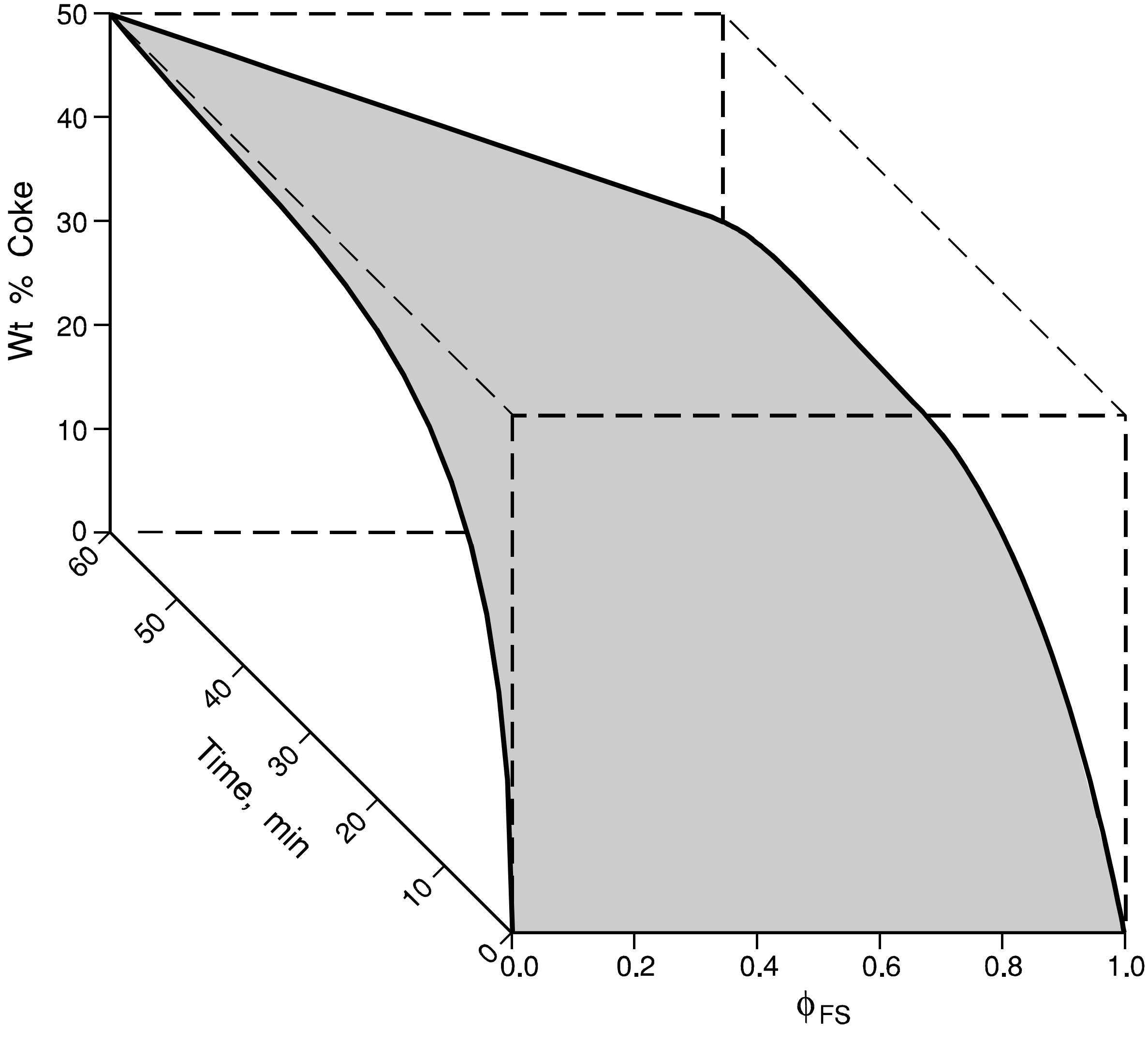

Figure 11. Three-Dimensional Coke Formation Predictability Map at 500 EC

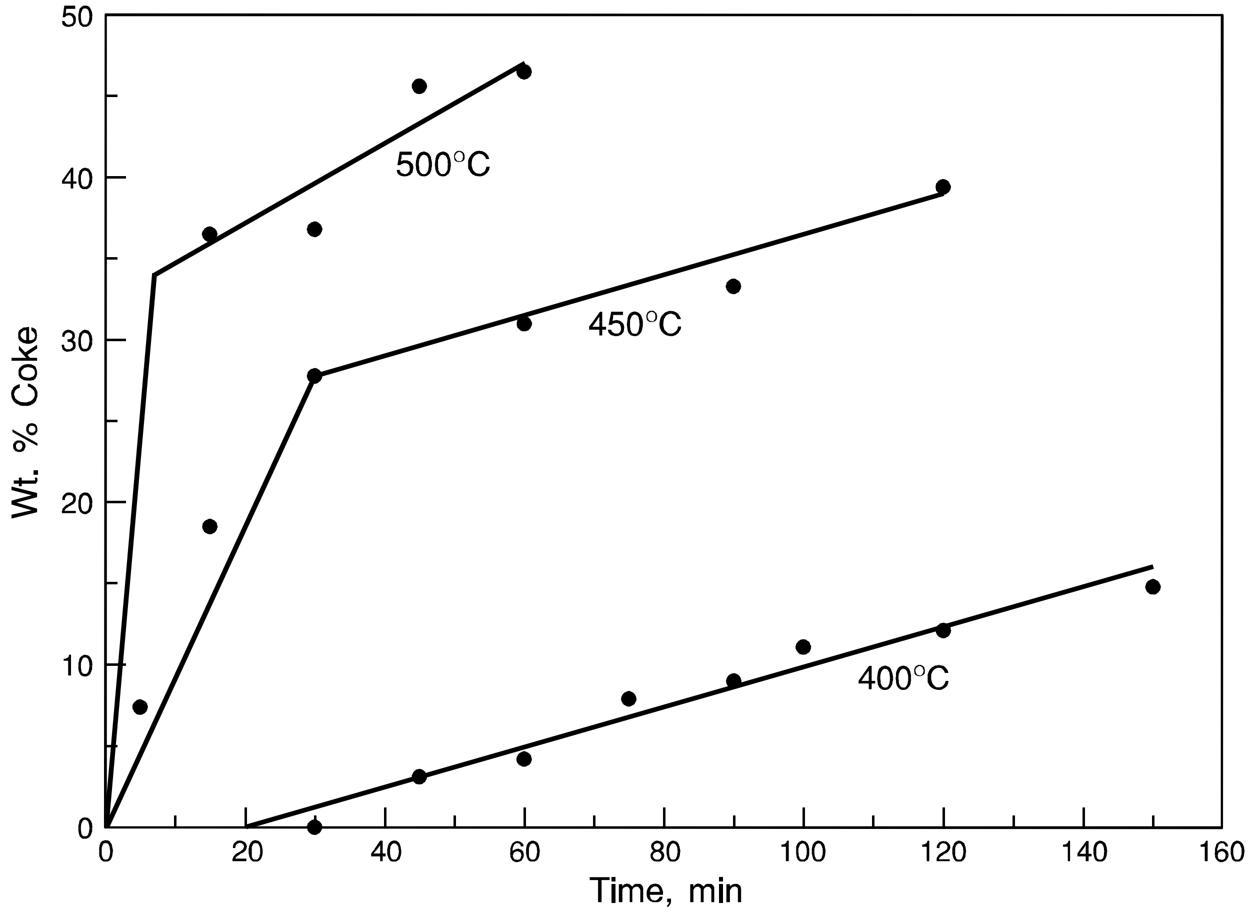

Figure 12. Coke Formation Lines for Boscan Residuum

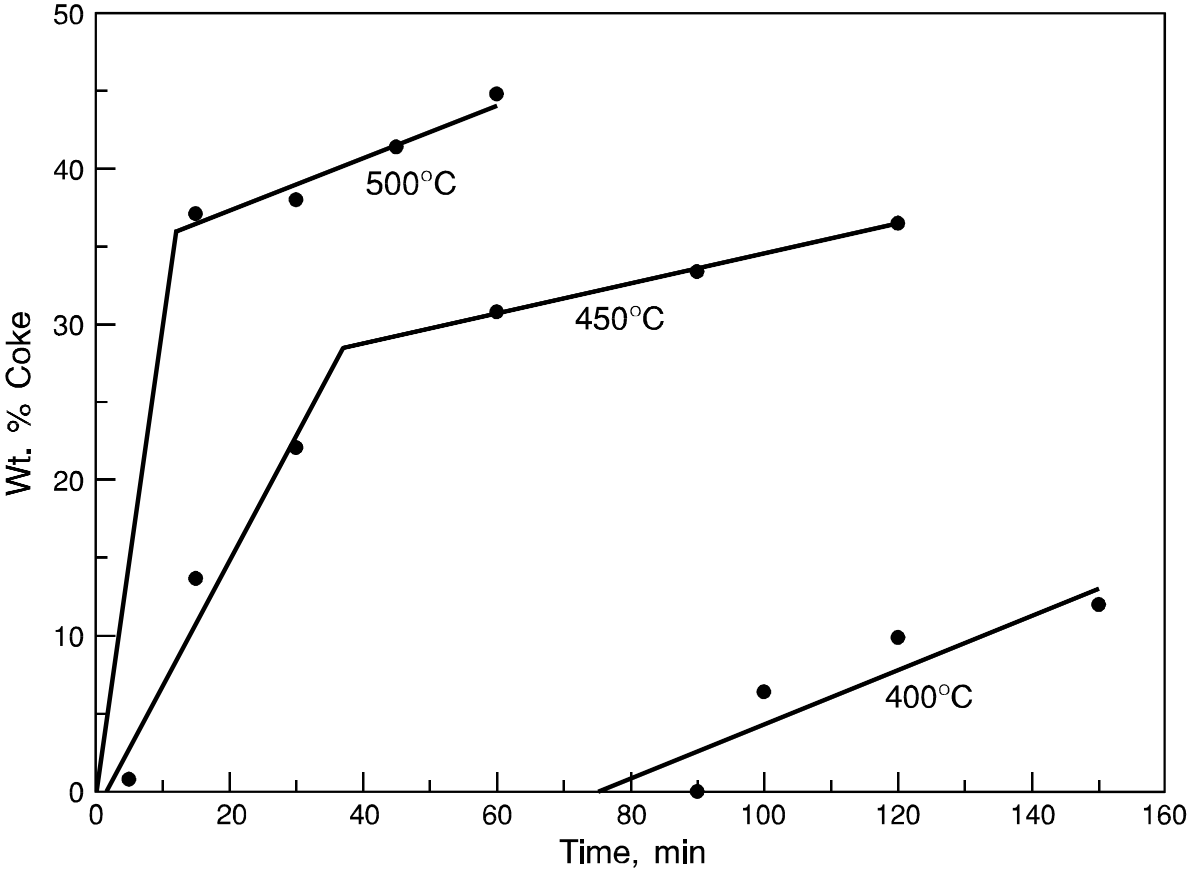

Figure 13. Coke Formation Lines for MaxCL Residuum

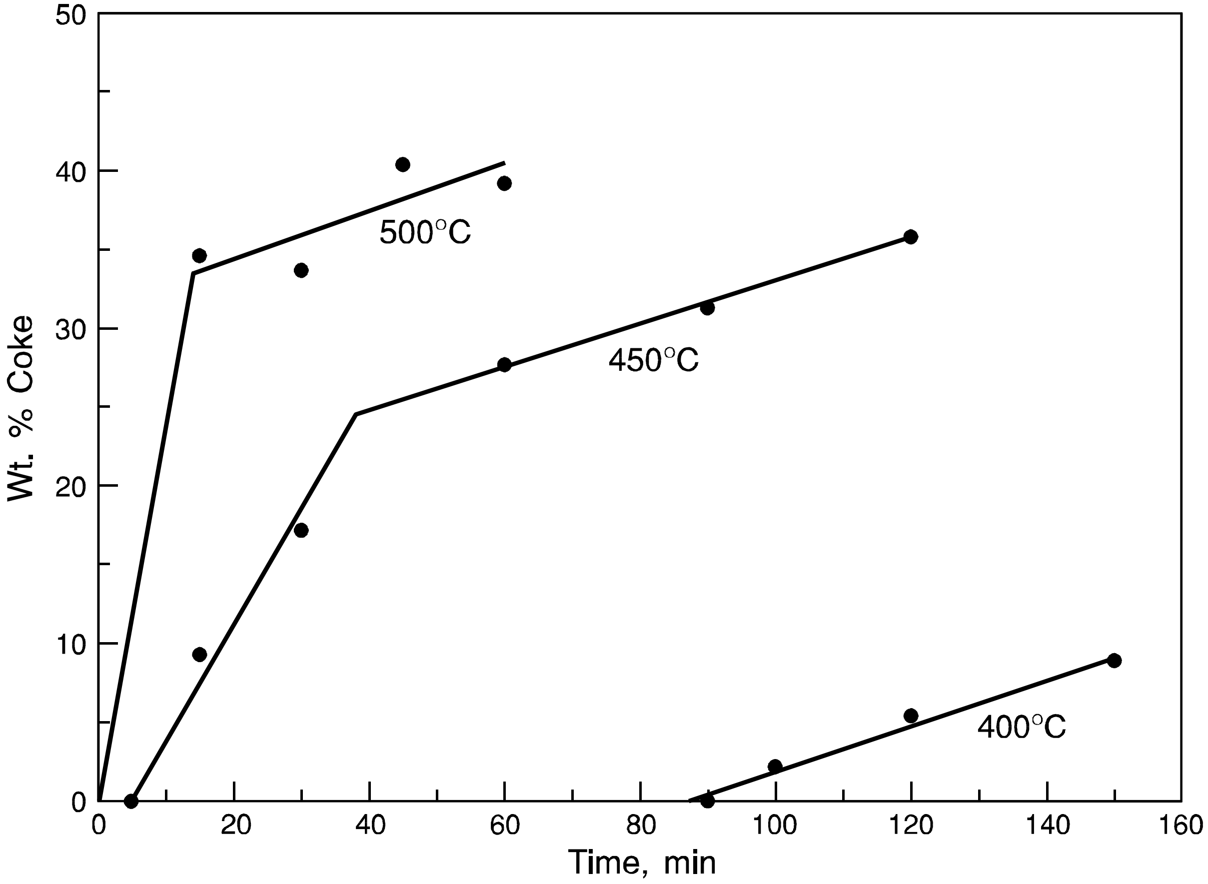

Figure 14. Coke Formation Lines for Lloydminster Residuum

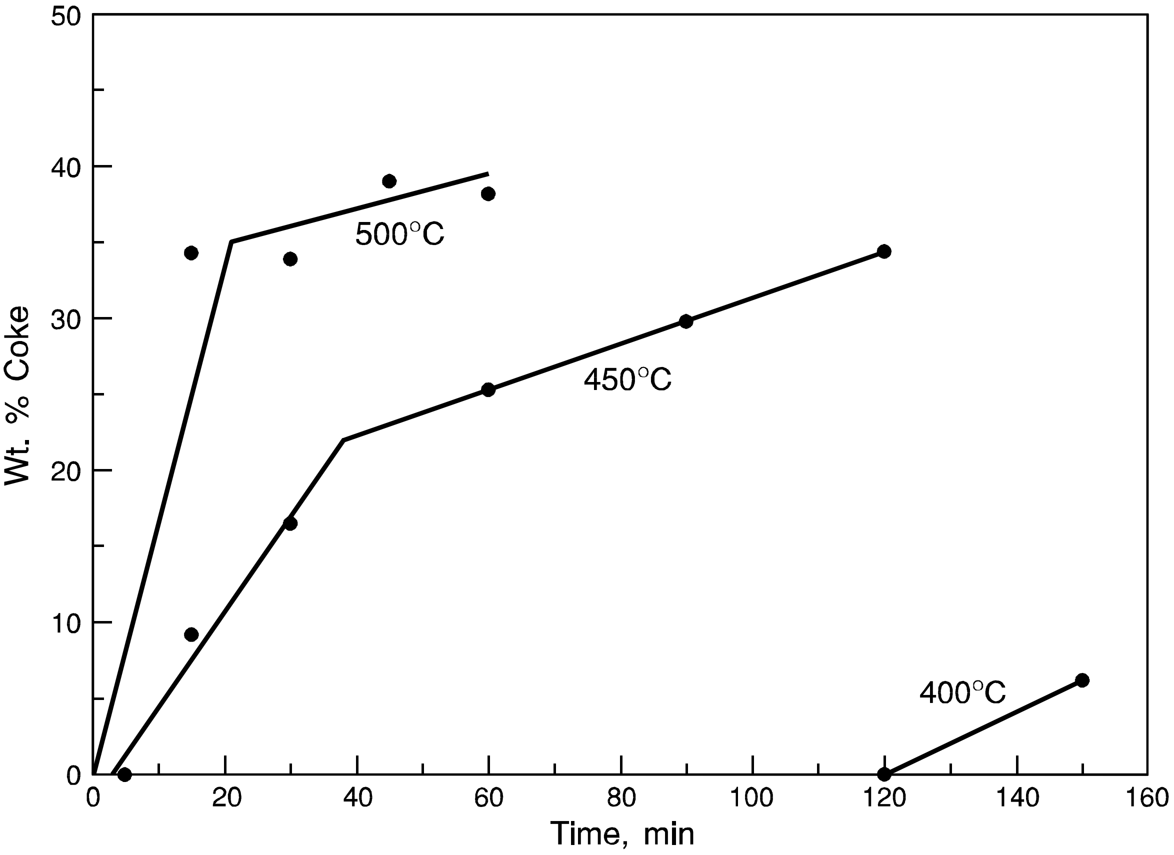

Figure 15. Coke Formation Lines for Redwater, B.C. Residuum

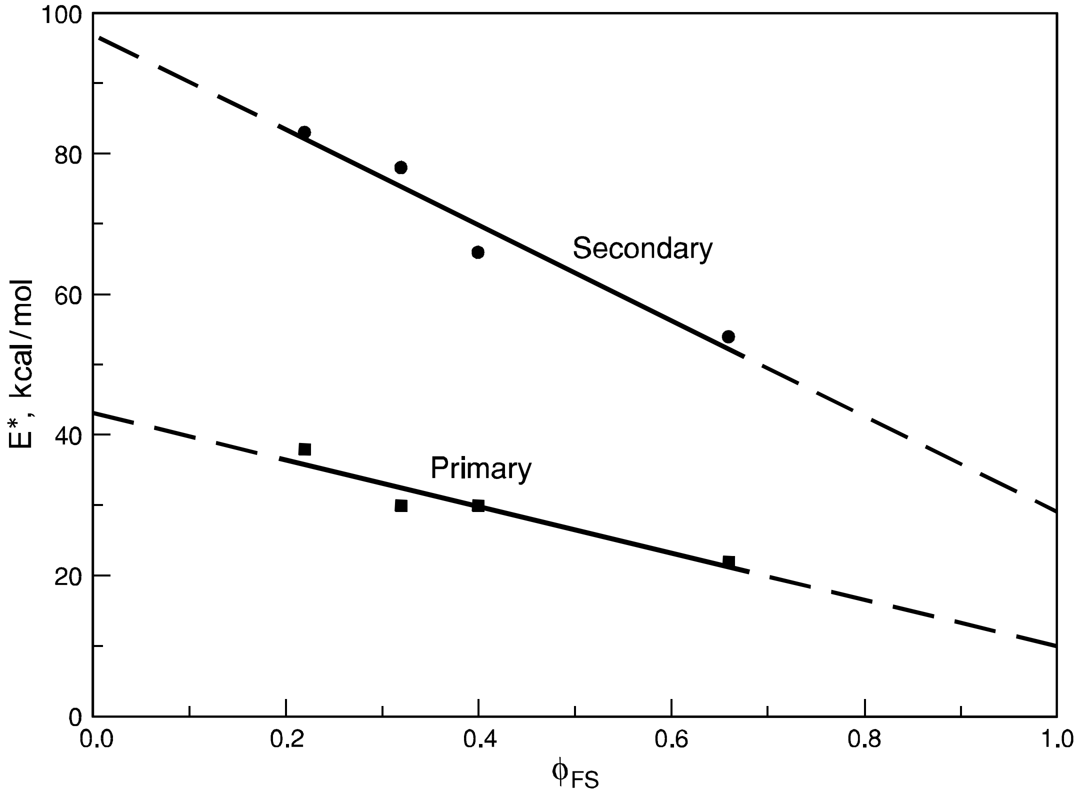

Figure 16. Activation Energy and Free Solvent Volume Correlation