

Predicting coke formation tendencies

John F. Schabron*, Adam T. Pauli, Joseph F. Rovani Jr., Francis P. Miknis

Western Research Institute, 365 North 9th Street, Laramie, WY 82072, USA

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Abstract

New coking indexes were developed to measure how near a pyrolysis system is to coke formation during the coke formation induction period. These are based on an asphaltene flocculation titration and the cyclohexane soluble portion of heptane asphaltenes. Coking indexes were determined for five residua before and after pyrolysis for 60 and 90 min at 400°C. The coking indexes appear to be universal for all the materials studied. The theoretical basis is based on the dispersed particle solution model of residua structure. Coking onset is coincidental with the destruction of the ordered structure and the formation of a bimodal system. Nuclear magnetic resonance (NMR) imaging showed the presence of two and three phase systems in the toluene soluble portions of residua pyrolyzed for 90 min. Results also show that initial coke formation can be related to the free solvent volume. A relationship was observed between free solvent volume and the amount of initial coke make at 400°C. The results provide a new tool for ranking residua, gauging proximity to coke formation, predicting initial coke make tendencies. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

1.1. New coking indexes

When a residuum is subjected to pyrolysis, there is typically an induction period before coke formation begins [1,2]. This can range from a few seconds to over an hour, depending on the residuum and the temperature. Heavy oils and petroleum residua consist of ordered systems of polar asphaltenes dispersed in a lower polarity solvent phase, held together by intermediate polarity materials usually referred to as resins. Refinery processes that convert heavy oils and residua to lighter distillate fuels require heating for distillation, hydrogen addition or carbon rejection (coking). The efficiency of conversion is limited by the formation of insoluble carbon-rich coke deposits [3,4]. Heat exchangers and other refinery units must be taken out of service for coke removal, resulting in a significant loss of output and revenue. In many cases, this heating is stopped sooner than need be, resulting in less than maximum product yield. Coking onset appears to coincide with the depletion of resin-type asphaltene solubilizing components in residua, resulting in a bimodal system [5]. This is consistent with observations of the formation of a neophase at the onset of coke formation [6,7]. Asphaltenes are complex associated species typically isolated as a solubility class obtained by

precipitation with a weak solvent such as heptane. There is a vast literature describing their chemical nature and properties [8]. The nature of asphaltenes changes irreversibly during pyrolysis [5].

A variety of measurements and indexes are in use to gauge stability, fouling, and coke formation tendencies. Common approaches involve precipitation of polar material from solutions of oils in aromatic solvents with the addition of low polarity solvents, or precipitation of polar material on the addition of a non-polar solvent directly to the oil [9,10]. These approaches utilize drops of the mixtures on filter paper or optical microscopic visualization to detect precipitation onset. Another approach involves taking the ratio of the amount of saturates plus asphaltenes to the amount of aromatics plus resins [11]. Precipitation of asphaltenes from solutions of Cold Lake residuum in pentane, xylenes, and naphtha have been studied in terms of the Gaestel stability index [12]. These approaches do not provide a universal gauge of how near a residuum is to forming coke on the coke induction time-line during pyrolysis. Two new coking indexes have been proposed recently for measuring the proximity to the coke formation onset in thermal treatment [5]. These are based on automated flocculation titration data and the solubility of asphaltenes. The first coking index is defined as the ratio of the Heithaus parameters, p_a/C_{\min} from an asphaltene flocculation titration [13]. A description of the automated titration procedure is provided in a companion paper on heat-induced deposition [14]. This is based on the observation that as pyrolysis progresses, p_a decreases as the

* Corresponding author. Tel.: +1-307-721-2445; fax: +1-307-721-2345.
E-mail address: jfschabr@uwyo.edu (J.F. Schabron).

polarity of the asphaltenes increases, and C_{\min} increases as the overall stability of the residuum matrix decreases. The second coking index is based on the amount of heptane asphaltenes that are soluble in cyclohexane, which is diagnostic of the state of the solubilizing resins in these materials [5]. The disappearance of the cyclohexane soluble portion of heptane asphaltenes is coincidental with the formation of a bimodal system and the onset of coke formation. The ratio of weight percent of cyclohexane soluble materials in heptane asphaltenes (Y) to weight percent of heptane asphaltenes (X), or Y/X gives a coking index value comparable in magnitude to the p_a/C_{\min} ratio. Ratios above 1 indicate relatively stable systems. As pyrolysis progresses, the ratios decrease. As they approach zero, coking begins. In the current work, the coking indexes were measured for unpyrolyzed residua, and toluene soluble products from pyrolysis at 400°C for 60 and 90 min.

1.2. Solvation shell considerations

As part of the Strategic Highway Research Program (SHRP), the dispersed particle solution model of residua was studied extensively [15,16]. Residua are considered to be suspensions of polar asphaltene materials dispersed in a solvent phase [17]. Pal and Rhodes developed a model for emulsions which has been applied to petroleum residua [18]. The model features resins and solvent layers around an asphaltene core, and solvated cores interacting with each other in an ordered system. Additional solvent is trapped between the asphaltene structures. A solvation shell magnitude term K ($K = K_S \cdot K_F$), includes terms representing the ratio of the volume of solvent adsorbed around a core particle plus the core particle volume to the core particle volume (K_S) and the ratio of the volume of solvent trapped in a group of solvated particles plus the solvated particle volume to the solvated particle volume (K_F). For petroleum residua, typical values of K range from [3–6]. When a residuum is heated, the value for K decreases with increasing temperature and there is less and less trapped solvent associated with the asphaltene structures, resulting in a flocculation of the polar asphaltenic core material [19,20]. Below pyrolysis temperatures (340°C), this appears to be reversible on cooling. Pauli and Branthaver [16] have demonstrated that the fraction of solvent bound in the ordered structure, α , is numerically equivalent to the Heithaus parameter, p_a . Thus, an asphaltene flocculation titration can be used to estimate K_F . K_S can be estimated from solubility data such as the differences between the amounts of heptane and iso-octane asphaltenes [21]. The fraction of solvent around a solvated asphaltene core also can be estimated by measuring the weight fraction of heptane asphaltenes that are soluble in cyclohexane. Therefore, values of K_S and K_F can be estimated using the equations below.

$$K_S = \frac{1}{1 - \chi_{cy}} \quad K_F = \frac{1}{1 - p_a}$$

In these equations, χ_{cy} is the weight fraction of heptane asphaltenes soluble in cyclohexane (volume fraction assuming a resin density of 1), and p_a is the Heithaus parameter. Results from the determination of K_S using more than one approach for a wide selection of materials show that for unpyrolyzed residua the typical value of K_S is 1.6 [21].

1.3. NMR imaging

Nuclear magnetic resonance (NMR) imaging is a powerful, relatively new technique that can be used for non-invasive chemical and physical characterization of local regions in the interior of intact samples [22,23]. In addition, NMR imaging is able to characterize chemical and physical processes non-invasively over time. Because of these abilities and the fact that petroleum residua are usually optically opaque, this technique has the potential to provide information about these systems not obtainable by other methods. The work reported here includes an exploratory application of NMR imaging to study phase separation in pyrolyzed residua. The application of NMR imaging to study phase separation in solvent precipitation of asphaltenes from asphalts has been reported previously [24].

2. Experimental

Five residua materials were evaluated. These included Redwater, B.C., California Coastal, and Boscan from prior non-proprietary work at WRI. The other two were MaxCL and Vistar provided by Conoco.

Automated asphaltene flocculation titrations were performed in toluene solutions using iso-octane as titrant. The procedures used are described in detail elsewhere [25]. Titrations were performed with concentrations ranging from about 5 to 20 wt% solutions in toluene. Test solutions were titrated with 2,2,4-trimethylpentane (iso-octane) at $25.0 \pm 0.1^\circ\text{C}$ using an average titrant flow-delivery rate of 0.35 ml/min. Flocculation ratio (FR) vs. dilution concentration (C g/ml) plots were made and Heithaus parameters were calculated using linear regression [9].

Bulk pyrolysis experiments were performed in a batch reactor system consisting of a stirred reactor constructed from a 24.1-cm (9.5-in.) length of 10.2-cm (4-in.) diameter schedule 40 pipe. The bottom of the reactor was sealed with a 0.6-cm (0.25-in.) thick steel plate fitted inside the pipe and welded in place. The reactor top was threaded to receive a mating pipe cap. The cap was fitted with ports for a thermocouple, nitrogen purge, and a vapor recovery line. A packing gland was located in the center of the cap to accommodate a stirring shaft. The insulated reactor was heated with two Chromalox type HBT heaters rated at 650 J/s each. The heaters were wired in series and controlled by Orion model E5CSX temperature controllers. Two controllers were employed in series to control the heaters. One controller was used to control the temperature of the heaters and was set to control below the maximum reaction temperature of

538°C. The second controlled the temperature of the reaction media, and was set at the temperature designated for that experiment. Distillate product was removed from the reactor through the vapor port in the cap, condensed in a water cooled condenser, and collected. The reactor was charged with about 120 g of residua and was heated to the desired set point temperature (400°C) for the duration of the experiment. The heat rate must be controlled carefully to provide repeatable temperature profiles. At the end of the experiment, the reactor was allowed to cool and the contents of the reactor were rinsed with toluene. Toluene insolubles (coke) were recovered by filtration. The solvent was removed and a material balance was calculated. For evaluation of the product oils, the distillate material was recombined with the residual material following coke removal.

The more precise pyrolysis experiments to obtain initial coke make values were performed with 5 g samples weighed into 0.5 × 6 in.² stainless steel reactor tubes heated in a fluidized sand bath. The tube was capped and atmospheric air was evacuated using a vacuum pump, then it was pressurized to 100 psig with nitrogen and leak checked in water. The tube was evacuated again and pressurized with 10 psig of nitrogen for the pyrolysis experiment and was then placed into a 400°C fluidized sand bath. The time to achieve 400°C was 3 min. After the tube was in the sand bath for 93 min, it was removed and cooled by immersing it in another fluidized sand bath at room temperature. The reaction products were collected in toluene and filtered using 10 micrometer PTFE filters to obtain toluene insolubles (coke).

NMR imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz using a Chemagnetics/Otsuka electronics microimaging probe. Samples for the imaging experiments were placed in 23 mm (OD) glass vials, which were then placed in 25 mm (OD) glass tubes. The tubes were inserted into the NMR probe and were positioned in the probe using O-rings such that the cross sections

to be imaged were contained in the experimental field of view (FOV). Images were acquired in the XZ plane which gave longitudinal images of the material in the sample vial. Any phase separation that might be present in the sample would be easily observable in this configuration. NMR images of the pyrolyzed vacuum residua were obtained using the spin echo method. Images were acquired using a pulse delay of 1 s, a free induction decay size of 256 data points, 128 phase encodes, and a gradient strength of 34 G/cm. The echo time was 30 ms. The number of image slices, their thickness and spacing are generally variable in an imaging experiment. In this study, eight slices, 1 mm thick and separated by 1 mm were obtained for each image set. Typically, eight acquisitions were obtained for each slice. The time required to obtain a set of images using these parameters was about 27 min.

3. Results and discussion

3.1. Pyrolysis experiments

The mass balances from the pyrolysis experiments at both 60 and 90 min are provided in Table 1. Pyrolysis data for the MaxCL are not available due to problems with the reactor run and the limited amount of sample available. The weight percent toluene insolubles (coke) formed is provided also. Two liquid phase systems were evident for the 90 min pyrolysis products following coke removal. The recombined toluene soluble and distillate products from MaxCL, Redwater, B.C., and CA Coastal from the 90 min pyrolysis experiments showed a light solvent upper and tar like lower phases, when these materials were refrigerated. When heated to 50°C, uniform mixtures were obtained. The recombined product from the Redwater, B.C. residuum was semi-solid when refrigerated, and did not separate into two layers. For the 60 min pyrolysis experiments, the recombined product oils mixed more readily.

Table 1
Material balances for bulk reactor pyrolysis at 400°C

Residuum	Distillate	Weight percent		Total
		Toluene solubles	Toluene insolubles (Coke)	
<i>Redwater, B.C.</i>				
60 min	17.3	81.8	0.2	99.3
90 min	33.7	63.3	2.9	99.9
<i>CA coastal</i>				
60 min	46.4	47.8	4.4	98.6
90 min	47.8	42.0	7.9	97.7
<i>Boscan</i>				
60 min	40.9	49.1	7.5	97.5
90 min	44.7	44.1	11.2	100.0
<i>MaxCL</i>				
90 min	33.2	56.5	7.0	96.7
<i>Vistar</i>				
60 min	18.0	81.6	0.2	99.8
90 min	40.0	52.9	6.2	99.1

Table 2
Heithaus titration results and p_a/C_{\min} coking indexes

Material	p_a	p_o	P	C_{\min}	WRI coking index p_a/C_{\min}
<i>Redwater, B.C.</i>					
Original	0.698	0.749	2.48	0.676	1.0
Pyrolyzed 60 min	0.422	0.753	1.30	3.19	0.13
Pyrolyzed 90 min	0.162	0.878	1.05	21.1	0.0076
<i>CA coastal</i>					
Original	0.614	1.12	2.89	0.529	1.2
<i>Boscan</i>					
Original	0.691	0.992	3.21	0.452	1.5
Pyrolyzed 60 min	0.245	0.905	1.20	5.00	0.049
Pyrolyzed 90 min	0.285	0.717	1.00	434	0.00
<i>MaxCL</i>					
Original	0.682	0.758	2.38	0.725	0.94
Pyrolyzed 90 min	0.152	0.973	1.15	6.80	0.022
<i>Vistar</i>					
Original	0.616	0.916	2.38	0.722	0.85
Pyrolyzed 60 min	0.373	0.831	1.32	3.08	0.12

3.2. Coking indexes

The results of the asphaltene flocculation titrations for the original five residua and the toluene soluble pyrolysis products from 60 and 90 min experiments at 400°C are provided in Table 2. Titrations could not be performed on the 60 or 90 min pyrolyzed CA Coastal material and the 90 min pyrolyzed Vistar material since these exhibited two-phase behavior and began precipitating asphaltenes at the beginning of the experiments. The P values (Table 2) suggest that of the original residua, the Boscan material is the most compatible, and the MaxCL is the least compatible. Values for p_a decrease modestly while concurrent values for C_{\min} increase dramatically. The amount of coke formed at

both 60 and 90 min pyrolysis times was evaluated in terms of the WRI coking indexes and the free solvent volume fraction. All of the recombined pyrolysis product oils were carefully homogenized prior to weighing for determination of the coking indexes. The coking indexes from Heithaus titrations are provided in Table 2 and a plot of weight percent coke vs. the p_a/C_{\min} coking index is provided in Fig. 1. The p_a value alone could possibly be used as a coking index also, with a threshold value of about 0.4, however by dividing this value by C_{\min} the effect is amplified significantly.

The heptane asphaltenes content of the five original residua and the toluene soluble pyrolysis products are provided in Table 3. For the unpyrolyzed residua, the Redwater, B.C.

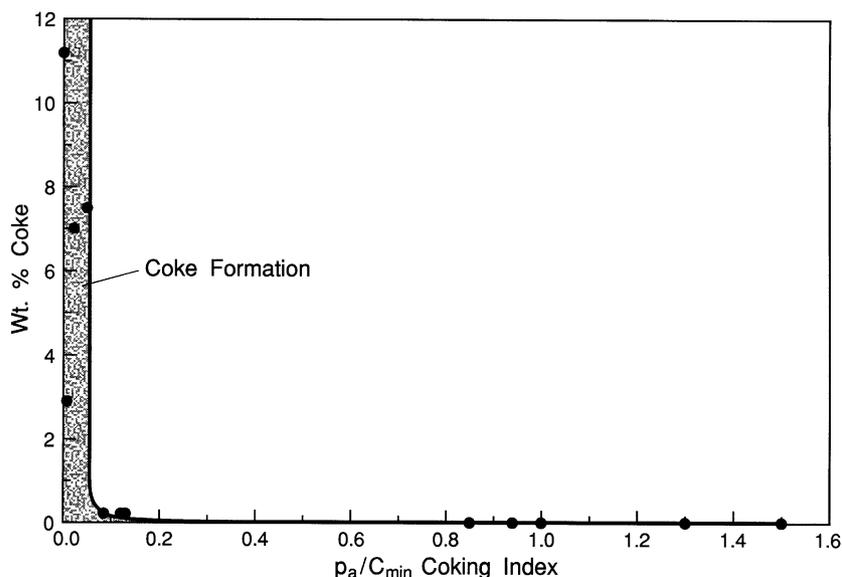


Fig. 1. Weight percent coke vs. p_a/C_{\min} coking index.

Table 3
Heptane asphaltenes and asphaltenes soluble in cyclohexane

Residuum	Weight percent		WRI coking index, Y/X	Wt% Toluene insolubles (Coke)
	X: Heptane asphaltenes ^a	Y: Asphaltenes soluble in cyclohexane		
<i>Redwater, B.C.</i>				
Original	11.7	41.4	3.5	< 0.01
Pyrolyzed				
60 min	15.9	14.7	0.92	0.2
90 min	17.1	6.0	0.35	2.9
<i>CA Coastal</i>				
Original	19.7	23.1	1.2	< 0.01
Pyrolyzed				
60 min	13.9	4.5	0.32	4.4
90 min	11.6	5.7	0.49	7.9
<i>Boscan</i>				
Original	19.8	40.6	2.1	< 0.01
Pyrolyzed				
60 min	15.6	5.3	0.34	7.5
90 min	12.5	2.6	0.21	11.2
<i>MaxCL</i>				
Original	18.1	45.8	2.5	< 0.01
Pyrolyzed				
90 min	19.8	3.6	0.18	7.0
<i>Vistar</i>				
Original	18.0	36.8	2.0	< 0.01
Pyrolyzed				
60 min	18.2	13.2	0.73	0.2
90 min	9.5	3.8	0.40	6.2

^a Weight percent of toluene soluble material.

material has the least amount of asphaltenes, 11.7 wt%, while the other four residua have similar asphaltene contents, ranging from 18.0 to 19.8 wt%. A ratio of the weight percent of cyclohexane soluble asphaltenes (Y) to

the weight percent of heptane asphaltenes (X) defines another coking index. The Y/X coking index values are listed in Table 3 and a plot of the Y/X coking index is provided in Fig. 2. The plots dramatically illustrate the

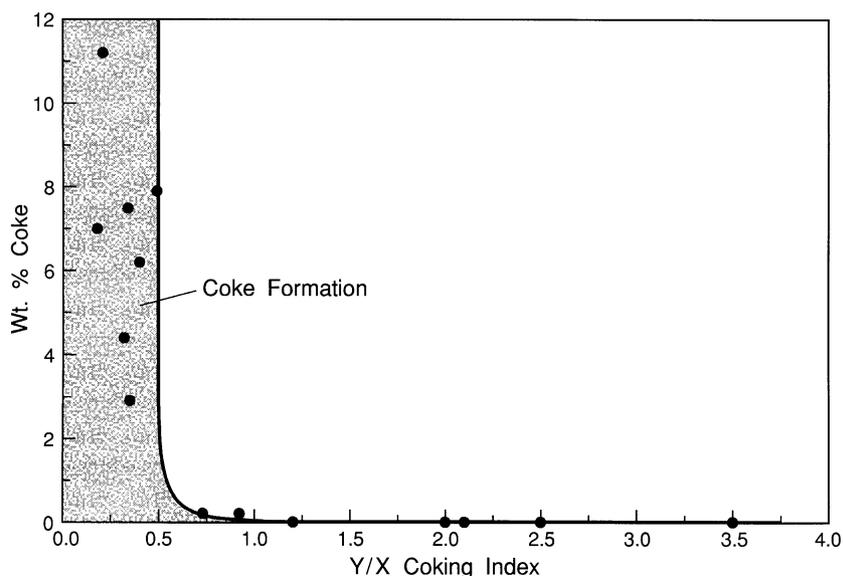


Fig. 2. Weight percent coke vs. Y/X coking index.

Table 4
Estimated K_S , K_F , and K values for the original and pyrolyzed residua

Residuum	$K_S = 1/(1 - \chi_{cy})$	$K_F = 1 - (1 - p_a)$	$K = K_S \cdot K_F$	Toluene insolubles (Coke), Wt% ^a
<i>Redwater, B.C.</i>				
Original	1.7	3.3	5.6	< 0.01
Pyrolyzed				
60 min	1.2	1.7	2.0	0.2
90 min	1.1	1.2	1.3	2.9
<i>CA Coastal</i>				
Original	1.3	2.6	3.4	< 0.01
Pyrolyzed				
60 min	1.0	– ^b	–	4.4
90 min	1.1	– ^b	–	7.9
<i>Boscan</i>				
Original	1.7	2.1	5.4	< 0.01
Pyrolyzed				
60 min	1.1	1.3	1.4	7.5
90 min	1.0	1.4	1.4	11.2
<i>MaxCL</i>				
Original	1.8	3.1	5.6	< 0.01
Pyrolyzed				
90 min	1.0	1.2	1.2	7.0
<i>Vistar</i>				
Original	1.6	2.6	4.2	< 0.01
Pyrolyzed				
60 min	1.2	1.6	1.9	0.2
90 min	1.0	– ^b	–	6.2

^a Weight percent of toluene soluble material.

^b Heithaus titration not possible due to multi phase product.

diagnostic potential of the coking indexes in measuring how close a residuum is to coke formation on the coke formation induction line. By evaluating a thermal process such as vacuum distillation using the coking

indexes, the possibility of optimizing distillate yield with confidence while avoiding undesired coking is evident. For example, vacuum distillation could be performed to a predetermined coking index threshold value

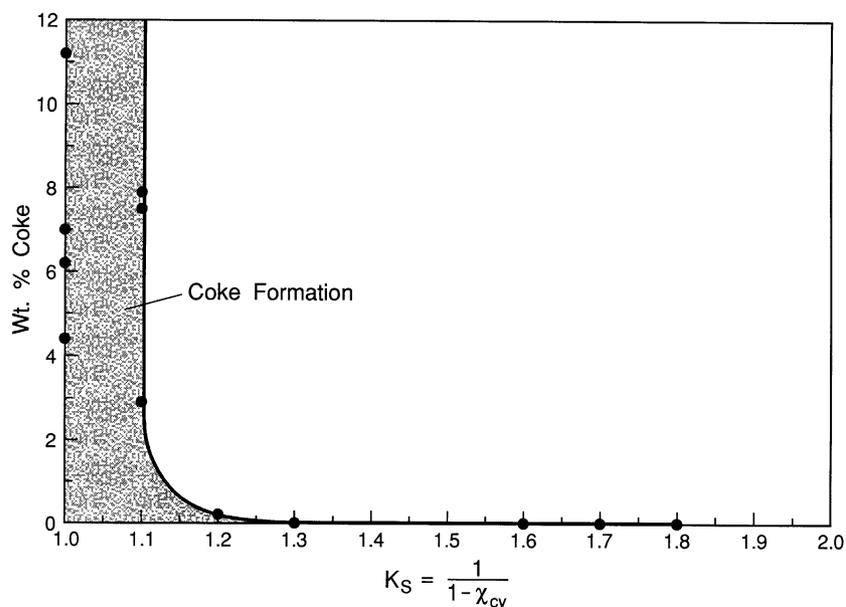


Fig. 3. Weight percent coke vs. estimated K_S values.

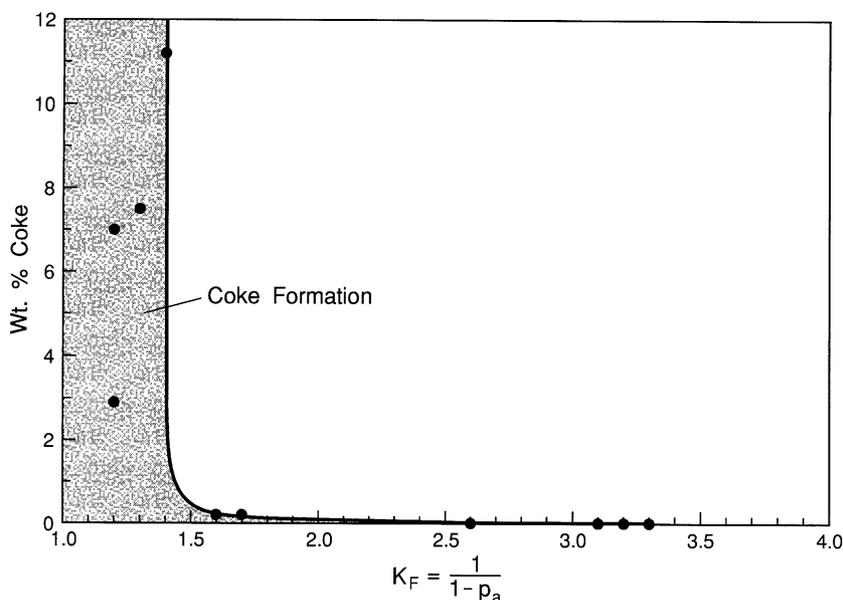


Fig. 4. Weight percent coke vs. estimated K_F values.

in a refinery before the bottoms are sent to a delayed coker unit.

Table 4 lists the estimated values of K_S , K_F , and K and weight percent coke for the five residua. The data are plotted in Figs. 3–5, respectively. It is apparent that as pyrolysis progresses, the values decrease and coke forms at estimated values of K_S below 1.2, K_F values below 1.5, and K values below 1.8. Thus, the coking indexes provide a means of observing the destruction of the ordered structure and the formation of an unstable bimodal system. To estimate K_S , simple solubility measurements are required. To estimate K_F , only the p_a value is required. Alternative physical or chemical methods may be developed in the future for

observing these fundamental properties of the ordered system and the destruction of the colloidal-like structure during pyrolysis, leading to coke formation. Some of these may be amenable to real-time on line analysis for process control to optimize distillate yields while minimizing the risks of unwanted coke formation. This will be explored in future work. It is important to note that the coking indexes do not predict how much coke will be formed, but only when the formation is likely to begin.

3.3. Free solvent volume correlations

A possible predictive tool is the free solvent volume of

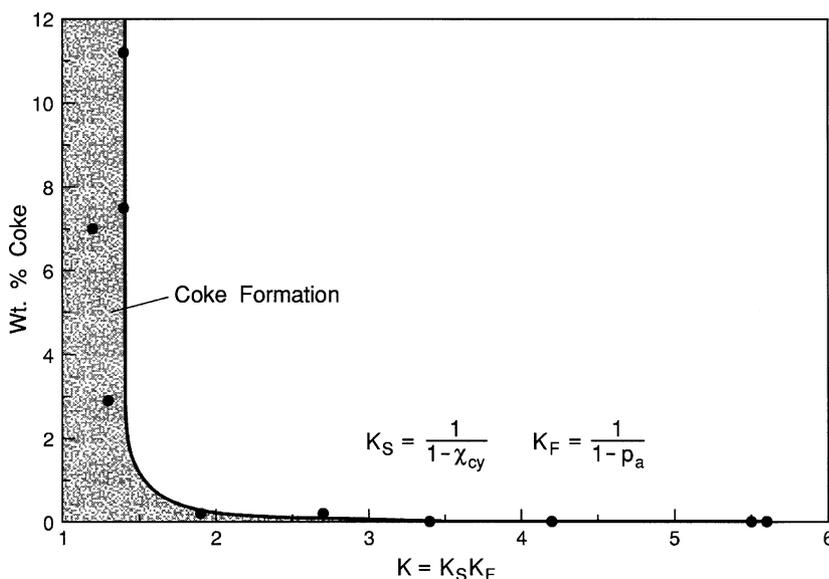


Fig. 5. Weight percent coke vs. estimated K values.

Table 5
Free solvent volumes at 25°C

Residuum	$\chi_a/1.2$	p_a	ϕ_{FS}^a
Redwater, B.C.	0.097	0.698	0.49
CA Coastal	0.164	0.614	0.32
Boscan	0.165	0.691	0.14
MaxCL	0.151	0.682	0.24
Vistar	0.150	0.616	0.38

^a $K_S = 1.6$.

the original residuum. This can be related to the amount of deposition below pyrolysis temperatures and the amount of coke make in the early stages of a pyrolytic process. The free solvent volume ϕ_{FS} can be calculated as

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

where $K_S = 1.6$ and $K_F = (1/(1 - p_a))$, and χ_a is the weight percent heptane asphaltenes divided by an assumed uniform density of 1.2 g/mol. The data used for the ϕ_{FS} calculations and the ϕ_{FS} values for the five original residua are provided in Table 5. Prior work has shown that the average K_S value for unpyrolyzed residua and asphalt colloidal type systems is 1.6 [21]. For the residua in the

Table 6
Initial coke make in tube reactor for 90 min at 400 °C

Residuum	Toluene insolubles (Coke), Wt%
Redwater, B.C.	1.3
CA Coastal	7.2
Boscan	10.6
MaxCL	8.4
Vistar	4.3

current study, a correlation of initial coke make with ϕ_{FS} can best be made if K_S is held constant. The correlation does not work well if estimated values of K_S based on the cyclohexane soluble portion of heptane asphaltenes are used. Thus, the only measurements required for calculation of ϕ_{FS} are the weight percent heptane asphaltenes and the Heithaus p_a value.

A plot of coke formation at 400°C vs. ϕ_{FS} for both 60 and 90 min is provided in Fig. 6. These results also show a distinct correlation, however the reactor used is difficult to control exactly. When the same residua are pyrolyzed in the small volume 5-g reactor tubes at 400°C for 90 min using the more precise fluidized sand bath reactor, a more exact relationship is defined (Table 6, Fig. 7). Plots of

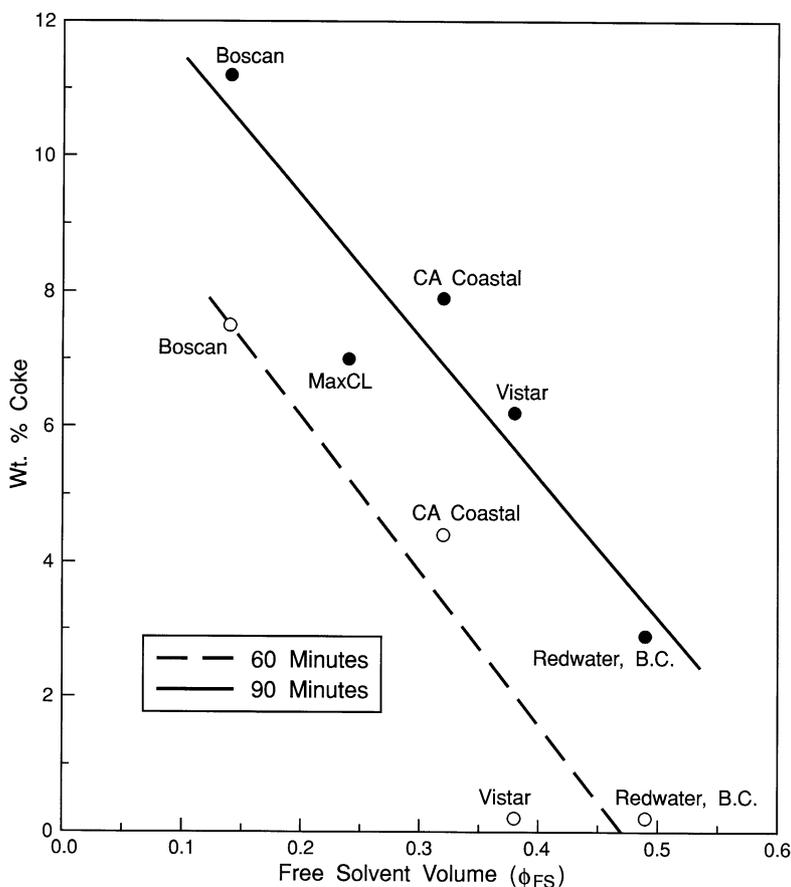


Fig. 6. Weight percent coke formed at 60 and 90 min in bulk reactor at 400°C vs. free solvent volume of unpyrolyzed residuum.

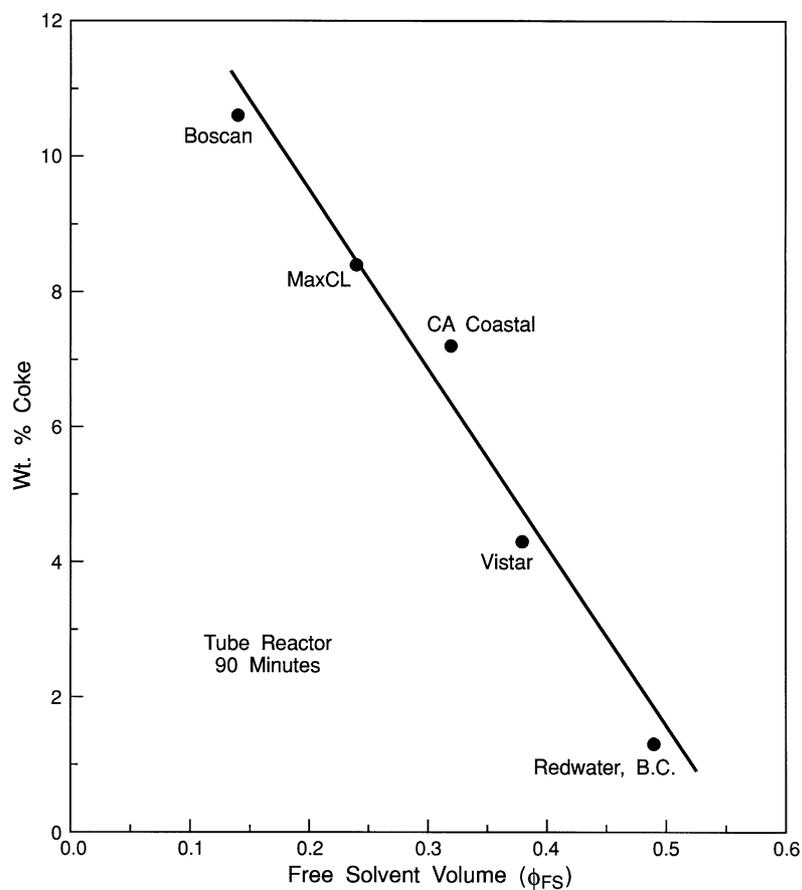


Fig. 7. Weight percent coke formed at 90 min in 5 g sand bath reactor tubes at 400°C vs. free solvent volume of unpyrolyzed residuum.

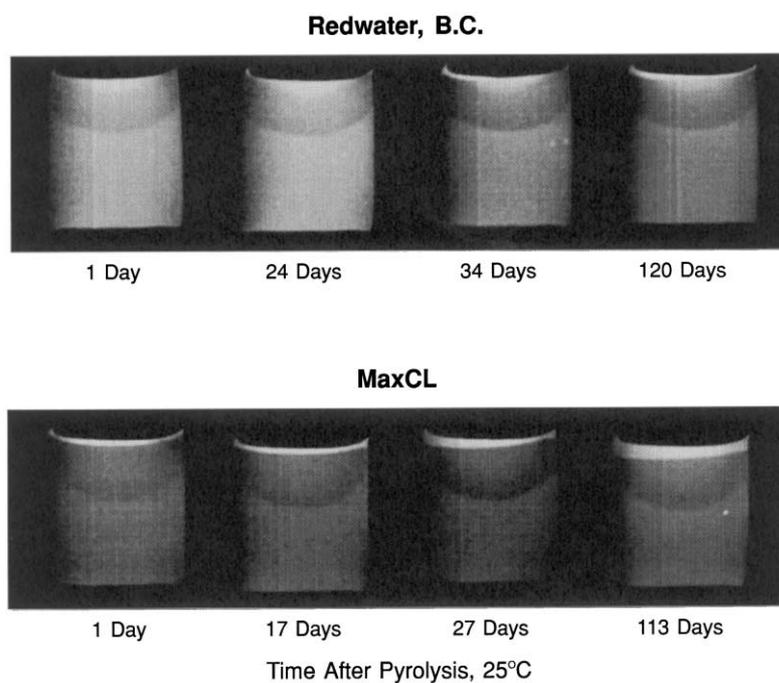


Fig. 8. NMR images of non-pourable pyrolysis product oils.

initial coke make vs. ϕ_{FS} could be generated for a variety of residua at a particular pyrolysis temperature for different pyrolysis times to rank them in terms of relative initial coke make potential. This could be related to the rate of coke formation, which can affect the nature of the coke formed. Such plots or predictive maps will be generated in future work. Modifications or refinements to the free solvent volume correlation may be made as more data with additional residua are generated. The free solvent volume correlation appears to relate to the amount of coke initially formed, but it does not predict the final amount of coke produced, which is determined by the atomic H/C ratio [26].

3.4. NMR imaging

A concern regarding the feasibility of using NMR imaging to study pyrolyzed residua was that the NMR relaxation time (T_2) of the residuum would be so short that images could not be obtained. In prior work with paving asphalts, it was not possible to acquire images at room temperature on asphalts for this very reason [22]. Generally,

NMR relaxation times are related to the mobility (viscosity) of the protons in the sample; the greater the viscosity, the shorter the T_2 . In order to image a petroleum residuum, some means must be employed to decrease the sample viscosity and increase the mobility of the protons. Previous work had shown that with increased pyrolysis times, the sample viscosity decreased. Consequently, it was possible to obtain images on these types of samples. In the case of coking, the viscosity of the pyrolyzed residua decreased significantly because of cracking and hydrogen incorporation in the distillate product as a result of carbon rejection due to coking. NMR imaging experiments were conducted on the toluene soluble products from residua that were pyrolyzed at 400°C for 60 and 90 min. The purpose of the imaging measurements was to determine the feasibility of using NMR imaging as a means of determining the instability of vacuum residua caused by incipient coke formation. Images of the 60 min product oils were dark since these materials were relatively viscous. Images of the 90 min product oils showed structures indicative of more than one phase, and thus provided the best prospects for imaging.

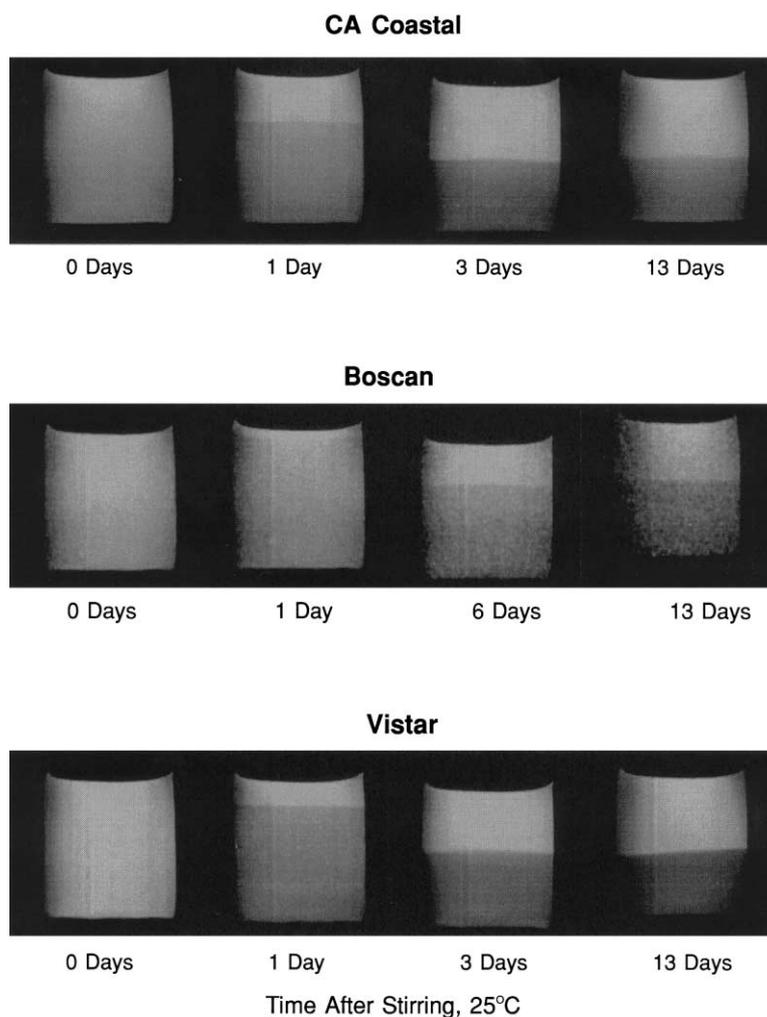


Fig. 9. NMR images of pourable pyrolysis product oils.

After pyrolysis for 90 min at 400°C in the bulk reactor, the coke (toluene insolubles) was removed and the distillate and product oil was recombined as described in the Experimental section. Three of the five pyrolyzed oils were pourable at room temperature (CA Coastal, Boscan, and Vistar), whereas two were not (Redwater, B.C., MaxCL). The non-pourable products were heated to about 80°C, stirred, and poured into the NMR imaging tubes, and cooled to room temperature prior to imaging. The pourable pyrolyzed residua were first stirred prior to imaging. Following the initial imaging, the samples were stored at room temperature and not stirred or agitated further between time intervals. The images were obtained at room temperature. In all cases, the samples were optically opaque so that none of the results obtained by NMR imaging could have been obtained visually.

Images of the non-pourable, pyrolyzed residua taken at different settling times after pyrolysis are shown in Fig. 8. Only the fourth slice of an 8 slice image set is shown. This is sufficient to illustrate the application of the technique. In both residua, there is evidence of three separate layers as evidenced by the different layers of contrast in the images. Areas of light contrast correspond to regions of the sample that have the lowest viscosity (greatest mobility), and areas of dark contrast correspond to regions of that have the highest viscosity. With increased settling time, the MaxCL and Redwater, B.C. samples showed increased creaming of the lighter materials at the top of the sample vial. The lower meniscus for the images in Fig. 8 are probably due to some surface area attraction between the sample material and the NMR imaging vial. NMR images of the pourable, pyrolyzed residua are shown in Fig. 9. The settling times in these images correspond to the settling times after the sample was first stirred before imaging. For these three materials, the residua separate into two major layers upon settling, with CA Coastal separating fastest and Boscan separating slowest of the three residua. The imaging results provide clear evidence of the presence of two and three phase systems in the toluene soluble product oils following pyrolysis. The chemical nature of the materials comprising the various layers were not characterized further since this was outside the scope of the current study.

4. Conclusions

Pyrolysis experiments were conducted with five residua at 400°C for 60 and 90 min residence times. The WRI coking indexes can be used to diagnose the nearness to coke formation during the coke formation induction period. The coking indexes indicate when coke formation will begin but they do not predict the amount of coke that will formed. The initial amount of coke formed with pyrolysis at a particular residence time correlates with the free solvent volume. When carried to completion, the amount of coke formed is related to the atomic H/C ratio. NMR images can be

acquired at room temperature on pyrolyzed residua in which sufficient cracking has occurred to cause increased mobility. In all five of the residua, the NMR images show separation into distinct layers upon standing after pyrolysis. The results suggest that NMR imaging can be used as an analytical technique to study the destruction of heavy oil colloidal systems during thermal treatment.

5. 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 agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute 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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