COKE FORMATION PROCESS MODEL FOR PETROLEUM REFINING EFFICIENCY IMPROVEMENT

Final Report

By
John F. Schabron
Francis P. Miknis
Daniel A. Netzel
A. Troy Pauli
Joseph F. Rovani, Jr.
Thomas F. Turner

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U.S. Department of Energy
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By
Western Research Institute
365 North 9th Street
Laramie, Wyoming 82072

Contact: John F. Schabron, Principal Scientist
phone: 307-721-2445 fax: 307-721-2345 jfschabr@uwyo.edu

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A. BRIEF SUMMARY OF THE ORIGINAL PROJECT GOALS

The current project was to determine the WRI Coking Indexes with a residuum material, which was pyrolyzed, and to explore potentially simpler analytical measurements that may correlate with the indexes such that real-time feedback and refinery process control is ultimately attained

B. VARIANCE FROM PROJECT GOALS

There was no variance from the project goals.

C. NARRATIVE DISCUSSION OF PROJECT RESULTS

EXECUTIVE SUMMARY

Refinery distillation efficiency is limited by the undesired coke deposition, resulting in a significant loss of revenue. When a residuum is heated to pyrolysis temperatures (>340 ?C, 650 ?F), there is typically an induction period before coke formation begins. To avoid fouling, refiners often stop heating well before coke forms, using arbitrary criteria. Often this heating is stopped sooner than it needs to be, resulting in less than maximum distillate yield. Western Research Institute (WRI) has developed innovative Coking Indexes that can be used for process control to heat residua to the threshold, but not beyond the point at which coke formation begins. These require either titration or solubility measurements. Alternative means of characterizing residua during pyrolysis are being explored. A Lloydminster vacuum residuum was pyrolyzed at 400?C (750 ?F) for 15, 30, 60, and 80 minutes. The 60 and 80 minute products contained coke. The WRI Coking Indexes were determined and the oils were analyzed by variety of analytical techniques including , near and mid infrared (IR) spectroscopy, absorbance and fluorescence spectroscopy, differential infrared functional group analyses, nuclear magnetic resonance (NMR) spectroscopy, atomic force microscopy (AFM), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). No significant differences which correlate with the WRI Coking Indexes were evident with the optical spectroscopy results. There were some differences noted in the differential infrared functional group data. Significant differences were evident with NMR relaxation times and AFM histograms. DSC and TGA results also showed significant differences between the original and pyrolyzed materials. These differences need to be explored further in future work using additional residua.

OBJECTIVES

The current project was to determine the WRI Coking Indexes with a residuum material, which was pyrolyzed, and to explore potentially simpler analytical measurements that may correlate with the indexes such that real-time feedback and refinery process control is ultimately attained. .

INTRODUCTION

Refinery processes that convert heavy oils to lighter distillate fuels require heating for distillation, hydrogen addition or carbon rejection (coking). Efficiency is limited by the formation of insoluble carbon-rich coke deposits. Heat exchangers and other refinery units must be shut down for mechanical coke removal, resulting in a significant loss of output and revenue. When a residuum is heated above the temperature at which pyrolysis occurs (340 ?C, 650 ?F), there is typically an induction period before coke formation begins (Magaril and Aksenova 1968, Wiehe 1993). To avoid fouling, refiners often stop heating a residuum before coke formation begins, using arbitrary criteria. In many cases, this heating is stopped sooner than need be, resulting in less than maximum product yield.

Western Research Institute (WRI) has developed innovative Coking Index concepts (patent pending) which can be used for process control by refiners to heat residua to the threshold, but not beyond the point at which coke formation begins when petroleum residua materials are heated at pyrolysis temperatures (Schabron et al. 2001). The development of this universal predictor solves a long standing problem in petroleum refining. These Coking Indexes have great potential value in improving the efficiency of distillation processes. The Coking Indexes were found to apply to residua in a universal manner, and the theoretical basis for the indexes has been established (Schabron et al. 2001a, 2001b, 2001c). For the first time, a few simple measurements indicates how close undesired coke formation is on the coke formation induction time line. The Coking Indexes can lead to new process controls that can improve refinery distillation efficiency by several percentage points. Petroleum residua consist of an ordered continuum of solvated polar materials usually referred to as asphaltenes dispersed in a lower polarity solvent phase held together by intermediate polarity materials usually referred to as resins. The Coking Indexes focus on the amount of these intermediate polarity species since coke formation begins when these are depleted. Currently the Coking Indexes are determined by either titration or solubility measurements which must be performed in a laboratory. In the current work, various spectral, microscopic, and thermal techniques possibly leading to on-line analysis were explored for measuring the Coking Indexes.

Benefits of Refinery Distillation Efficiency Improvement The WRI Coking Indexes can be used to minimize or eliminate downtime disruptions from fouling due to coking. With the Coking Indexes, coking propensity becomes predictable. The financial losses due to such unscheduled downtime events are difficult to quantify, but they are important. Another aspect is efficiency improvement during upgrading. In 1997 the average U.S. atmospheric and vacuum distillation refinery capacity was about 23 million barrels per day (USDOE 1998). Solvent deasphalting capacity was about 0.3 million barrels per day. About 1.8 million barrels per day of heavy end feedstocks produced in 1997 from atmospheric and vacuum distillation columns and solvent-deasphalting units were input to thermal cracking and coking operations. This represents about 10% of the crude run. An additional 6.5 million barrels per day went into catalytic cracking and hydrotreating units. Use of the patented Coking Indexes could improve the efficiency of atmospheric and vacuum distillation operations. Based on the total of 1.8 million barrels of total heavy ends minus about 0.3 million from solvent deasphalting, about 1.5 million barrels of heavy ends per day of thermal cracking and coking feed are produced from distillation operations. Assuming a conservative estimate of a 1% increase in U.S. distillate output due to efficiency improvements from the new Coking Indexes, an average increase of about 15,000 barrels per day of distillate and a corresponding reduction of heavy ends would result. Efficiency increases well above 1% are possible. Energy savings are significant since coking operations use about 166,000-258,000 Btu per barrel of feed. The differential price between distillate and residual oils is usually about $10 per barrel. Therefore, value added with each 1% efficiency improvement described above would be about $150,000 per day. Each 1% royalty applied to this incremental financial improvement would be $1,500 per day for total U.S. operations. Sales of on-line process control analyzers would include similar provisions. There is a significant energy savings involved, since coking operations use about 166,000-258,000 Btu per barrel of feed. Hydrotreater energy use is comparable, and a similar consideration applies. There would be only minimal extra heat required for a 1% improvement of distillate output at a particular temperature, since most of the energy is used initially to heat all of the feed material for distillation. For each 1% decrease in distillation residue coker feed of 15,000 barrels per day, there would be a potential savings of about 2.5-3.9 billion Btu in residua that do not need to be heated for coking, since they will have been recovered in an optimized distillate stream. An energy savings of about 2.5-3.9 billion Btu per day, as discussed above, results in a corresponding lowering of carbon dioxide from fuel that is not burned in coking operations. Residual fuel used as the heat source produces about 174 pounds of carbon dioxide per million Btu generated. Thus, in the U.S., the reduction in carbon dioxide emissions for each 1% industry-wide efficiency improvement is about 218-679 tons per day.

EXPERIMENTAL

Residuum The residuum material used was a Lloydminster vacuum residuum from non-proprietary work at Western Research Institute.

Heptane Asphaltenes Heptane asphaltenes were isolated by heating a 40:1 (v:w) mixture of reagent-grade –heptane and residuum to 70 ?C (158 ?F) for about ½ hour while stirring, followed by overnight stirring at room temperature. The stirring was stopped for 30 minutes prior to filtering. Vacuum filtration was performed using Ace, 140-mL, 10-20 micron, sintered glass filters. Residual solvent was removed from the asphaltenes on filters using a vacuum oven set at 120 ?C (248 ?F) for 30 minutes. The asphaltenes were cooled in a desiccator and weighed.

Cyclohexane Soluble Heptane Asphaltenes To determine the cyclohexane soluble portion of heptane asphaltenes, a portion of –heptane asphaltenes was ground to a fine powder using a mortar and pestle. A 0.5 g portion of this was stirred overnight with 100 mL of cyclohexane. The stirring was stopped 30 minutes prior to vacuum filtering 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 using a vacuum oven at 100 ?C (212 ?F) for 15 minutes. The cyclohexane solubles were cooled in a desiccator and weighed.

Asphaltene Flocculation Titration Automated asphaltene flocculation titrations were performed with a WRI Automated Flocculation Titrimeter using 5 - 20 wt.% toluene solutions of residua and isooctane as titrant at 25.0 ? 0.1?C using a titrant delivery rate of 0.35 mL/min (Pauli 1996). Flocculation ratio (FR) versus dilution concentration (C(g/mL)) plots were made and WRI Coking Indexes were calculated as described elsewhere (Schabron et al. 2001c).

Pyrolysis Experiments Pyrolysis experiments were performed with 80 g sample portions weighed into 12" long x1.4" o.d. stainless steel reactor tubes with a 120 cc volume capacity. The tube was capped and atmospheric air was evacuated using a vacuum pump. The tube 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 in a 400 ?C (750 ?F) fluidized sand bath. Two tubes containing residua and a third containing a thermocouple were run simultaneously in a tube rack. Timing was started when the thermocouple temperature equaled the set point temperature. The rack was removed and cooled by immersing it in another fluidized sand bath at room temperature. The reaction products were poured into glass vials and stored under nitrogen in a refrigerator prior to analysis. Small portions of the stirred reaction products were dissolved in toluene and filtered using 10 micron PTFE filters to obtain a gravimetric measurement of toluene insolubles (coke).

Optical Spectroscopy Near and mid-range infrared (IR) spectra were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer equipped with a Multiscope FTIR microscope. Spectra were obtained on neat samples pressed between KBr plates and 5 wt.% solutions in carbon disulfide. Absorption spectra were obtained from toluene solutions in 1-cm pathlength quartz cuvettes with a Shimadzu model UV-265 spectrophotometer. Fluorescence spectra were obtained with a Perkin-Elmer LS-50B luminescence spectrophotometer. Both the excitation and emission slits were set at their minimum aperture settings of 2.5 nm. A 1-cm square pathlength quartz fluorescence cell was used. Emission spectra were obtained from toluene solutions of residua using an excitation wavelength of 350 nm.

Differential Infrared Functional Group Analysis Determination of the different functional groups was performed by an IR method developed at Western Research Institute (WRI) (Petersen 1986). The functional groups are carboxylic acids and their salts, 2-quinolones, phenolics, pyrrolics, ketones, anhydrides, and sulfoxides. Data were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer.

Nuclear Magnetic Resonance Spectroscopy Nuclear magnetic resonance (NMR) images and solid state spectra were obtained with a Varian/Chemagnetics CMX-100/200 solids NMR spectrometer equipped with two superconducting magnets. One magnet has a field strength of 2.34 Tesla (100 MHz ^{1}H frequency) and the other magnet has a field strength of 4.7 Tesla (200 MHz ^{1}H frequency). The 2.34 Tesla magnet is used primarily for observation of ^{13}C resonances in solids using techniques of cross polarization with magic-angle spinning (CP/MAS), and single pulse measurements. This system has a standard 9.5 mm probe, a 12 mm large-volume probe and a low background, variable temperature 7.5 mm probe. The 4.7 Tesla magnet is used for observation of ^{1}H resonances in solids using the technique of combined rotation and multiple pulse spectroscopy (CRAMPS). The NMR spectrometer is also equipped with a micro-imaging probe for conducting magnetic resonance imaging (MRI) experiments at 4.7 Tesla.

For solution spectra, the residua samples were dissolved in $CDCl_3$ containing 0.1 wt. % tetramethylsilane (TMS). The $CDCl_3$ solutions studied were approximately 30 mg/mL for the proton spectra, 170 mg/mL for the carbon spectra in 5 mm NMR tubes. A JEOL GSX-270 NMR spectrometer was used to obtain both the ^{1}H and ^{13}C liquid-state NMR spectra. The experimental conditions to obtain a ^{1}H spectrum were 6 scans, a pulse width of 5.0 µs (? $45^?$), an acquisition time of 2.0 s, a pulse delay of 20 s, and 32K time domain data points. The conditions for obtaining a ^{13}C spectrum were 1500 scans, a pulse width of 4 µs ($68^?$), an acquisition time of 0.5 s, a pulse delay of 2.0 s, 32K time domain data points, and broadband developing.

Atomic Force Microscopy Height and phase-contrast atomic force microscopy (AFM) experiments were performed under ambient conditions with a Digital Instruments MultiMode scanning probe microscope equipped with a Nanoscope-III controller, operated in the tapping mode. Etched silicon probe cantilevers that varied in spring constant between 20-100 N/m were used at scan rates fro. 1-2 Hz, and phase contrast angles varied between 6° and 129°. **For thin**

film AFM imaging, residua samples were dissolved in HPLC grade toluene to make solutions of ~ 7mg oil/mL solution. A small volume of solution was deposited on the surface of a 1.2 cm diameter glass sample disk, and the disk was rocked back and forth while the toluene solvent evaporated. Solution volumes were measured to provide the oil volume needed to form a uniform film of ~1 ?m thickness. The actual films formed as the solvent evaporated were not uniform and exhibited visibly thicker areas around the perimeter of the evaporating drops. Thus, the film thickness around the perimeter was somewhat greater than 1?m with the remaining area being less than 1?m in thickness. AFM images of the samples were collected from the films in areas where the thickness was less than 1?m. All of the images were collected within a few hours of each other, and the same silicone cantilever and tip was used for each image. 20 ?m X 20 ?m areas were scanned for each sample. The same drive amplitude, set point, scan rate, and feedback gain settings were used for each image so that the images are directly comparable. Scaling of both the height and phase images was changed to accommodate features of the individual samples (surface topography was very smooth, only a few nm of variation, for the 0 min. sample, and quite rough, several hundred nm of variation for the 60 min. sample).

Differential Scanning Calorimetry and Thermogravimetric Analysis Differential Scanning Calorimetry (DSC) **measurements were performed over the temperature range 30?C to 290?C using a TA Instruments 2920 modulated differential scanning calorimeter (DSC). Average heating rates were 2?C per minute. The modulation amplitude was ?0.5?C, and the modulation period was 80 seconds. Although hermetic pans were used for both sample and reference, a pinhole in each of the lids allowed pressure equalization with the DSC cell. The TA2920 DSC was calibrated using standard procedures. Three materials were used for temperature calibration: indium (mp 156.60?C), water (mp 0.01?C), and n-octane (mp -56.76). Enthalpy was calibrated using an indium metal standard (heat of fusion 28.57 J/g). Heat capacity was calibrated using sapphire. All tests were performed using sealed hermetic aluminum DSC pans with pin hole vents, and helium was used to purge the DSC cell. Thermogravimetric analysis (TGA) profiles were obtained with a TA Instruments model TGA 2950 Thermogravimetric Analyzer. Sample weight was 15 - 30 mg. Samples were heated under a nitrogen sweep from 20 - 600 °C at a rate of 10 °**C/min.

RESULTS AND DISCUSSION

WRI Coking Indexes The first Coking Index is defined as the ratio of the Heithaus parameters, p_a/C_{min} from an asphaltene flocculation titration (Schabron 2001c). As pyrolysis progresses, p_a decreases as the polarity of the asphaltenes increases, and C_{min} increases as the overall stability of the residuum matrix decreases. The second Coking Index is the ratio of the weight percent of the cyclohexane soluble portion of heptane asphaltenes (Y) to the weight percent of heptane asphaltenes (X) (3). The amount of cyclohexane soluble components of the asphaltenes is diagnostic of the state of the solubilizing resins in these materials. The disappearance of the cyclohexane soluble portion of heptane asphaltenes is coincidental with the formation of a multi-phase system and the onset of coke formation. The Y/X ratio 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 a threshold value, coking begins (Figures 1 - 2). The Coking Indexes do not predict how much coke will be formed, but only when coking is likely to begin.

Pyrolysis Portions of a Lloydminster vacuum residuum were pyrolyzed at 400?C (750 ?F) for residence times of 15, 30, 60, and 80 minutes. The original material and the 15 and 30 minute products contained <0.03 wt.% coke. The 60 and 80 minute products contained 4.2 and 8.0 wt.% coke, respectively. For these two oils, the coke amount increased somewhat after a two week period after pyrolysis due to the instability of these materials. The WRI Coking Indexes were determined for the original and pyrolyzed materials. The data are provided in Table 1. The original and product materials were analyzed by optical spectroscopy including near and mid infrared (IR), absorbance, and fluorescence spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and atomic force microscopy (AFM). The results are described below.

Table 1. WRI Coking Indexes and Amount of Coke Formed after Pyrolysis at 400 ˝ C

Pyrolysis Time, Minutes	Wt. % Coke	WRI Coking Indexes	
		p_a/C_{min}	Y/X
0	<0.03	1.6	2.9
15	<0.03	0.67	1.6
30	<0.03	0.33	1.0
60	4.2[b]	0.04	0.6
80	5.9[a], 8.0[b]	-	0.5

a. Coke amount one day after pyrolysis b. Coke amount two weeks after pyrolysis

Optical Spectroscopy

Infrared Spectroscopy IR spectra were obtained from both neat samples pressed between two KBr window plates and from 5 wt. % solutions in carbon disulfide. The wavelengths included the standard mid IR range (450 - 4,000 cm^{-1}) and the near IR range (4000 - 12,800 cm^{-1}). The spectra of neat samples are provided in Figure 3. The spectra of the carbon disulfide solutions are provided in Figure 4. The spectra are all very similar and a spectroscopic marker that correlates with the Coking Indexes is not apparent. There is a decrease in the carboxyl carbonyl band at about 16,900 cm^{-1} as pyrolysis progresses due to the loss of carboxylic acid functionality. There is evidence of a steady increase in the amount of aromatic C-H functionality with increasing pyrolysis time as evidenced by the relative increases in the aromatic C-H stretching band at 3,050 cm^{-1} and in the aromatic C-H bending bands at 673 and 738 cm^{-1}.

<u>Absorbance Spectroscopy</u> Absorbance spectra were obtained in toluene solutions at concentrations of 39 - 56 mg/mL against a toluene reference, from 320 - 700 nm. The spectra are shown in Figure 5. There is little difference evident in the spectra of the original and pyrolyzed materials except for the Soret peak due to porphyrins at 410 nm (Branthaver 1976). This peak disappears as pyrolysis progresses, indicating that the ordered porphyrin structures are destroyed during pyrolysis.

<u>Fluorescence Spectroscopy</u> Emission spectra were obtained in toluene solutions at concentrations of 39 - 56 mg/mL with an excitation wavelength of 350 nm. The spectra are shown in Figure 6. There is no significant qualitative difference between the spectra.

It appears that none of the various types of direct optical spectra evaluated will provide a means of correlating with the WRI Coking indexes.

<u>Differential Infrared Functional Group Analysis</u> The various functional groups in the original residuum and the 15 and 30 minute pyrolysis oils were characterized using an IR spectroscopic method (Petersen 1986). These include carboxylic acids and their salts, 2-quinolones, phenolics, pyrrolics, ketones, anhydrides, and sulfoxides. The functional groups are shown in Figure 7 and results of the functional group analyses are listed in Table 2.

Table 2. Results of IR Functional Group Analysis, mol/kg

Functional Group	Original Residuum	Pyrolyzed 15 min.	Pyrolyzed 30 min.
Carboxylic Acid & Salts	0.022	0.014	0.016
Carboxylic Acid Anhydride	<0.001	<0.001	<0.001

Ketone	0.005	0.006	0.006
Phenolic OH	0.022	0.102	0.120
Pyrrolic OH	0.192	0.058	0.006
2-Quinolone	0.003	0.017	0.015
Sulfoxide	0.043	0.054	0.063

The results show that there is a slight decrease in carboxylic acids between the original residuum and the 15 minute pyrolysis oil. Carboxylate levels are about the same for the 15 and 30 minute pyrolysis oils. Acid anhydrides were not detected. The ketone content remains unchanged. Phenolics increase with increasing pyrolysis severity, while pyrroles decrease. The 2-quinolone content increases from the original residuum to the 15 minute pyrolysis product, and it remains the same for the 30 minute product oil. Sulfoxide content increases slightly with increasing pyrolysis severity. The above results indicate that the phenolic OH, the pyrrolic OH, and the sulfoxide functionalities could be evaluated with additional residua to see if the changes observed with Lloydminster residuum correlate universally with the Coking Indexes.

Nuclear Magnetic Resonance Spectroscopy

NMR Images of Pyrolyzed Residua NMR imaging techniques were used to determine possible phase separation during coking (Miknis and Michon 1998, Miknis et al.1998). This information was evaluated for its applicability as a coking indicator. Imaging experiments were conducted on the product oils that were pyrolyzed at 400 ?C for 15, 30, 60, and 80 minutes. The objective of these experiments was to determine the feasibility of using NMR imaging as a means of determining the instability of vacuum residua caused by incipient coke formation. Imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz using a Chemagnetics/Otsuka Electronics micro-imaging 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). NMR images of the pyrolyzed residua were made 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 10 ms. Eight slices, each 1 mm thick and separated by 1 mm were obtained for each image set. The time required to obtain a set of images was about 32 minutes using these parameters. A set of NMR images of the pyrolyzed residua is shown in Figure 8. In all cases the images were obtained at room temperature. Also, for each pyrolysis time, only the 4th slice of an 8 slice image set is shown. This slice corresponds to a slice approximately through the longitudinal center of the cylindrical sample vial.

The set of images in Figure 8 show that as the residence time increases, images are more easily formed due to the decreased viscosity of the pyrolyzed residua as a result of cracking reactions taking place at 400 ?C. The longer the residence time, the greater the degree of cracking and hence greater amount of lower molecular weight, lower viscosity materials in the sample.

A concern regarding the feasibility of using NMR imaging to study the pyrolyzed residua was that the NMR relaxation time (T_2) of the residua would be too short for imaging (Schabron et al. 2001) . 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. If the T_2's are too short an image can not be formed by the spin echo method. Such is the case for the residuum pyrolyzed for 15 minutes (Figure 8). The viscosity of the residuum pyrolyzed for 30 minutes is decreased sufficiently so that an NMR image was obtained that shows the cross-section of the sample vial. With longer residence times, more detailed images are formed. Two separate phases are visible in the 80 minutes sample and to a lesser extent two phases are visible in 60 minute pyrolyzed sample. These are the samples in which coke has formed. The phase separation is probably due to cracking reactions that take place during pyrolysis to the point of concomitant coke formation. The presence of more than one phase is not evident to the human eye since the samples are all optically opaque. NMR imaging clearly shows that two liquid phases form in the sample once coke begins to form as noted by the different areas of grey contrast in the images. During pyrolysis, hydrogen is abstracted from portions of the residuum to stabilize and lower the molecular weights of the products. As a result, a material begins to form which is more carbonaceous and coke-like. The images do show a lighter contrast at the top of the sample, similar to what might be observed upon creaming in which lighter, cracked materials appear at the top surface. The lower layer is immiscible with the upper layer. In future work, chemical analyses will be performed to define the chemical composition of the two layers that appear as coke begins to form.

Wide-line NMR Measurements Wide-line NMR measurements were made at a nominal proton frequency of 100 MHz using a pulse delay of 1 s, and a pulse width of 2 µs. In these measurements, the response of the protons in the residuum sample to a radio frequency pulse is measured. This measurement is called the Free Induction Decay (FID) and is the basic measurement made in pulsed NMR (Farrar and Becker 1971). The FID represents the rate at which the magnetization from the protons in the sample decays following application of an rf pulse. The FID s of the pyrolyzed residua are shown in Figure 9. The lengthening of the decay curves with increasing pyrolysis time is due to a decrease in viscosity. The characteristic time for the decay is called the spin-spin relaxation time, and is denoted as T_2. Generally for non-viscous liquids like water, the decay is exponential. However, in complex materials such as residua, the decay is usually non-exponential and can be fitted to a sum of exponential functions, each having a characteristic T_2. In the current work, the residua FID s were fitted with a 2-component exponential function of the form,

$$M(t) = M_{0a}\exp(-t/T_{2a}) + M_{0b}\exp(-t/T_{2b}) \qquad (1)$$

M_{0a}, M_{0b}, are the populations of protons in environments a, b, and T_{2a}, T_{2b}, are the relaxation times for those protons. The relaxation time data are given in Table 3.

Table 3. Two Component Fit of NMR Relaxation Data for Pyrolyzed Residua

Pyrolysis Time, min	M_{0a}	M_{0b}	T_{2a}, µs	T_{2b}, µs
0	0.52	0.48	55	226
15	0.47	0.53	229	1056
30	0.38	0.62	255	1274
60	0.22	0.78	254	1607

It should be stressed that the fitting of the relaxation data is arbitrary and there is no *a priori* reason to fit the data using the sum of two exponential functions, other than the data do not follow a single exponential function. Nevertheless, the longer relaxation time, T_{2b}, which increases significantly with pyrolysis appears to correlate with the solubility-based coking indicators (Figure 10). However, we do not yet have a model for the NMR relaxation behavior and thus do not have a physico-chemical basis for such correlations.

Proton and Carbon Solution NMR Solution NMR spectra were obtained in deuterated chloroform solutions. The proton and carbon aromaticities calculated from the integrated spectra are listed in Table 4 and are plotted in Figure 11. There is clearly a trend toward increasing aromaticities as pyrolysis progresses. Additional residua will need to be tested to determine whether or not the numerical values correlate with the Coking Indexes in a universal manner.

Table 4. Proton and Carbon Aromaticities for Original and Pyrolyzed Residua

Pyrolysis Time, min	Proton Aromaticity, f_a^H	Carbon Aromaticity, f_a^C

0	0.066	0.19
15	0.072	0.23
30	0.079	0.24
60	0.091	0.25
80	0.094	0.28

<u>Atomic Force Microscopy</u> In tapping mode (TM) AFM phase contrast imaging a rectangular cantilever of spring constant k is oscillated at a driving frequency and amplitude of ? **and A, respectively, above/near or in periodic contact with the surface of the sample** (Bar et al. 2000, Delineau et al. 2000, Wang 1999). **As the cantilever is oscillated, or tapped across a surface, the damping in the cantilever occurs due to the attractive (viscous damping) and repulsive (elastic) forces manifest between features of the sample encountered by the cantilever tip and the tip itself. The dynamics of a dampened oscillating cantilever in tapping mode may be expressed in terms of a second order non-homogeneous differential equation:**

(2)

where t is time, ? **is the damping constant, m is the point mass of the cantilever, z is the cantilever-tip surface distance, and F(z) is the force acting between the cantilever tip and the surface at distance z. The damping of the cantilever results in a change in the frequency,** ? ? **, and the amplitude** ? **A of the cantilever as the cantilever tip surface distance z is changed. The damping of the cantilever that takes place during the downward motion of the cantilever as it approaches the surface of the material under investigation constitutes a dissipation of energy, W_d, associated with the tapping cantilever system. The resulting change in energy corresponds to a phase lag,** ? ? **, observed in A(amplitude) versus** ? **(frequency) plots.** In effect, TM-AFM constitutes a method for measuring multiple single-point cantilever tip-surface interaction forces over a comparatively large area. These measurable areas may be as large as 100 X 100 microns compared to a cantilever-tip contact area that would be less than 500 nm. Thus, Q^{eff} may be a convenient means of mapping surface forces in residua fine structures.

Phase contrast images are often observed as light and dark contrasted regions in a phase shift image. When sharp cantilever tips are used, lighter regions observed in phase contrast micrographs correspond to features that represent greater forces of adhesion, or viscous damping. In a residuum system, the lighter regions are believed to represent hard, polar surfaces and the darker areas are believed to represent soft, less polar surfaces.

Thick Smear Images AFM height images of neat thick smears of the residua pyrolyzed at 400 °C (750 °F) for 30 minutes (<0.03 wt.% coke) and 60 minutes (4.2 wt.% coke) are shown in Figure 12. Before coke begins to form, the material appears to be a uniform single phase structure. The images at 0, 15, and 30 minutes all exhibited a similar single-phase appearance. At 60 minutes, as coke is beginning to form, the ordered structure has broken down and a bimodal system consisting of two immiscible liquids appears to be present.

Thin Film Images AFM images of thin films obtained from dilute toluene solutions evaporated onto glass plates show more fine structural differences between the materials pyrolyzed at various residence times. AFM height (left) and phase-contrast (right) images were obtained for original and pyrolyzed residua. These are shown in Figure 13. Clearly, small agglomerate species observed in the unpyrolyzed sample appear to further aggregate as pyrolysis progresses. These observations suggest that AFM may be used to image the formation life cycle of micro-coke particles. Image analysis software (Image-Pro Plus, version 4.1 for Windows) was used to develop spatial calibration (SC) histograms of phase-contrast images of each of the four samples. In the histograms, the dark to light regions are assigned x-axis number values ranging from 0 (darkest) to 250 (white). The y axis corresponds to a relative pixel count corresponding to each intensity of dark or light. These histograms are shown in Figure 14. Comparison between SC histogram shape and intensities may be exploited to differentiate between materials that have undergone different degrees of pyrolysis. One approach is to take the ratio of peak height to peak width at half height (Table 5). When these values are plotted against the WRI Coking Indexes, there appears to be a distinct correlation (Figure 15). This correlation should be studied with additional residua to determine if the trend is universal.

Table 5. Ratio of AFM Histogram Peak Height to Peak Width at Half Height for Original and Pyrolyzed Residua

Pyrolysis Time, min	$H/W_{1/2}$
0	5.9
15	4.3
30	3.0
60	0.36

Thermal Analyses

Differential Scanning Calorimetry One untreated and two thermally pretreated samples pyrolyzed for 15 and 30 minutes were examined. None of thee samples were producing coke. Samples pyrolyzed for longer periods which produced coke were not evaluated since these are multi-phase systems and it is difficult to obtain a representative sample in the 1-5 mg range. **The heat capacity profiles for the three experiments are shown in Figure 16. There are distinct differences among the profiles that are dependent on pyrolysis. Higher severity pretreatment generates products with lower heat capacity. All three samples lost weight through vaporization of light hydrocarbons at the higher temperatures. Some of the curvature of the heat capacity profiles above 100 °C is due to this loss. At 290 °C the losses were 3.2, 16.6, and 18.4 wt.% for the original, 15 minutes, and 30 minutes pyrolysis oils, respectively. Values of the heat capacities at 100?C are listed in Table 6. There is a significant difference between the heat capacities of the original and pyrolyzed oils. The difference between the oils can be measured at any temperature from 20 0 290 °C. The heat capacities correlate with the WRI Coking Indexes (Figure 17). The results suggest that the technique of measuring heat capacities could possibly be developed into on-line process control instrumentation. This will have to be investigated with a variety of residua to see if this concept is universally applicable.**

Table 6. Heat Capacities for Original and Pyrolyzed Residua

Pyrolysis Time, min	C_p at 100 °C, J/g K
0	2.056
15	1.832
30	1.530

Thermogravimetric Analysis Thermogravimetric analysis showed increased losses of light components with increasing pyrolysis severity. This is not surprising since cracking reactions have taken place and lighter, distillable components have been formed. TGA profiles are shown in Figure 18. The weight loss and residue data are presented in Table 7. The weight losses at 400 °C provide an estimate of conversion of the residuum to lighter distillable products by pyrolysis. The residue is the carbonaceous material remaining in the pan at 600 °C. This is analogous but not identical to coke formation as determined by the Conradson Carbon value for the original residuum (500 °C), which is 16.4 wt. % (Schabron et al 2001d).

Table 7. Thermogravimetric Analysis Data

Pyrolysis Time, min	Weight % Loss at 400 °C	Residue at 600 °C, wt.%
0	37.4	12.2
15	49.2	13.8
30	55.2	15.3
60	62.2	15.6

Derivative TGA profiles are shown in Figure 19. The profiles for the various oils are quite different and the results suggest that the progress of pyrolysis could possibly be monitored by TGA analyses. There is a region near 310 °C where weight loss is about the same for the original and pyrolyzed materials. At temperatures above this, the rate of weight loss is higher for the unpyrolyzed material than the pyrolyzed material, and it decreases as pyrolysis time increases. This is due to the presence of more high boiling material in the original material than in the pyrolyzed materials. This high boiling material is cracked during pyrolysis to form lower boiling material. Below 310 °C the opposite effect is observed, with larger rates of weight loss of lower boiling material in the more severely pyrolyzed materials than in the less severely pyrolyzed materials and the original material.

CONCLUSIONS

Portions of a Lloydminster vacuum residuum were pyrolyzed at 400?C (752 ?F) for residence times of 15, 30, 60, and 80 minutes. The original material and the 15 and 30 minute products contained <0.03 wt.% coke. The 60 and 80 minute products contained 4.2 and 8.0 wt.% coke, respectively. The WRI Coking Indexes were determined for the original and pyrolyzed materials. The original and product materials were analyzed by variety of analytical techniques including near and mid infrared (IR) spectroscopy, absorbance and fluorescence spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and atomic force microscopy (AFM). No significant differences which correlate with the WRI Coking Indexes were evident with the optical spectroscopy results. There were significant differences noted with NMR relaxation times and AFM histograms. DSC and TGA results also showed significant differences between the original and pyrolyzed materials. These differences need to be explored further in future work using additional residua.

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