

**RESIDUA UPGRADING EFFICIENCY IMPROVEMENT MODELS:  
WRI COKING INDEXES**

**Topical Report**

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## ABSTRACT

Pyrolysis experiments were conducted with three residua at 400 °C (752 °F) at various residence times. The wt % coke and gaseous products were measured for the product oils. The Western Research Institute (WRI) Coking Indexes were determined for the product oils. Measurements were made using techniques that might correlate with the Coking Indexes. These included spin-echo proton nuclear magnetic resonance spectroscopy, heat capacity measurements at 280 °C (536 °F), and ultrasonic attenuation.

The two immiscible liquid phases that form once coke formation begins were isolated and characterized for a Boscan residuum pyrolyzed at 400 °C (752 °F) for 55 minutes. These materials were analyzed for elemental composition (CHNS), porphyrins, and metals (Ni,V) content.

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## EXECUTIVE SUMMARY

Approaches to performing rapid laboratory diagnostic analyses or on-line analytical concepts that can be related to the WRI Coking Indexes were studied. These may eventually provide rapid and possibly on-line analyses for refinery process control. This should result in significant efficiency improvement as well as less down time and heat wasted in refinery operations.

Pyrolysis experiments at various residence times at 400 °C (752 °F) were performed with four residua to obtain sufficient samples for subsequent analysis. Residence times were selected to provide materials that are at various points in the coke formation induction period time line. The amount of gas formed was measured. A portion of the product oils was dissolved in toluene to measure the amount of toluene insolubles (coke) by filtration. The WRI Coking Indexes were measured for the original and pyrolyzed oils. This involved performing asphaltene flocculation titrations, determining heptane asphaltenes, and measuring the amount of the heptane asphaltenes that are soluble in cyclohexane. Various analyses on the original and product oils were conducted to determine the measurement technique that best correlates with the WRI Coking Indexes. The goal is to identify the most rapid measurement possible and ideally, the technique that is amenable to possible on-line analysis. Techniques investigated in this study included spin-echo proton nuclear magnetic resonance (NMR) induction decay times, heat capacity measurements, and ultrasonic attenuation.

Changes that occur during residua pyrolysis were studied with Boscan residuum pyrolyzed at 400 °C (752 °F) for 25 and 55 minutes. The nature of the two immiscible liquid phases that are present when pyrolytic coke formation begins was explored also. The results provide insight into the chemical changes that occur as coke formation begins. The two immiscible phases visualized by nuclear magnetic resonance imaging (NMRI) from Boscan residuum pyrolyzed at 400 °C (752 °F) for 55 minutes were isolated. These materials were analyzed for elemental composition (CHNS), porphyrins, and metals (Ni,V) content.



## OBJECTIVES

Approaches to performing rapid laboratory diagnostic analyses or on-line analytical concepts that can be related to the WRI Coking Indexes were studied. These may provide rapid analysis approaches for refinery process control resulting in significant efficiency improvement, with less down time and heat wasted in refinery operations. In addition, the two immiscible liquid phases that appear once coke begins to form were isolated and characterized for Boscan residuum.

## INTRODUCTION

Heavy oil and residua conversion processes require heating for distillation and thermal treatment. The many sources of residua behave differently in refining processes. The so-called opportunity resids are often purchased for their low prices. No longer does the refiner have the luxury of upgrading the same known material year after year. More often than not, blends are used with different day-to-day compositions. With different feed sources, unexpected fouling due to coke formation often occurs. To avoid this, many refiners select relatively conservative heating profiles that result in less than optimal distillation efficiency. Western Research Institute (WRI) has developed new Coking Index concepts to measure how close a residuum is to coke formation when it is heated above pyrolysis temperatures (340 °C, 650 °F) (Schabron et al. 2001a). In the current work, we are developing approaches to performing rapid laboratory diagnostic analyses or on-line analytical concepts that can be related to the WRI Coking Indexes. These may eventually provide rapid and possibly on-line analyses for refinery process control, which will result in significant efficiency improvement and less down time and heat wasted in refinery operations.

### The Ordered Structure of Petroleum Residua

Petroleum residua are highly ordered structures consisting of a variety of components. The system free energy is minimized by the alignment of available components. The ordered structure can be described by the Pal and Rhodes suspended particle solution model (Pal and Rhodes 1989, Schabron et al. 2001b). The model considers dispersed solvated particles in a solvent matrix. For residua, the volume fraction of the core of particles can be considered as the volume fraction of heptane asphaltenes  $N_a$ . The volume of the core is increased by a solvation shell  $K_S$ . Several solvated shells bind a portion of solvent and increase the effective particle volume by a term  $K_F$ . The term  $K_S K_F$  is called the solvation constant  $K$ . The effective particle volume  $N_{EFF}$  is equal to the core asphaltene fraction volume increased by the solvation terms, as shown by the following equation.

$$\phi_{EFF} = K\phi_a = K_F K_S \phi_a \quad (1)$$

The residua free solvent volume fraction ( $N_{FS}$ ) can be calculated using the equation below.

$$\phi_{FS} = 1 - K_S K_F \phi_a = 1 - 1.6 \left( \frac{1}{1 - p_a} \right) \left( \frac{\chi_a}{1.2} \right) \quad (2)$$

In the equation,  $P_a$  is the mass fraction of heptane asphaltenes divided by an assumed density of 1.2 g/cm<sup>3</sup> to yield the volume fraction of asphaltenes,  $N_a$ . 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). The free solvent volume fraction ranges from 0 to 1. A small free solvent volume fraction represents a residuum that requires a highly ordered structure to maintain stability. Residua with low free solvent volume values have higher viscosities than those with relatively lower values. The ordered structure of a residuum with a relatively low free solvent volume fraction is more easily disrupted by heating than the structure of residua with relatively higher free solvent volumes (Schabron et al. 2001b, 2002a).

### **Asphaltenes**

Asphaltenes are a solubility class of molecules that self associate to maintain minimum system free energy. They are isolated from a petroleum matrix by mixing the oil with an excess of a low-polarity hydrocarbon solvent such as heptane, pentane, or isooctane. The temperature of mixing is important. Higher temperatures result in significantly lower asphaltene yields than lower temperatures (Andersen et al. 1997). Apparent molecular weights of asphaltenes are a function of measurement conditions such as temperature, solvent, and concentration. For example, the molecular weights of asphaltene subfractions in toluene were found to range from 1,260–23,000 g/mol when measured by vapor pressure osmometry at solution concentrations of 2–5 wt % (Schabron et al. 2001c). Dilute size exclusion chromatography measurements of the same fractions at concentrations in toluene of about 0.06–0.3 wt % yielded number average molecular weights relative to polystyrene of 523–772 g/mol, with polydispersity ratio values ranging from 2.6–4.0. These later measurements were probably below the critical micelle concentration (CMC) of the asphaltene subfractions in toluene. In an unrelated study, calorimetry measurements in toluene provided a CMC value for asphaltenes near 0.38 wt % (Andersen and Birdi 1991). In a whole residuum, the situation is different. Asphaltenes are not in toluene solution, and they interact directly in a continuum with the residuum solvent matrix.

### **Non-Pyrolytic Heat-Induced Deposition**

When a residuum is heated below pyrolysis temperatures (340 °C, 650 °F), the solvation shell is partially removed in a reversible manner and the solvation constant  $K$  decreases. On cooling, the shell is restored, although the time for restoring the original structure can vary. On heating, the polar asphaltene core is partially exposed, and the core material can attach to polar metal

surfaces such as surfaces in heat exchangers. These deposits are enriched in nickel and vanadium. Heat-induced deposition studied with five residua materials suggest that the heat-induced deposition process is not significant at 100 °C (212 °F). It is just beginning at 175 °C (347 °F), and is very evident at 250 °C (482 °F) (Schabron et al. 2001b). At the latter temperature, the amount of deposition correlates with the residua free solvent volume. Residua with low free solvent volumes exhibit higher heat-induced deposition tendencies than residua with relatively higher free solvent volumes. The activation energies of shell removal were found to range from 470–1,600 cal/mol, which is similar to energies determined by Storm et al. (1995, 1996). These results suggest that to minimize heat-induced fouling when residua are heated for pumping or storage, the lowest possible temperature should be used to keep the polar asphaltene cores as solvated as possible.

### **Pyrolysis and Coking**

When a residuum is heated above the temperature at which pyrolysis occurs (340 °C, 650 °F), there typically is an induction period ranging from a few seconds to over an hour after which coke formation begins (Magaril and Aksenova 1968, Phillips et al. 1985, Wiehe 1993). As pyrolysis progresses, the intermediate polarity material decreases during the induction period. 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). The apparent molecular weight of asphaltenes in toluene measured by VPO decreases, and they become more polar (Schabron et al. 2001c). The polar asphaltenes agglomerate within the whole oil matrix and the particle size of the agglomerated complexes increases. For example, asphaltene particles in unpyrolyzed Lloydminster residuum were visualized by atomic force microscopy to be about 0.5 micron in diameter (Schabron et al. 2002a). At a pyrolysis time of 15 minutes at 400 °C (752 °F), the particles increased to a diameter of about 2 microns. At 30 minutes, they were about 5 microns. At 60 minutes, coke formation had begun.

In an unpyrolyzed residuum, as much as 50 wt % of the heptane asphaltenes are soluble in cyclohexane, which has a solubility parameter midway between toluene, in which the asphaltenes are fully soluble, and heptane (Schabron et al. 2001a, 2001c). As pyrolysis progresses, less and less of the heptane asphaltenes dissolve in cyclohexane. This is an indicator of the destruction of the intermediate polarity, or resins material. An unstable system results when the depletion of the resins disables the ability of the asphaltene/resin complexes to self-adjust their apparent molecular weights to closely match the solubility parameter of the matrix. At that point on the coke formation induction time line, the ordered system breaks down and the polar asphaltene material is no longer stabilized, and coke begins to form. Once the amount of cyclohexane-soluble asphaltenes approaches zero, coke formation begins. Coke formation is coincidental with the disappearance of the intermediate polarity material and the formation of a bimodal system. This is consistent with observations of the formation of a neophase at coke formation onset (Shenghua et al. 1999). The bimodal system has been visualized as two apparently immiscible liquid phases by atomic force microscopy and by proton nuclear magnetic resonance imaging (Schabron et al. 2002b).

Three-dimensional predictability maps for coke formation were developed at 400 °C (752 °F), 450 °C (842 °F), and 500 °C (932 °F) (Schabron et al. 2002a). The maps are comprised of plots of free solvent volume (x), amount of coke formed (y), and pyrolysis residence time (z). The initial amount of coke formed correlates with residence time and free solvent volume at 400 °C (752 °F) and 450 °C (842 °F). At 500 °C (932 °F), coke formation is very rapid. The structure of residua with low free solvent volumes is more easily destroyed during pyrolysis than the residua with relatively higher free solvent volumes, and thus they produce more coke initially than residua with relatively higher free solvent volumes. Coke formation was studied in terms of two stages of zero-order (decomposition) kinetics. The first stage appears to be dominated by bond cleavage reactions with activation energies ranging from 22,000 to 38,000 cal/mol. The second stage is probably dominated by coke formation reactions and has activation energies ranging from 54,000 to 83,000 cal/mol. The activation energies appear to correlate with the initial residua free solvent volume. When carried to completion, the amount of coke formed is related to the atomic H/C ratio. The results provide a new tool for ranking residua and predicting initial coke make tendencies.

### **Asphaltene Flocculation Titration**

The automated asphaltene flocculation titration (AFT) is performed with the toluene-soluble components of residua. Two or more toluene solutions at different concentrations of residuum are titrated with a weak solvent such as isooctane. The weight of residuum or asphalt ( $W_a$ ), the volume of toluene ( $V_s$ ), and volume of isooctane titrant ( $V_t$ ) are recorded at the flocculation point where asphaltenes just begin to precipitate for each solution. The flocculation ratio and dilution concentration are calculated as follows:

$$FR = \text{Flocculation Ratio} = V_s / (V_s + V_t) \quad (3)$$

$$C = \text{Dilution Concentration} = W_a / (V_s + V_t) \quad (4)$$

A linear plot of FR vs C is made and the intercepts are determined ( $FR_{MAX}$  and  $C_{min}$ ). The AFT stability parameters are defined as follows (Heithaus 1962):

$$p_a = 1 - FR_{MAX} \quad \text{Peptizability of Asphaltenes} \quad (5)$$

$$P = P_o / (1 - P_a) = 1 / C_{min} + 1 \quad \text{Overall Compatibility of Residuum} \quad (6)$$

Larger values of  $p_a$  and  $P$  indicate peptizable asphaltenes and an overall compatible system, respectively.  $FR_{MAX}$  is the volume fraction of toluene in a toluene and isooctane mixture, and is a direct measurement of the solubility parameter at which asphaltenes begin to precipitate (Schabron et al. 2001c).  $C_{min}$  is the ratio of residuum to titrant (isooctane) at which asphaltenes begin to precipitate, and this value can be used to calculate the solubility parameter of the whole oil.

## **WRI Coking Indexes**

A common problem in the refining industry is to ascertain how close a pyrolysis system is to forming coke on the coke induction period time line. This has resulted in undesired coking events in distillation units, resulting in significant down time and economic loss. To avoid this problem, conservative heating profiles are often used. This results in less than optimal distillate yield, and less profitability. In response to this need, WRI Coking Indexes were developed. The Coking Indexes are calculations made from relatively simple analyses of a residuum. One of the measurements used is the  $p_a/C_{\min}$  ratio from the AFT titration. As pyrolysis proceeds, the value of  $p_a$  decreases, and the value of  $C_{\min}$  increases. The  $p_a/C_{\min}$  ratio drops from an initial value near one or higher to a threshold value of about 0.2, below which coke formation begins. Once coke is present, the product oil consists of an unstable multiphase liquid system, and it is difficult to obtain reliable AFT data from the material.

An alternative Coking Index is obtained by determining the weight percent, the weight percent heptane asphaltenes (X), and the weight percent of cyclohexane-soluble material in heptane asphaltenes (Y). The ratio Y/X is calculated. The initial value for a stable residuum can range from 2–4 or higher. As pyrolysis proceeds, the amount of cyclohexane-soluble asphaltenes decreases and the Y/X value decreases to a threshold value of about 1.0, below which coke begins to form. Unlike the AFT titration, the Y/X analysis can be reliable when performed after coke formation begins. The Coking Indexes do not predict the amount of coke formed; however, the initial amount of coke formed with pyrolysis at a particular residence is influenced by the unpyrolyzed residua free solvent volume.

Determination of the Coking Indexes requires that a sample be taken and analyzed in a laboratory. This is a relatively time-consuming operation in terms of real-time plant process control. Efforts have begun to identify alternative instrumental analyses that could possibly correlate with the Coking Indexes and lead to the development of a real-time on-line analysis system. Initial studies were performed with a single Lloydminster residuum that was pyrolyzed at 400 °C (752 °F) prior to and beyond the point of coke formation (Schabron et al. 2002b). Atomic force microscopy histograms visualized the formation of agglomerated particles correlated with the Coking Indexes. However, this is a laboratory technique not amenable to on-line analysis. Wide line nuclear magnetic resonance signal decay measurements were found to correlate with the Coking Indexes. Heat capacity measurements also showed a correlation with the Coking Indexes. The purpose of the current work is to study additional residua and explore potential alternative techniques that could correlate with the WRI Coking Indexes.

## **Ultrasonic Spectroscopy**

The ultrasonic region is defined by sound waves with frequencies above the upper audible limit of 20 kHz. Ultrasonic measurements are widely used for nondestructive testing of materials including medical diagnostics. The wavelengths commonly used for testing are in the range of about

0.1 to 100 MHz. One of the more common methods for characterizing materials is based on wave velocity. The specific acoustic impedance is a function of the material density, and is expressed as:

$$Z = DV \quad (7)$$

where  $D$  is the material density and  $V$  is the wave velocity (Halmshaw 1991). In ultrasonic testing, material boundaries with different  $Z$  values, such as metal/air or oil/water interfaces, cause reflection of ultrasonic waves. This allows thicknesses of materials and defects not visible to the eye to be detected and imaged.

For characterizing particles dispersed within a material such as emulsions or dispersions, ultrasonic attenuation is used. Ultrasonic absorption,  $u$ , results from the sum of two effects:

$$u = u_t + u_s \quad (8)$$

where  $u_t$  is absorption due to internal friction between particles and  $u_s$  is scattering due to dispersed particles in the material (Cartz 1995). The average size of the suspended particle,  $D$ , and the frequency,  $\nu$ , have a significant effect on the scattering at a particular wavelength  $\lambda$ :

- (a) When  $\lambda$  is greater than  $D$ ,  $u_s$  is proportional to  $D^3\nu^4$
- (b) When  $\lambda$  is about the same as  $D$ ,  $u_s$  is proportional to  $D\nu^2$
- (c) When  $\lambda$  is less than or equal to  $D$ ,  $u_s$  is proportional to  $1/D$ .

In ultrasonic testing of liquids and solids, the speed of sound ranges from about 1–10 km/s depending on the matrix, and the wavelengths are in the range of about 1–10 mm. For asphaltene complexes and agglomerated particles leading to coke formation in a petroleum residuum matrix, the particle diameter has been visualized by atomic force microscopy to be in the range of about 0.5–5 microns, depending on pyrolysis residence time (Schabron et al. 2002b). The speed of sound varies by the material. Therefore, for heavy oils containing asphaltenes, the first case above applies and the attenuation due to scattering is a function of the particle diameter cubed. Thus, it seems likely that for changes in particle diameter during pyrolytic processing, ultrasonic attenuation could prove to be a valuable monitoring tool. The number of particles in suspension is also expected to change during pyrolysis as agglomeration occurs. Some preliminary experiments were performed in the present work that support the potential utility of ultrasonic attenuation measurements.

Ultrasonic attenuation is commonly given in terms of Neper per distance  $x$  such as Neper/cm. This is calculated as  $u = -1/x \ln A_x/A_0$  where  $A$  is the signal amplitude at distance 0 and distance  $x$ . To obtain attenuation in decibels, Neper is multiplied by 8.686 (Cartz 1995). The Neper value is loosely analogous to the absorbance term in optical spectroscopy.

## **Benefits of Improving Distillation Efficiency**

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, with a significant energy savings. In the United States, coking operations use about 166,000–258,000 Btu per barrel of feed (USDOE 1998). 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 residua 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. Since the difference in price between residua and distillates is about \$10 per barrel, each 1% increase in distillate yield could be worth about \$150,000 per day. 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 United States, the reduction in carbon dioxide emissions for each 1% industry-wide efficiency improvement is about 218–679 tons per day. Although the above is a crude workup of potential savings, it serves to demonstrate that significant benefits can occur with the use of the Coking Indexes.

## **Technical Approach**

The current work is divided into two parts. The first is to explore possible instrumental alternatives to measuring the WRI Coking Indexes. Pyrolysis experiments at various residence times at 400 °C (752 °F) were performed with four residua to obtain sufficient samples for subsequent analysis. Residence times were selected to provide materials that are at various points in the coke formation induction period time line. The amounts of coke (toluene insolubles) and gas were measured. The WRI Coking Indexes were measured for the original and pyrolyzed oils. This involved performing asphaltene flocculation titrations and determining heptane asphaltenes and the amount of the heptane asphaltenes that are soluble in cyclohexane. Various analyses on the original and product oils were performed to evaluate potential measurement techniques that could correlate with the WRI Coking Indexes. The goal is to identify the most rapid measurement possible, and establish a technique that is amenable to possible on-line analysis. Techniques included spin-echo proton nuclear magnetic resonance (NMR) induction decay times, heat capacity measurements, and ultrasonic attenuation.

The second part involved characterizing the two immiscible liquid phases that appear once coke begins to form. This was studied with Boscan residuum. The results provide insight into the chemical changes that occur as coke formation begins. This could lead to the development of procedures or additives to increase the induction period time to allow for additional distillate yield.

Boscan residuum was pyrolyzed at 400 °C (752 °F) for 25 and 55 minutes. The longer residence time produced coke, and the two liquid phases were isolated for elemental and metals analysis.

## **EXPERIMENTAL DETAILS**

### **Residua Materials**

Four residua materials were used in the current work. These were Boscan, Lloydminster, and Redwater, B.C. from prior nonproprietary work at Western Research Institute (WRI). The MaxCL2 was provided by ConocoPhillips, 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 °C (158 °F) for about ½ hour on a heated stir plate while stirring with a magnetic stir bar. This was followed by overnight stirring at room temperature. The following morning, the stirring was stopped for 30 minutes prior to vacuum filtration using Ace, 140-mL, 10–20 micron, sintered glass filters. Residual solvent was removed from the asphaltenes on the filters using a vacuum oven set at 120 °C (248 °F) 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. The mixture was allowed to settle for 30 minutes prior to vacuum filtration 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 °C (212 °F) for 15 minutes. The cyclohexane-soluble materials 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  $25.0 \pm 0.1$  °C ( $77 \pm 0.2$  °F) 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. The procedures are described in detail elsewhere (Pauli 1996).

### **Pyrolysis**



Pyrolysis experiments were performed using 3.5 cm o.d. x 30 cm tube reactors (2.4 cm i.d. x 29 cm nominal internal dimensions) constructed from 316 stainless steel. The total internal volume of the reactor assembly was about 135 cc. Each reactor was charged with about 50 g of residuum. 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 two tube reactors were attached to a rack that contained a third tube 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 three tubes on the rack. The rack was placed into a Techne, 4,000-watt, fluidized sand bath. The pyrolysis time frame was started after about twelve minutes 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 residence time, they were removed and cooled by immersing them in another fluidized sand bath at room temperature. The reactors were then placed in ice water for 30 minutes. The amount of gas produced was measured at room temperature using a pressure gauge. The product oils were poured from the reactor tubes at room temperature, and the collected product was stirred. A portion of the product oil was dissolved in toluene and filtered to determine wt % coke.

### **Nuclear Magnetic Resonance Spectroscopy**

Nuclear magnetic resonance images (NMRI) 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  $^1\text{H}$  frequency) and the other magnet has a field strength of 4.7 Tesla (200 MHz  $^1\text{H}$  frequency). The 2.34 Tesla magnet is used primarily for observation of  $^{13}\text{C}$  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  $^1\text{H}$  resonances in solids using the technique of combined rotation and multiple-pulse spectroscopy (CRAMPS).

Imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz at 4.7 Tesla using a Varian/Chemagnetics microimaging probe. NMR images of the pyrolyzed residua were obtained by the spin-echo method 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.

Wide-line NMR measurements were made at a nominal proton frequency of 200 MHz using the imaging probe. 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. The FID represents the rate at which the

magnetization from the protons in the sample decays following application of an RF pulse. However, to compensate for inhomogeneities in the magnet that might compromise the relaxation time measurements, the spin-echo method was used for the relaxation time measurements. Typically, 40 echoes were recorded for each residuum.

### **Heat Capacity Measurements**

Differential Scanning Calorimetry (DSC) measurements were performed over the temperature range of 30 °C to 290 °C (86 °F to 554 °F) using a TA Instrument 2920 modulated differential scanning calorimeter (DSC). Average heating rates were 2 °C (35.6 °F) per minute. The modulation amplitude was  $\pm 0.5$  °C ( $\pm 32.9$  °F), 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.

### **Ultrasonic Attenuation**

Ultrasonic attenuation measurements were obtained from three different companies that provide ultrasonic instrumentation. Different samples of original and pyrolyzed residua were sent to these vendors, who offered to make measurements to demonstrate the potential utility of the technique. Although trends can be compared, the numerical values generated cannot be directly compared with one another. Spectra for Redwater, B.C. samples were provided by Dr. Wes Cobb, University of Denver Research Institute, Denver, Colorado using an in-house fabricated instrument. Ultrasonic Scientific, Dublin, Ireland, provided data for the Boscan material using an HR-US 102 spectrometer. Matec Instruments, Northboro, Massachusetts, provided data for the Lloydminster residuum samples using a Matec TB 100 computer card as pulser and receiver. Measurements were made at frequencies ranging from 1–3 MHz. Data were converted to Neper/cm ultrasonic attenuation.

### **Porphyryns, Metals, and Elemental Determinations**

Porphyryns were determined from the absorbance of the Soret band for porphyryns at 410 nm using methylene chloride solutions. Absorption spectra were obtained in 10-mm pathlength quartz cuvettes with a Shimadzu model UV-265 scanning spectrophotometer. The standard used was a low-molecular-weight size exclusion chromatography fraction from Boscan pentane asphaltenes known to contain 110 micromoles per gram of vanadium porphyrin (Branthaver 1976). The conversion factor used was absorbance per g/mL  $\times 0.23 =$  mg/kg porphyryns.

To determine Ni and V, a 0.3-g or smaller portion of sample was weighed into a 50-mL borosilicate glass beaker. About 1 mL of concentrated trace metals-grade sulfuric acid was added, and the beaker was heated on a hot plate until a dry char was obtained. The char was ashed in a muffle furnace at 520 °C (968 °F) overnight. After cooling, 2 mL of concentrated trace metals-grade nitric acid was added to the sample, which was warmed on a hot plate until the ash dissolved. This solution was made up to 10 mL or 25 mL in a volumetric flask with deionized type I water. Ni and V were determined by inductively coupled plasma (ICP) spectrometry using a Thermo Elemental AtomScan Advantage ICP spectrometer. A digestion blank, a duplicate sample, and a quality control sample of Unitar Round Robin Athabasca Bitumen were digested with each batch. Elemental analyses (CHNS) were performed by Huffman Labs, Golden, Colorado.

## **RESULTS AND DISCUSSION**

### **Pyrolysis Experiments**

The residua used in the current study are Boscan, MaxCL2 (Conoco), Redwater, B.C., and Lloydminster residua. Most of the pyrolysis work was performed with the first three residua, and only limited pyrolysis experiments were conducted with Lloydminster residuum. Pyrolysis results, especially at the lower temperature employed in the current study, 400 °C (752 °F), require very careful time and temperature control. This is because the coke formation reactions are 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 significant differences in the amount of coke formed. This requires very careful and repeatable operation of the equipment. In the current study, pyrolysis experiments were performed at 400 °C (752 °F) in larger reactor tubes (135 cc) rather than the 20-cc tubes we have used in the past for precision time studies. The larger reactor tubes generated about 50 g of product oil for each pyrolysis condition to provide sufficient sample for subsequent characterization. These larger reactor tubes do not allow for as precise a control of total heat flux to the sample as the smaller tubes; however, the purpose of the current study was to generate sufficient material portions for characterization rather than to document the effect of a particular time on changes in the oil. Characterization results were related directly to the WRI Coking Index values for the corresponding materials, and not to precise pyrolysis residence times.

### **WRI Coking Indexes**

Asphaltene content, solubility data, and AFT data for original and pyrolyzed residua are provided in Table 1. The WRI Coking Index values include Y/X, which is the weight percent of heptane asphaltene soluble in cyclohexane (Y) divided by the weight percent of heptane asphaltene in the oil (X). The other Coking Index values are the ratios of AFT parameters,  $p_a/C_{min}$ . The Coking Index results are provided in Table 2. The values for the four unpyrolyzed residua are all above unity, indicating that the residua are far from producing coke on the coke formation

induction time line (Schabron et al. 2001a). In general, the data show decreasing Coking Index values with increased residence time. However, since the heat transfer is difficult to control for the larger reactor tubes, this was not always the case. For example, the Coking Index data for Redwater, B.C. indicates that the 30-minute product oil was pyrolyzed more severely than the 45-minute material. The data in Table 1 are ranked in decreasing values of  $p_a/C_{\min}$  to reflect increasing severity of pyrolysis.

### **NMR Images of Pyrolyzed Residua**

NMR imaging experiments were conducted on the three residua samples that were pyrolyzed at 400 °C (752 °F), well beyond the point of coke formation. The objective of these experiments was to demonstrate the presence of two immiscible liquid phases in these materials. The NMR images of pyrolyzed residua are shown in Figure 1. For each pyrolysis time, only the fourth slice of an eight-slice image set is shown. This slice corresponds to a cross section approximately through the longitudinal center of the cylindrical sample vial.

The set of images in Figure 1 is for the longest pyrolysis residence times for Boscan, MacCL2, and Redwater, B.C. residua. Images taken at these residence times are more easily formed and visualized due to the decreased viscosity resulting from the pyrolysis cracking reactions. 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. Two immiscible phases with different relaxation times are visible in the images. Once coke begins to form, phase separation occurs (Schabron et al. 2001a). During pyrolysis, hydrogen is abstracted from the residua to stabilize and reduce the molecular weights of the products. The lighter contrast phase at the top of the samples is probably due to the predominance of less viscous, lower molecular weight materials.

### **Wide-Line NMR Relaxation Time Measurements**

The wide-line Free Induction Decay (FID) is the basic measurement made in pulsed NMR. In these measurements, the response of the protons in the residua sample to a radio frequency pulse is measured. The FID represents the rate at which the magnetization from the protons in the sample decays following application of an RF pulse. To compensate for inhomogeneities in the magnet that might compromise the relaxation time measurements, the spin-echo method was used for the relaxation time measurements. As an example, echo decay profile curves of original and pyrolyzed Boscan residuum are shown in Figure 2. The lengthening of the decay curves with increasing pyrolysis time is due to decreased viscosity of the pyrolyzed material at longer residence times.

The characteristic time for the decay is usually 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  $T_2$ . We have chosen to fit the residua FIDs with a two-component exponential function of the form,

$$M(t) = M_a \exp(-t/T_{2a}) + M_b \exp(-t/T_{2b}) \quad (9)$$

where  $M_a$  and  $M_b$  are the populations of protons in environments a and b, and  $T_{2a}$  and  $T_{2b}$  are the relaxation times for those protons. The relaxation time data are given in Table 2. 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. The two populations can be considered as a less viscous material (long decay time) in the presence of a more viscous component (short decay time).

Relaxation decay times were plotted against the WRI Coking Indexes to evaluate possible relationships between the values (Figure 3). In general, coking has occurred below the Y/X threshold value of 1 and the  $p_a/C_{\min}$  threshold value of 0.2, with two exceptions. The Y/X value for the MaxCL2 residuum pyrolyzed for 30 minutes was 0.7, and no coke was observed; however, a 40-minute pyrolysis time yielded 0.1 wt % coke. A more significant exception is the  $p_a/C_{\min}$  value for the Redwater, B.C. residuum pyrolyzed for 60 minutes, which was 0.55. This material contained 0.1 wt % coke. The AFT titration is difficult to perform on residua that have been pyrolyzed beyond the point of coke formation. Since these are multiphase systems, the  $p_a/C_{\min}$  can often be erratic, and thus have no meaning.

The plots show definite trends between the Coking Indexes and the signal decay times. Significant scattering of the data is evident in both the short and long decay correlation curves with Y/X and the long decay correlation curve with  $p_a/C_{\min}$  (Figure 3). The least amount of scattering is observed in the short decay time correlation with  $p_a/C_{\min}$ , which appears to provide the best correlation. In a dispersed particle system modeled as consisting of two components, the short decay time component could be considered to consist of the bound material, and the long component could be considered as the unbound solvent phase. The decay time data are an indicator of the viscosity of the material at ambient room temperature. At elevated temperature in a refinery operation such as vacuum distillation, residua materials have very low viscosity, and the short and long decay time pattern observed at room temperature probably does exist. Thus, a correlation with NMR proton relaxation time measurements and the Coking Indexes at process temperatures such as 340 °C (644 °F) or higher is not expected.

### **Heat Capacity Measurements**

Some initial prior experiments with Lloydminster residuum suggested that heat capacity measurements could correlate with the Coking Indexes for original and pyrolyzed residua. A good correlation for this residuum was evident (Schabron et al. 2002b). To explore this further, heat

capacity measurements were made for Redwater, B.C. and MaxCL2 original and pyrolyzed product oils. The data are provided in Table 2. The data do not show a correlation between the Coking Indexes and heat capacity for the Redwater, B.C. and MaxCL2 original and pyrolyzed residua. These pyrolyzed product oils also contain lighter product oils from cracking reactions. Additional experiments will be performed in the future with pyrolyzed residua from which the lighter distillate product oils have been removed.

### **Ultrasonic Attenuation**

Ultrasonic spectroscopy is a technique used to detect various types of materials in a wide variety of configurations. It is used to establish the presence of water in oil, evaluate liquid levels and the presence of the interface boundaries of two immiscible liquids, and measure density or viscosity differences in liquids. It is used to measure various properties of emulsions and slurries, such as particle sizes and amounts (McClements 1998). It is used to measure properties of gels, and to assess the integrity of various solid materials relative to corrosion, cracking, and compositional changes. It is also used in agricultural and food applications to measure product consistency, such as for cheese, butter, and vegetable oil. Ultrasonic spectroscopy is becoming widely used in the chemicals industry as an on-line process control tool.

There are many applications of ultrasonic spectroscopy that have not yet been explored. One application not yet studied pertains to petroleum residua, which consist of ordered dispersed particle systems that determine their viscoelastic behavior. For example, ultrasonic spectroscopy could be used to detect the changes in the ordered structure leading to deposition phenomena when residua are heated both below and above pyrolysis temperatures. Thus, it could be used to gauge low-temperature blending and fouling. Ultrasonic spectroscopy is a non-invasive, non-destructive technique having various measurement parameters, but no moving mechanical parts. The technique can be easily applied in its modular form to chemical processes, even in hostile environments.

In the current study, data were obtained from three different vendors of ultrasonic instrumentation to evaluate the potential for ultrasonic spectroscopy to correlate with the WRI Coking Indexes. Data for Lloydminster were provided by Matec Instrument Companies, Northboro, Massachusetts. Data for Redwater, B.C. were provided by Dr. Wes Cobb, University of Denver Research Institute, Denver, Colorado. Data for Boscan were provided by Ultrasonic Scientific, Dublin, Ireland.

An ordered system with suspended or dispersed particles present absorbs and scatters more ultrasonic energy than a similar system with less ordering and/or fewer suspended particles. Pyrolysis destroys the ordering of a residuum system. Ultrasonic attenuation data for original and pyrolyzed petroleum residua at 1–3 MHz frequency are provided in Table 3. As mentioned, the data were generated by three different vendors of ultrasonic equipment, so the results for the different residua cannot be compared directly with each other. Cell pathlength, signal profiles, and applied

signal energies varied. However, the trend is clear: ultrasonic attenuation decreases with increasing pyrolysis time, as the ordered system is being destroyed. The ultrasonic attenuation data for Lloydminster residuum are plotted against the WRI Coking Indexes in Figure 4. The results show that this technique has the potential to provide rapid non-intrusive measurement that correlated with the WRI Coking Indexes. This could lead to the development of an on-line process control system to improve refinery distillation efficiency and minimize undesired fouling incidents. This will be studied further under a variety of conditions.

### **Characterization of Product Oils and Upper and Lower Immiscible Product Phases**

Portions of 50 g of Boscan residuum were pyrolyzed for 25- and 55-minute residence times at 400 °C (752 °F). The amount of coke and volatiles and the WRI Coking Indexes for the starting and product oils are listed in Table 4. The 25-minute product oil did not contain any coke, and the 55-minute product oil contained on average 6.4 wt % coke. A 30-mL NMR vial containing the two phases from the 55-minute product oil (Figure 1c) was frozen and sliced in two at the boundary mark with a Norton Clipper circular masonry saw with a diamond cutting blade. In this manner the upper and lower phase immiscible product oils were isolated for subsequent characterization. There is no substantial difference in n-heptane asphaltenes or coke content between the upper and lower phases. The data for coke and asphaltenes are somewhat higher than for a different batch of whole 55-minute product oil. This is probably due to some reactions continuing in the product oils and changes in the layered oil samples during the experimental workup.

The analyses included determination of elemental content (CHNS), metals (Ni,V), and porphyrins. Data for the original and pyrolyzed product oils are provided in Table 5. The H/C ratios of the original unpyrolyzed oil and the heptane asphaltenes are 1.5 and 1.2, respectively. As pyrolysis progresses, the H/C ratio of the whole product oil is nearly constant, at 1.4–1.5. As expected, the H/C ratio for the asphaltenes decreases significantly with increasing residence time. From the elemental total values, it is apparent that the asphaltenes probably contain about 2 wt % oxygen by difference. The nitrogen content of asphaltenes and coke is 2–5 times higher than in the corresponding maltenes. The sulfur content of asphaltenes and coke is only slightly higher than in the corresponding maltenes, about 1–2 wt %. The elemental composition of cyclohexane-soluble and insoluble asphaltenes is similar for a given residence time.

Elemental analysis data are essentially identical within experimental error for the upper and lower 55-minute product oil phases. Despite this, the fact that they are imaged as two phases by NMR suggests that there are actually some differences between these materials that are not discernable by bulk elemental content. The results show no significant differences within experimental error for elemental content between the upper and lower phases from the 55-minute pyrolysis product oil.

Pyrolysis destroys the porphyrin structure that absorbs light at 410 nm, and the porphyrin content of the maltenes is lowered during pyrolysis (Table 5). The porphyrins content of the original and pyrolyzed asphaltenes is about the same. The porphyrins content of the upper and lower phases from the 55-minute product oil are the same. The numerical value of 230 mg/kg in Table 1 as compared to the bulk 55-minute product oil value of 180 mg/kg is due to the analysis of different pyrolysis batches. The vanadium content of any of the oils or subfractions is about ten times greater than the nickel content of the particular oil or subfraction. Metals (Ni,V) are transferred from the maltene phases into the asphaltenes. The metals content of the cyclohexane-soluble and insoluble asphaltenes is similar for the unpyrolyzed oil. For the 25-minute pyrolysis oil, the metals content of the cyclohexane-insoluble asphaltenes is about 64% higher than the cyclohexane-soluble asphaltene material. The metals are concentrated from the asphaltenes into the coke once coke begins to form. These observations are consistent with results of Reynolds and Biggs (1985) in earlier work. The results show a potential difference for metals content between the upper and lower phases from the 55-minute pyrolysis product oil. The lower phase appears to contain about 18% more nickel and vanadium than the upper phase. Experimental error of these measurements is usually less than 5% difference. Additional testing will be done in the future to explore this further. In addition, spectroscopic or chromatographic analyses for the upper and lower phases will be pursued to see what differences might be evident.

### **Future Work**

The pyrolyzed residua materials studied in the current work were obtained from sealed reactor tubes. Thus, the samples are representative of visbroken product oils. Additional work needs to be performed with residua that have the lighter product, or distillate oils removed under vacuum distillate during pyrolysis. This will provide samples that are analogous to vacuum bottoms during distillation processes. In prior work WRI demonstrated that the Coking Indexes apply to both visbroken oils and distillate bottom types of product materials; however, heat capacity measurements and ultrasonic attenuation need to be measured for distillate bottom materials from pyrolysis for various residua sources. In the current work, ultrasonic attenuation data were obtained from three vendors of equipment. In future work, ultrasonic spectroscopy equipment will be obtained and all measurements will be made in an identical manner. This will allow the data to be compared for a variety of residua materials and pyrolysis conditions.

## **CONCLUSIONS**

Pyrolysis experiments were conducted with four residua at 400 °C (752 °F) at various residence times. Wt % coke and gaseous products were measured for the product oils and the WRI Coking Indexes were determined. Measurements were made using techniques that could correlate with the Coking Indexes. These included NMR imaging, spin-echo proton nuclear magnetic resonance spectroscopy, heat capacity at 280 °C (536 °F), and ultrasonic attenuation. NMR imaging showed the presence of two immiscible liquid phases for residua pyrolyzed beyond the



point of coke formation. NMR spin-echo proton magnetization decay results were interpreted in terms of a two-component system, with short (viscous material) and long (less viscous material) signal decay times. The decay time data showed correlations with the Coking Indexes; however, since decay times are a function of material viscosity, the correlations are not expected to exist at elevated process temperatures where residua materials have low viscosity. Heat capacity measurements for original and pyrolyzed residua showed no correlation with the Coking Indexes. Ultrasonic attenuation data provided by three instrument vendors for three different sets of original and pyrolyzed residua showed significant differences between the original and pyrolyzed materials within each set. As pyrolysis progressed, the ultrasonic attenuation near 1 MHz decreased significantly. In future work, ultrasonic instrumentation will be acquired and used to generate data for a variety of residua materials prior to and after pyrolysis. Although the initial development of the Coking Indexes was with pyrolyzed stripper bottom materials, most of the recent Coking Index data generated have been with residua pyrolyzed in sealed reactor tubes. These product materials contain lighter oils, which would be removed during refinery distillation processes. In the future, additional samples will be generated with the removal of the lighter materials prior to determination of the Coking Indexes and additional data that could correspond to the Coking Indexes will be obtained.

The upper and lower phases visualized by NMRI from Boscan residuum pyrolyzed at 400 °C (752 °F) for 55 minutes, beyond the point of coke formation, were isolated for subsequent characterization. The original and product oils were separated into asphaltene and maltene fractions using n-heptane. The heptane maltenes, heptane asphaltenes, and the portion of heptane asphaltenes soluble in cyclohexane were measured and characterized. Characterization included determination of the WRI Coking Indexes, elemental content (CHNS), metals (Ni,V), and porphyrins. There were no differences in the elemental analyses results for the upper and lower phase product oils; however, the lower phase seems to contain about 18% more nickel and vanadium than the upper phase. Additional spectroscopic or chromatographic analyses will be pursued to see what differences might be evident.

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**Table 1. Asphaltene Content, Solubility Data, and AFT Data at Various Pyrolysis Residence Times at 400 °C (752 °F)**

<u>Residuum</u>	<u>X: Wt % n-C7</u>	<u>Y: Wt % CyC6</u>	<u>AFT Parameters</u>		<u>Weight Percent</u>	
	<u>Asphaltenes</u>	<u>Sol. Asphaltenes</u>	<u>p<sub>a</sub></u>	<u>C<sub>min</sub></u>	<u>Coke</u>	<u>Volatiles</u>
<u>Boscan</u>						
0 min.	18.4	37.3, 34.6	0.659,0.666	0.407,0.476	<0.05	-
10	16.5	27.5	0.581	0.486	<0.05	0.6
20	16.5	18.2	0.452	0.941	<0.05	1.2
30	17.7	18.3, 18.2	0.472	0.920	<0.05	1.1
40	19.2	8.5	0.198	1.39	0.2	2.1
55	13.0,14.0	4.8	nd	nd	6.9,5.9	2.2
<u>MaxCL2</u>						
0 min.	17.8	39.2, 41.1	0.641	0.444	<0.05	-
10	17.0	39.6	0.623	0.606	<0.05	0.2
20	18.0	19.5	0.443	0.855	<0.05	1.0
30	20.3	13.3	0.372	1.06	<0.05	1.2
40	21.7	10.3	0.249	1.94	0.1	1.9
55	21.6	7.6	0.199	1.42	0.3	1.6
<u>Redwater, B.C.</u>						
0 min.	6.2,6.1,6.2	34.2,34.1,35.3	0.668	0.563	<0.05	-
15	11.6	26.8	0.564	0.912	<0.05	0.5
45	12.3,13.0	25.5	0.494	1.04	<0.05	0.7
30	13.5	15.2	0.445	1.65	<0.05	0.9
60	13.5	9.8	0.465	0.841	0.1	1.1
75	14.4	6.9	0.210	1.31	2.1	1.5
<u>Lloydminster</u>						
0 min.	16.8	51.2	0.677,0.660	0.54,0.60	<0.05	-
20a	15.1,16.2	19.8	0.41	1.14	<0.05	-
20b	16.4	18.6	0.28	1.82	<0.05	-

**Table 2. WRI Coking Indexes, NMR Relaxation Data, and Heat Capacities at Various Pyrolysis Residence Times at 400 °C (752 °F)**

<u>Residuum</u>	<u>Coking Indexes</u>		<u>Wide Line NMR Proton Decay Data</u>				<u>Heat Capacity</u>
	<u>Y/X</u>	<u>p<sub>a</sub>/C<sub>min</sub></u>	<u>Populations</u>		<u>Relaxation Times*10<sup>4</sup> sec.</u>		<u>C<sub>p</sub>, 280 °C</u>
			<u>Ms</u>	<u>Ml</u>	<u>T2s</u>	<u>T2l</u>	
<u>Boscan</u>							
0 min.	2.0	1.51	0.60	0.40	0.61	1.69	-
10	1.7	1.20	0.48	0.52	1.10	2.75	-
20	1.1	0.48	0.47	0.53	1.72	5.05	-
30	1.0	0.51	0.46	0.54	1.70	5.31	-
40 (coke)	0.4	0.14	0.42	0.48	2.89	9.89	-
55 (coke)	0.4	-	0.45	0.54	4.80	18.1	-
<u>MaxCL2</u>							
0 min.	2.3	1.44	0.68	0.32	0.58	1.85	2.55
10	2.3	1.03	0.53	0.47	0.75	2.44	2.53
20	1.1	0.51	0.47	0.53	1.68	6.70	2.42
30	0.7	0.35	0.52	0.48	2.88	10.0	2.52
40 (coke)	0.5	0.13	0.45	0.55	4.09	15.7	2.21
55 (coke)	0.4	0.14	0.52	0.48	4.65	16.4	2.74
<u>Redwater, B.C.</u>							
0 min.	5.6	1.20	0.57	0.43	0.72	2.27	2.65
15	2.3	0.62	0.51	0.49	1.77	6.85	2.67
45	2.0	0.47	0.58	0.42	3.38	11.2	-
30	1.1	0.27	0.47	0.53	3.31	13.1	2.72
60 (coke)	0.7	0.55	0.72	0.28	5.26	15.0	2.26
75 (coke)	0.5	0.16	0.37	0.63	5.94	35.2	-

**Table 3. Ultrasonic Attenuation (1–3 MHz) and WRI Coking Indexes for Original Residua and Residua Pyrolyzed at 400 °C (752 °F)**

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<u>Residuum</u>	<u>Pyrolysis Time, min.</u>	<u>WRI Coking Indexes</u>		<u>US Attenuation Compared To Original Residuum, Neper/cm</u>
		<u>Y/X</u>	<u><math>p_a/C_{min}</math></u>	
Boscan (2–3 MHz)	0	2.0	1.51	0.00
	20	1.1	0.48	-0.55
Redwater,B.C. (1 MHz)	0	5.6	1.20	0.00
	15	2.3	0.62	-0.31
Lloydminster (1.3 MHz)	0	3.0	1.12	0.00
	20	1.3	0.36	-1.85
	20	1.1	0.15	-2.11

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**Table 4. Asphaltene Solubility Data, AFT Data, and Coking Indexes for Original and Pyrolyzed (400 °C, 752 °F) Boscan Residuum**

Boscan Residuum	X: Wt % n-C7	Y: Wt % CyC6	AFT Parameters		Weight Percent		WRI Coking Indexes	
	<u>Asphaltenes</u>	<u>Sol. Asphaltenes</u>	$p_a$	$C_{min}$	<u>Coke</u>	<u>Volatiles</u>	<u>Y/X</u>	$p_a/C_{min}$
0 min.	18.4,18.4, 18.3	37.3, 34.6, 41.6,36.3	0.659,0.666	0.407,0.476	<0.05	-	2.04	1.51
25 min.	18.9,17.9	18.2,14.7	0.463	0.919	<0.05	1.4	0.89	0.49
55 min.	13.0,14.0	4.8,5.0	nd	nd	6.9,5.9	2.2,2.2	0.36	nd
Upper Layer								
0.28 vol. frac.	18.3 <sup>a</sup>	-	-	-	9.7	-	-	nd
Lower Layer								
0.72 vol. frac.	18.8 <sup>a</sup>	-	-	-	7.7	-	-	nd

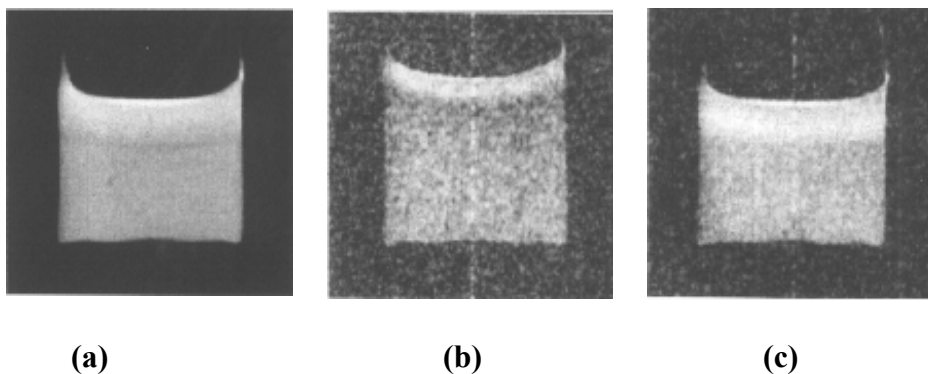
<sup>a</sup> Asphaltene content following removal of toluene and loss of about 24 wt % of volatile product oils



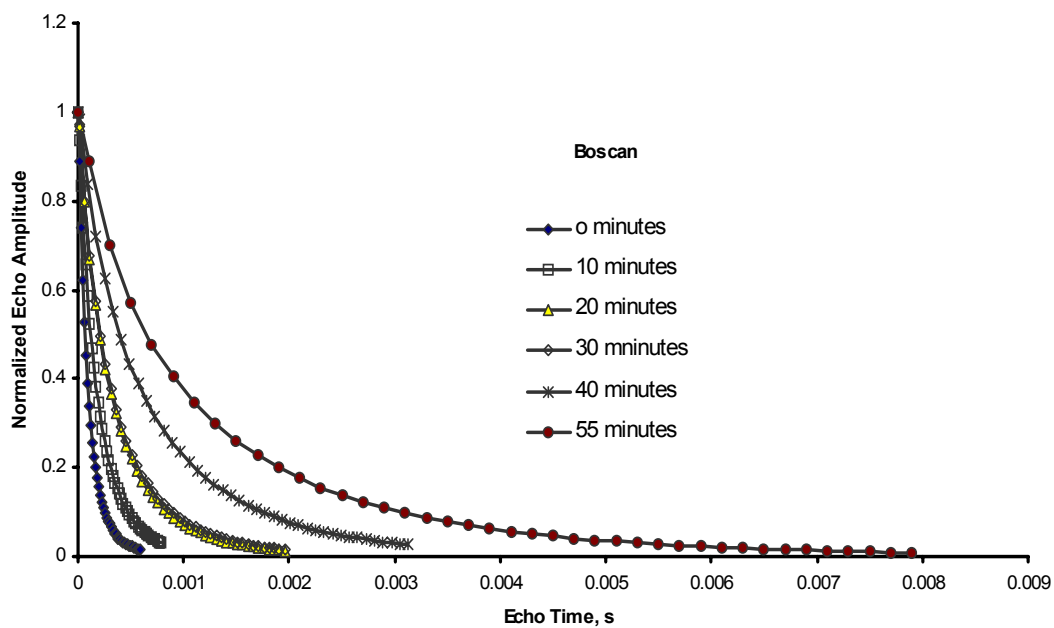
**Table 5. Elemental and Metals Analysis Data for Original and Pyrolyzed (400 °C, 752 °F) Boscan Residuum and Fractions**

<u>Boscan Residuum</u>	<u>Weight Fraction</u>	<u>Weight Percent</u>					<u>Total</u>	<u>H/C Ratio</u>	<u>Metals and Porphyrins, mg/kg</u>		
		<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>				<u>Ni</u>	<u>V</u>	<u>Porphyrins</u>
<u>0 min.</u>	1.000	83.1	10.3	0.8	5.5	99.7	1.5	130	1300	480	
Maltenes	0.816	83.2	10.6	0.5	5.0	99.3	1.5	59	530	350	
Asphaltenes	0.184	81.6	7.9	1.8	6.6	97.9	1.2	450	4700	1100	
<i>CyC6 Sol.</i>	<i>0.360</i>	81.4	8.0	1.7	-	-	1.2	390	4000	1100	
<i>CyC6 Insol.</i>	<i>0.640</i>	81.7	7.8	1.9	6.6	98.0	1.2	470	4800	1000	
Balance to Whole	1.000	82.9	10.1	0.7	5.3	-	1.5	130	1300	490	
<u>25 min.</u>	1.000	83.6	9.7	0.5	5.0	98.8	1.4	140	1300	310	
Maltenes	0.811	83.9	10.8	0.4	4.5	99.6	1.5	38	300	180	
Asphaltenes	0.189	82.3	6.7	2.3	6.4	97.7	0.98	580	6100	1000	
<i>CyC6 Sol.</i>	<i>0.182</i>	82.5	7.2	1.9	-	-	1.0	370	4100	1100	
<i>CyC6 Insol.</i>	<i>0.818</i>	82.3	6.5	2.4	6.5	97.7	0.95	610	6700	1000	
Balance to Whole	1.000	83.6	10.0	0.8	4.8	-	1.4	140	1400	330	
<u>55 min.</u>	1.000	84.3	9.5	0.8	4.8	99.4	1.4	140	1400	180	
Maltenes	0.801	83.8	10.6	0.4	4.1	98.9	1.5	21	120	36	
Asphaltenes	0.135	83.2	6.2	2.2	5.9	97.5	0.89	450	5000	1000	
<i>CyC6 Sol.</i>	<i>0.048</i>	-	-	-	-	-	-	-	-	-	
<i>CyC6 Insol.</i>	<i>0.952</i>	-	-	-	-	-	-	-	-	-	
Coke	0.064	83.2	5.4	2.6	6.2	97.4	0.78	770	7700	-	
Balance to Whole	1.000	83.6	9.7	0.8	4.5	-	1.4	130	1300	160	
<u>55 min.</u>											
<i>Upper Layer</i>	0.28 <sup>a</sup>	84.3	8.9	0.9	-	-	1.3	110	1100	230	
<i>Lower Layer</i>	0.72 <sup>a</sup>	84.5	8.9	0.9	-	-	1.3	130	1300	230	

<sup>a</sup> Volume fraction

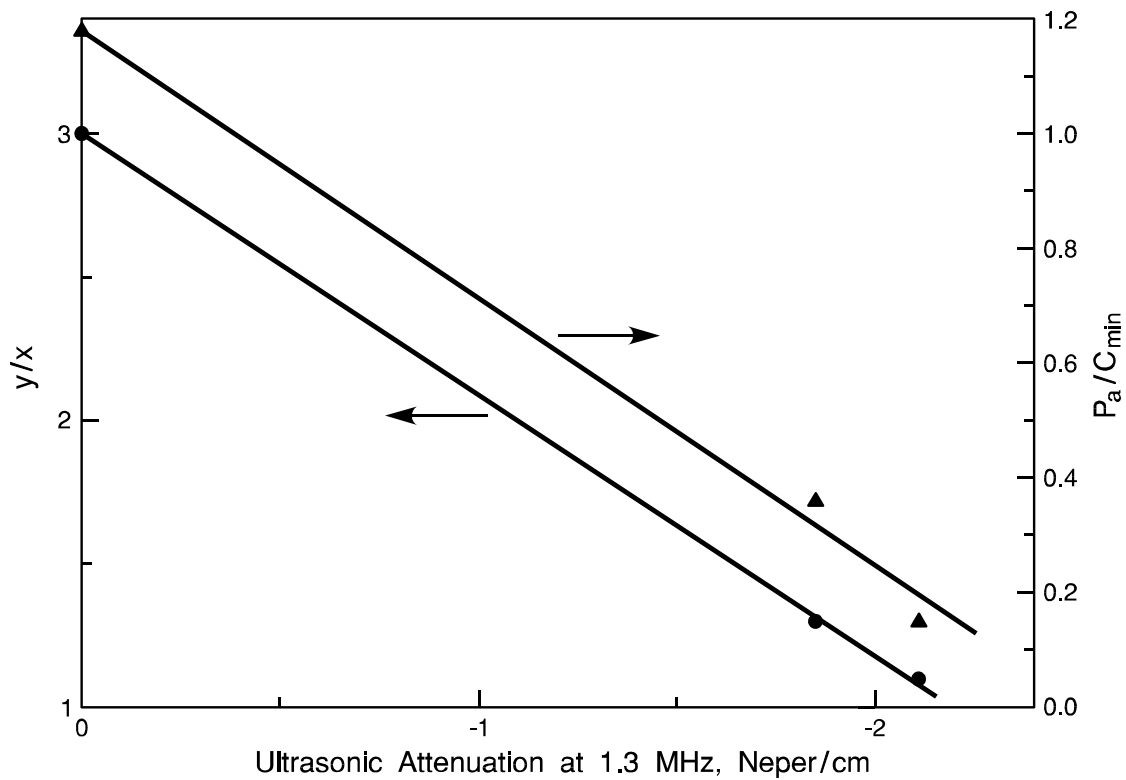


**Figure 1. NMR Images of Residua Pyrolyzed at 400 °C: (a) Redwater, B.C. (75 min), (b) MaxCL2 (55 min), (c) Boscan (55 min)**



**Figure 2. NMR Proton Spin-Echo Decay Profile for Boscan Residuum**





**Figure 4. WRI Coking Indexes vs Ultrasonic Attenuation for Original and Pyrolyzed Lloydminster Residuum**