

# analytical chemistry feature

## Complex Fluid Analysis with the Advanced Distillation Curve Approach

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**An improved method for measuring distillation curves reveals the physicochemical properties of complex fluids such as fuels.**

In their landmark review, Marshall and Rodgers assert that the application of ultrahigh resolution MS to complex fluids made possible the new field of petroleomics.<sup>1</sup> Petroleomics, according to these authors, is the “relationship between the chemical composition of a fossil fuel and its properties and reactivity”. Indeed, in recent years, many analytical methods have been applied to crude oils, the finished fuels derived from them, and the waste products we generate in the course of using them.

The analytical methods that have been applied to crude oils and finished fuels are too numerous to list in detail here.<sup>2</sup> They include nearly all types of gas, liquid, and supercritical fluid chromatography coupled with virtually all types of detectors and sampling methods. Almost every spectroscopic method has been applied as well. Ultrahigh resolution mass spectroscopic methods, such as Fourier transform ion cyclotron resonance (FTICR), are perhaps the pinnacle of analytical techniques applied to such complex fluids.<sup>3</sup> Current limitations in the advancement of petroleomics, as asserted by Marshall and Rodgers, include quantitation of species, modeling, and informatics. Indeed, most of the strikingly successful work has been in very detailed compound identification. Lacking is the relationship between the chemical composition and the properties of the fluid, specifically the physicochemical properties. Most papers reporting petroleomics compositional details imply that once chemical composition is known, physicochemical properties must follow. An inherent limitation of this notion results from the intermolecular interactions that occur among species present in a complex fluid such as a crude oil or finished fuel. Thus, fundamental physical properties (thermodynamic and transport) have not been easily obtainable from a composition suite, however detailed.

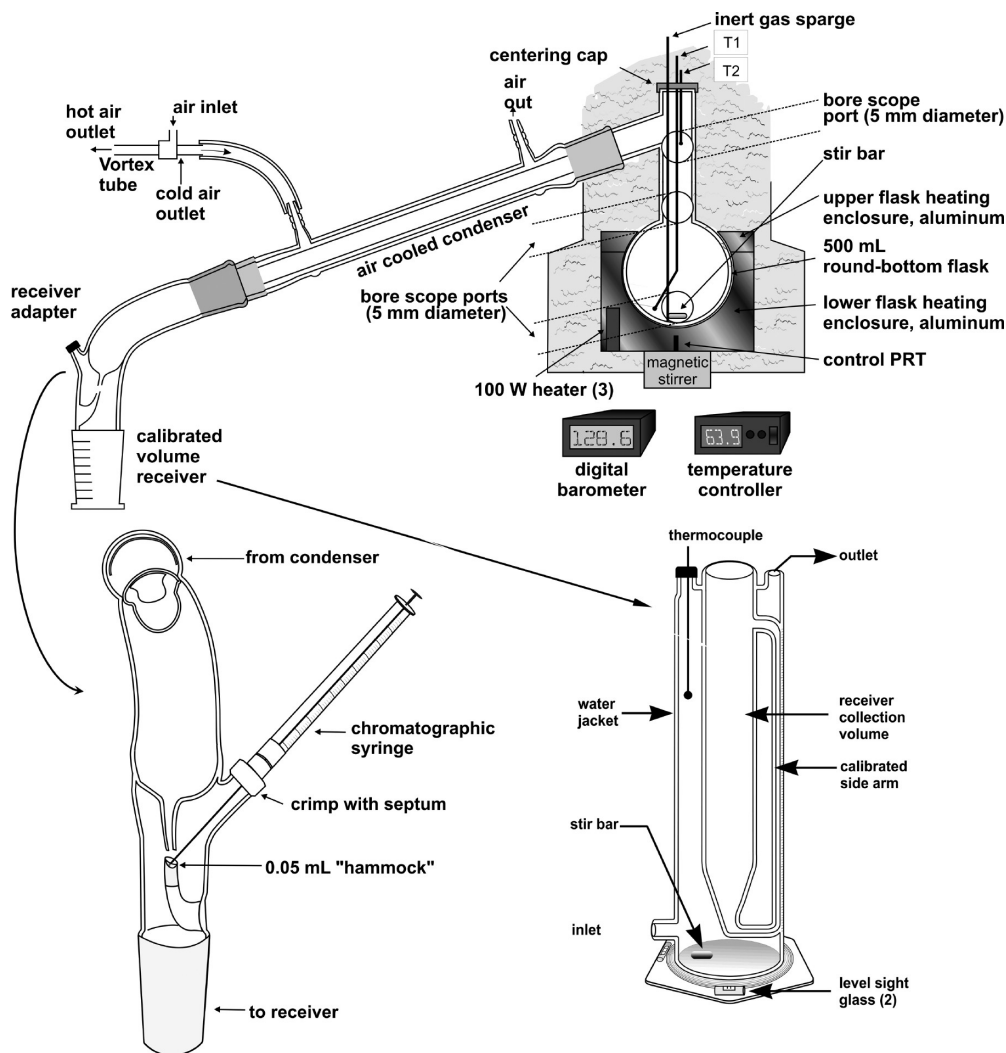
To at least approximately establish the relationship of petroleomics to physicochemical properties, we recently introduced an improved method for measuring distillation curves of complex



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fluids. The distillation curve provides the only practical avenue to assess the vapor/liquid equilibrium (volatility) of a complex mixture. The classical distillation or boiling curve of a complex fluid is a graph of boiling temperature versus volume fraction distilled, a procedure embodied in the ASTM D-86 standard. Unfortunately, this method suffers from significant limitations.<sup>4</sup> Measurements made with this approach have no theoretical significance; the initial boiling temperatures are systematically incorrect; and the uncertainties in temperature, volume, and pressure are high. The major historical value of the method is that everyone does it the same way.

Our improved method, called the composition-explicit or advanced distillation curve (ADC), is a significant improvement, featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state; (3)



**Figure 1.** Schematic diagram of the apparatus used for an ADC measurement. Expanded views of the sampling adapter and the stabilized receiver are shown in the lower half of the figure.

temperature, volume, and pressure measurements of low uncertainty; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6) trace chemical analysis of each distillate fraction;<sup>5–16</sup> and (7) corrosivity assessment of each distillate fraction.<sup>5–16</sup> As an analytical strategy for complex fluids, the ADC presents the analyst with a sample that has been simplified on the basis of a physicochemical property (vapor/liquid equilibrium). One can often apply simpler analytical methods to fractions to avoid complexities such as multiple chromatographic columns, backflushing, etc. We have applied the ADC to mixtures that include simple n-alkanes,<sup>9</sup> simple azeotropes,<sup>17</sup> gas turbine fuels,<sup>6,8,10,18–20</sup> diesel and biodiesel fuels,<sup>21–25</sup> gasolines,<sup>7,26,27</sup> rocket propellants,<sup>10,28,29</sup> and crude oils.<sup>13,14,16,30</sup>

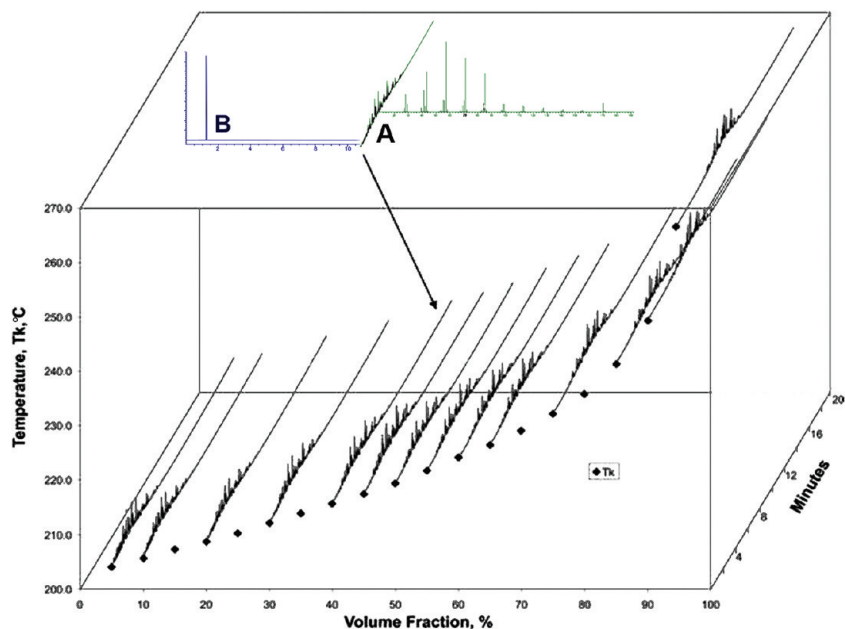
### ADVANCED DISTILLATION CURVE METHOD

The apparatus and procedure for the measurement of the ADC have been discussed in detail elsewhere; only a brief description will be provided here.<sup>9,10</sup> The apparatus is depicted schematically in Figure 1. The distillation flask is placed in an aluminum heating jacket contoured to fit the flask. Heaters are controlled by a model predictive proportional-integral-derivative (PID) controller that

applies a precise thermal profile to the fluid. Three observation ports are provided in the insulation to observe the stirred fluid with a flexible, illuminated borescope.

Above the distillation flask, a centering adapter holds two thermally tempered, calibrated thermocouples. One thermocouple (T1) is submerged in the fluid and the other (T2) is centered at the low point of distillate take-off. Also in the head is an inert gas capillary line for use with thermally-unstable fluids. Distillate taken off the flask enters a forced-air condenser chilled with a vortex tube.<sup>31–33</sup> Following the condenser, the distillate enters an adapter that allows instantaneous sampling of distillate for analysis. When the sample leaves the adapter, it flows into the calibrated, level-stabilized receiver for a precise volume measurement.

To measure a distillation curve, fluid (40–200 mL) is placed in the flask, and the heating profile begins. The profile typically has the sigmoidal shape of a distillation curve but continuously leads the fluid in temperature by ~20 °C.<sup>15</sup> For each ADC measurement, we can record a data grid consisting of the temperature measured in the fluid ( $T_k$ , measured with T1), the temperature in the head ( $T_h$ , measured with T2), the corresponding fluid volume, the elapsed time, and the external (atmospheric) pressure. The estimated uncertainty (with a



**Figure 2.** A distillation curve for RP-1 showing  $T_k$  versus volume fraction in the  $x$ - $y$  plane and the composition as measured by GC along the  $z$ -axis, represented as retention time versus peak intensity. Inset (A) shows the mass spectrum of the major peak of the 40% fraction, n-dodecane; Inset (B) shows a total sulfur chromatographic peak.

coverage factor  $k = 2$ ) in the  $T_k$  and  $T_h$  is typically  $<0.5$  °C, the uncertainty in the volume is typically 0.05 mL, and the uncertainty in the pressure measurement (assessed by automatically logging a pressure measurement every 15 seconds) is typically 0.001 kPa. We typically adjust the measured temperatures for the effects of atmospheric pressure (or elevation) with the Sydney Young equation.<sup>34,35</sup>

Along with measuring these data, one withdraws a sample for detailed analysis. This procedure provides access to the detailed composition, energy content, corrosivity, etc. that correspond to each datum in the grid.

## EXAMPLES OF MEASUREMENTS AND APPLICATIONS

**Detailed Analysis: Rocket Propellant.** Though modern rocket motors can operate on a liquid or a solid fuel package, the former is more easily controlled and flexible. This led to the development in the 1950s of RP-1 kerosene,<sup>36</sup> which continues to be widely used. The desire in recent years to reuse rocket motors many times has led to reformulations of RP-1 with low sulfur, olefin, and aromatic content.<sup>37–48</sup> Reformulation has required a reassessment of the physicochemical properties; we have used the ADC metrology for this purpose.<sup>49</sup> We show in Figure 2 a distillation curve of RP-1 with the composition measurement superimposed. First, focusing on the plot of  $T_k$  versus volume fraction, we note that the plot shape is a subtle sigmoid, which is characteristic of a complex fluid with many components. ADC data such as these are used in the design and specification of many engine operational parameters and in equation of state development. Because the  $T_k$  data are thermodynamic state points, the plot represents a cut through the fluid phase diagram that has theoretical meaning.

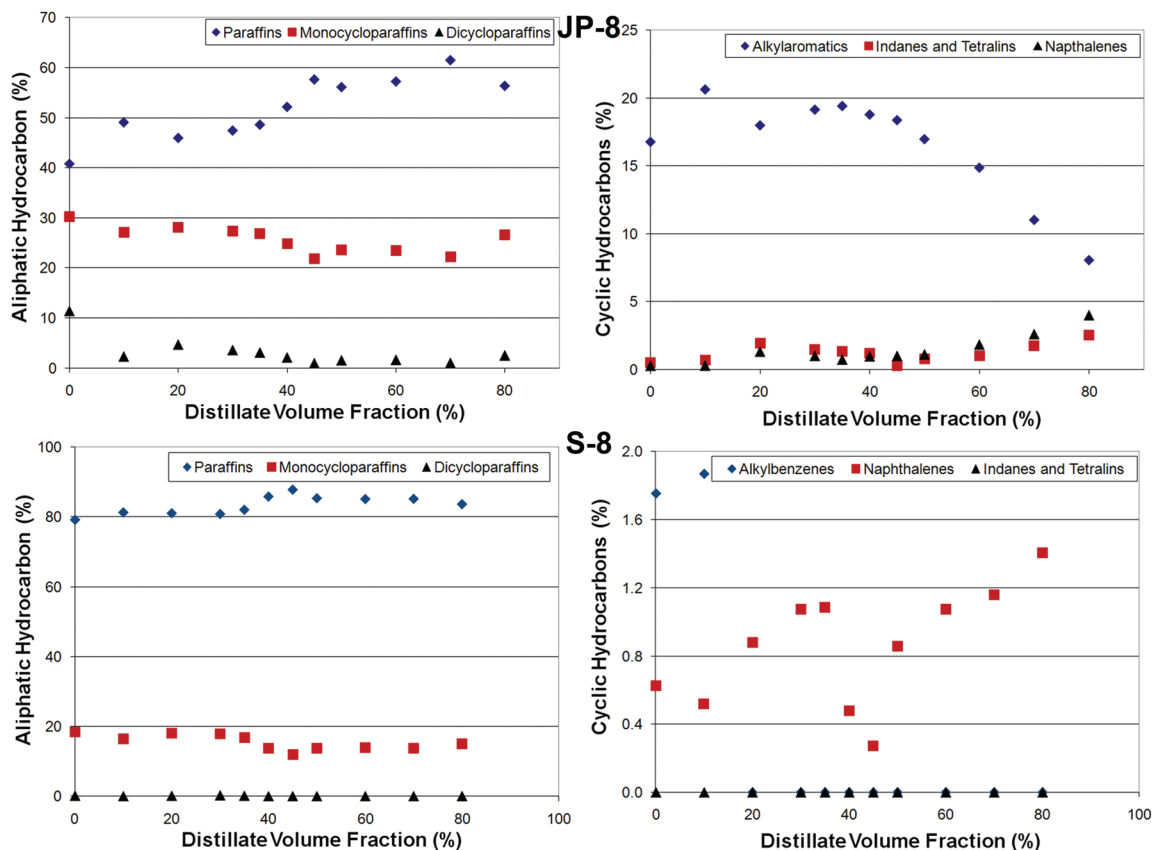
The composition-explicit channel provides additional information for the data grid. In Figure 2, the composition was measured by GC/MS. Additional detail is shown in the insets: (A) the mass

spectrum of the largest peak is identified as n-dodecane and (B) a sulfur analysis is done with a post-column split (a chromatographic fitting made from two sections of fused silica tubing) to a sulfur chemiluminescence detector (GC/SCD). What is most significant is that this compositional information is now joined with the temperature grid measurement discussed above; the temperature, pressure, and composition can all be modeled with an equation of state.

**Hydrocarbon Type Analysis: Aviation Fuels.** A detailed analysis for each line of the data grid is not always necessary. It is often enough to simply classify the chemical families that are present. We routinely apply mass spectrometric moiety classification (similar to ASTM Method D-2789),<sup>50</sup> in which one characterizes hydrocarbons into six types: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralins (grouped), and naphthalenes. We show the application of this approach to the comparison of the distillation curve data grid of two aviation turbine fuels, JP-8 and S-8.<sup>10,18–20</sup>

JP-8 is the major turbine fuel currently used by the U.S. military.<sup>36,51–54</sup> Environmental concerns and potential disruptions in supply have led to the development of synthetics. One such fuel made from natural gas is S-8, a hydrocarbon mixture rich in C7–C18 linear and branched alkanes. A key engineering parameter to facilitate application of S-8—and even mixtures of S-8 with JP-8—is the ADC. By adding the chemical family classifications to the data grid, the distillation curve becomes more information rich. In Figure 3, we present the classification results as a function of distillate cut for typical batches of JP-8 and S-8. The differences are striking. We note that S-8 has a high level of paraffinic species and very few aromatics (as expected from its natural gas feedstock), and JP-8 has a high aromatic content decreasing as distillation proceeds (as expected from petroleum feedstock).

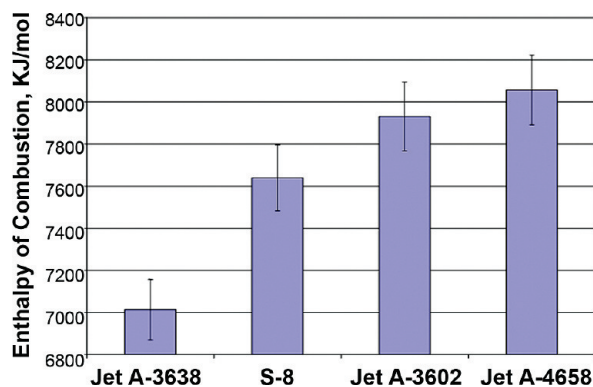
**Enthalpic Analysis.** The ability to apply a detailed quantitative analysis to each distillate fraction offers the potential of assessing



**Figure 3.** Plots showing the distribution of chemical families present in aviation fuels JP-8 and S-8 as determined by MS.

thermal properties such as energy content of a fuel. If the enthalpy of combustion is known (or predictable) for the components of a mixture, the composite enthalpy of combustion of a mixture of these components can be derived.<sup>12</sup> We illustrate this with a comparison of different samples of Jet-A, the most common turbine fuel used commercially in the U.S. (800 billion liters in 2006).<sup>55</sup> The ADC was applied to three different batches of Jet-A (designated numerically as 3638, 3602, and 4658) that represent the composition gamut very well. Sample 3638 was known to be unusual in that the aromatic content was relatively low. We noted a divergence in the distillation curves of these three fluids at the 70% fraction, so we performed a quantitative analysis on each and determined the enthalpy of combustion. The results are shown in Figure 4, along with a comparison to the synthetic fluid S-8. The spread in the enthalpies is striking; the atypical fluid shows the lowest value. The combination of the distillation data grid with the composition analysis and the enthalpic analysis thus permits a more complete understanding of the fuel properties and how they relate to composition.<sup>56</sup>

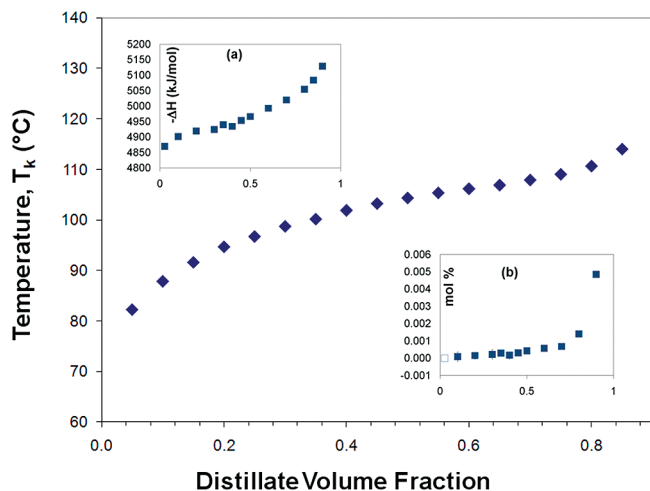
**Trace Analysis: Avgas 100LL.** Although motor fuels used today do not contain lead additives, most general aviation gasoline (avgas 100LL) still contains tetraethyl lead (TEL). Because TEL was banned from motor gasoline, avgas 100LL is now one of the largest contributors of lead in the atmosphere in the U.S. Significant efforts have been made to develop a low-cost, lead-free alternative fuel to replace avgas 100LL for aircraft that use piston engines. Ideally, this alternative should be a drop-in replacement. The examination of avgas 100LL with the ADC provides the opportunity to ultimately develop an equation of state for this fuel and to track the presence of the lead compound



**Figure 4.** The composite enthalpy of combustion of the 70% distillate fraction for three samples of Jet-A and the sample of S-8. The fluids are presented in increasing enthalpy of combustion of the 70% distillate fraction.

through the full range of the distillation curve. In Figure 5, we apply the ADC to avgas 100LL.<sup>57</sup> The y-axis presents the thermodynamically consistent temperatures, while some analytical information is presented in the insets. In inset (a), we present the enthalpy of combustion as a function of distillate cut (from a quantitative analysis). This allows the energy content to be related to the other fuel properties. In inset (b), we present the composition profile of TEL as a function of distillate cut, which is derived from specific trace analysis applied to the distillate cuts. We note that there is far more TEL in later distillate fractions. This allows the composition profile of this fuel to be predicted with confidence.

**Corrosivity Analysis.** Crude oil is an economic driving force in the developed world. Many properties of crude oil (color,

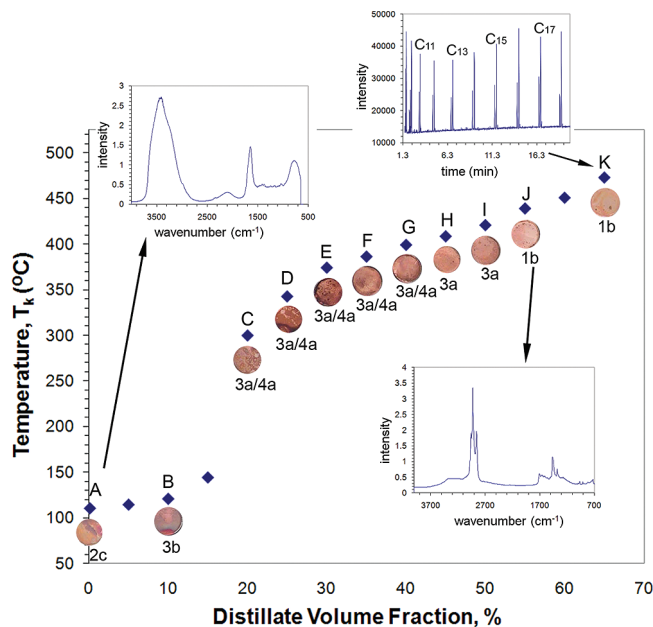


**Figure 5.** Distillation curve of avgas 100LL with the enthalpy of combustion in inset (a) and the concentration of TEL in inset (b), both as a function of distillate cut.

viscosity, and amount and type of impurities) are dependent on source. Impurities of primary concern are sulfur species, which are often corrosive. Crude oils containing relatively few sulfur impurities are referred to as “sweet”; they are considered “sour” if they contain large amounts of sulfur impurities. The corrosivity of crude oil streams is always an important issue—one that can account for serious financial liabilities to producers and refiners. The corrosivity of certain sulfur species in fluids is determined by the copper strip corrosion test (CSCT), described in ASTM test methods D-1838 or D-130.<sup>4,58–63</sup> A strip of cleaned, polished copper is placed in a vessel and then filled with an appropriate quantity of the fluid to be tested. The filled vessel is then maintained at an elevated temperature for a predetermined amount of time, and the strip is removed from the fluid and immediately rated by comparison with a lithographed standard. There are four levels of increasing corrosion on the standard, with level one corresponding to slight tarnishing and level four corresponding to severe corrosion.

Although the CSCT is a well-established standard, it is both qualitative and subjective. We improved the interpretation of CSCT by analyzing strips in a mathematical color space, specifically  $L^*a^*b^*$  color space (the most complete, perceptually linear color model).<sup>64</sup> We adapted the dimensionless  $L^*$  axis of this space, which describes the “lightness” of an image, to measure the corrosion of copper strips. Lightly tarnished strips generally have high  $L^*$  values (180–210), whereas severely tarnished strips generally have low  $L^*$  values (120–150). Whereas the usual CSCT was designed for 30 mL fluid samples and large copper strips (75 × 12.5 mm, up to 3.0 mm thick), we used very small, circular copper coupons that fit in the bottom of GC autosampler vials.<sup>14</sup> Moreover, the symmetric circular geometry facilitates the analysis of the images with  $L^*a^*b^*$  color space, and the small size of the coupons can actually facilitate corrosion testing.

We applied the ADC approach to several crude oils and a sand crude (dense, viscous petroleum in sand or clay, also called bitumen, usually extracted with a solvent).<sup>30</sup> In a more exotic application, we measured a “crude oil” made from swine manure.<sup>16</sup> To make this oil, swine manure is suspended in water, pressurized in a reactor with CO, and heated to ~300 °C. The overall yield of



**Figure 6.** The distillation curve of the crude oil made from swine manure is shown (diamonds), along with the CSCT coupons for each fraction. The FTIR spectra for an early (A) and a late (J) fraction and GC/MS results for a late (K) fraction are shown in the insets.

oil from the reactor is ~11% (mass/mass). In Figure 6, we present a distillation curve, along with the CSCT results. Insets show FTIR spectra of an early and late fraction and GC/MS of a late fraction. The relatively high water content of this oil causes the distillation temperatures to start at a low value and jump when the organics begin to distill. The high water content early in the distillation is reflected in the FTIR data, as is the high hydrocarbon content that develops later. The CSCT shows the fluid to be somewhat corrosive through much of the distillation curve. The  $L^*$  values (not listed here) correlated well with the CSCT ratings.

Analyses by GC/MS showed that the swine manure crude is a very complex mixture: even when investigating only the main peaks (those with an abundance >1%), 83 different organic compounds were identified. The main peaks from the low boiling region distillate samples were identified as nitrogenous heterocycles: substituted pyrazines and pyrroles. Also identified in fraction A were thiophenes. The sulfur in the thiophenes was also quantitated by GC/SCD. The high boiling fractions were dominated by long-chain hydrocarbons: fluids from octane to octadecane were identified. In addition to these hydrocarbons, an interesting component identified on the basis of its mass spectrum was coprostane. Coprostane is the parent hydrocarbon of coprostanol (also called coprosterol, CAS Number 360-68-9), which is a main sterol found in swine fecal matter. Its presence indicates that the thermal conversion conditions of swine manure to crude oil were not sufficient to thermally crack this polycyclic compound.

Unlike our experiences with finished fuels or other crudes, a large fraction of particulate char remained after distillation. The ADC allows recovery and analysis of this material. A powder X-ray diffraction pattern was inconclusive. Consequently, the char was analyzed with instrumental neutron activation analysis and cold neutron prompt gamma activation analysis. These complementary neutron activation analysis techniques detected the presence of Fe, Zn, Ag, Co, Cr, La, Sc, W, and very small amounts of Au and

Hf. Metals such as Fe have been found elsewhere in swine manure and lagoon sludge.

**Thermodynamic Modeling.** We have mentioned above that because the ADC provides state point temperatures (along with the composition profile), we can model the results with a sound thermodynamic model.<sup>65–68</sup> We finish our discussion of the ADC with just a few sentences on this aspect, which is peripheral to the analytical aspects.

Our approach is to represent the molar Helmholtz energy (*a*) of a mixture as a sum of an ideal solution contribution and an excess contribution. Though the details are beyond the scope of this review, we can use the theoretical formalism in two different ways. First, we can correlate experimental property data to produce a model that represents the data within experimental uncertainty. Second, we can use the model predictively to estimate property values, even when based on limited experimental data. With the ADC as a primary experimental input, we have used both of these approaches for aviation fuels, rocket propellants, and diesel fuels.

## CONCLUSIONS

We have shown that the ADC provides a thermodynamically consistent description of the volatility (or vapor/liquid equilibrium) of a complex fluid such as a fossil fuel. The composition channel of the ADC allows us to relate and indeed explain the thermal properties on the basis of the composition of each fraction. We can apply any specific analytical technique that might be deemed useful. Our initial efforts using equations of state to correlate the physicochemical properties with the composition information suggest that the ADC approach will have a place in advancing the field of petroleomics. We hope in the future to apply the high resolution technique of FTICR to the ADC.

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*manure biofuel, visit [http://www.nist.gov/public\\_affairs/techbeat/tb2008\\_0610.htm#crude](http://www.nist.gov/public_affairs/techbeat/tb2008_0610.htm#crude).)*

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