

CHARACTERIZATION OF COAL LIQUEFACTION RESIDS BY FIELD IONIZATION MASS SPECTROMETRY: CORRELATING SPECTRAL FEATURES WITH PROCESSING PARAMETERS

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INTRODUCTION

Under a contract with the U.S. Department of Energy, Consolidation Coal Company (Consol) has provided a range of well-documented samples obtained from process development units to various analytical researchers, who then apply their chosen methodology to determine the value of the method to process understanding and development (1). One objective of Consol's program is to provide a bridge between direct coal liquefaction process development and analytical chemistry. At SRI International, we have analyzed 15 resid samples, taken from three sampling points in five close-coupled two-stage liquefaction runs at the Wilsonville facility by field ionization mass spectrometry (FIMS) to help answer several questions relating to the chemistry of liquefaction, specifically as it relates to resid conversion, and how to improve the overall process.

The technique of field ionization (FI) consists of passing the vapors of a material through a region of intense electric field to polarize and ultimately ionize the molecules. The ions are then mass analyzed using standard mass spectrometric techniques. For most organic compounds, this procedure causes minimal fragmentation and produces only the molecular ions (2). The resulting spectra are thus true representations of the molecular weight profiles of the volatilized materials. FIMS has been used for a variety of applications relevant to coal liquefaction. However, its ability to answer the very difficult questions pertaining to the chemistry of resid reactivity has not been demonstrated. The objective of the task on FIMS analysis was to evaluate the utility of FIMS for addressing the issue of resid reactivity by analyzing a reasonably large set of related samples.

EXPERIMENTAL PROCEDURES

The samples were the vacuum resid portions of the oils samples collected at the end of the first stage, the second stage and following the ROSE-SR deashing unit. They are referred to as the interstage oil (V1235), product oil (V1067), and recycle oil (V131B) respectively. These samples are from five different two-stage liquefaction runs: Lignite (Run 255), Wyo-dak (Run 251-II), Illinois No. 6 (run 250) in the thermal-catalytic mode, and Illinois No. 6 (Run 257) and Pittsburgh (Run 259) in the catalytic-catalytic mode.

The analyses were conducted using SRI's FIMS instrument, which consists of a foil-type field ionizer interfaced with a 60-degree magnetic-sector mass analyzer and a PDP 11/23 computer for instrument control, data acquisition, and report production. The spectrometer has a resolving power ($M/\Delta M$) of 1300, although it is capable of scanning up to 3000 Da. Typically, approximately 20 μg of the sample is taken in a melting point capillary and introduced into the spectrometer with a heatable direct insertion probe. The sample is heated at a fixed rate from ambient (or $\sim 67^\circ\text{C}$ for samples with sufficiently high vapor pressure) to about 700°C . The pressure in the ion source chamber is generally in the 10^{-6} Torr range, although the pressure in the capillary sample holder is considerably higher. We estimate the sample pressure to be around 10^{-4} Torr. Under these conditions, materials with atmospheric equivalent boiling points (AEBP) up to about 1400°F are expected to vaporize completely, and those with AEBPs in between 1400° and 1600°F to vaporize at least partially. What often limits the vaporization of these high boiling materials are the coupling reactions with other species present in the sample. Hence the quoted limits should be regarded as a rough guide. (Similarly, other pyrolytic reactions can occur that produce volatile species not present at such in the original mixture.) The spectra of the evolving volatiles are continuously recorded, and at the end of a run, they are added to produce a "sum" spectrum of the total volatiles.

RESULTS AND DISCUSSION

General Spectral Features

Figure 1 shows the spectrum of the recycle oil from cat-cat run with the Pittsburgh coal (Run 259), and is typical of the entire set. All of the spectra consist of a broad distribution of molecular weights ranging from about 200 to 1000 Da. There is an additional group of peaks in the 50 to 120 Da range corresponding to small fragment ions. The total intensity of this low-mass group is typically extremely low compared to that of the main profile, reflecting the minimal ion fragmentation that is typical of most liquefaction product streams during FIMS analysis. Immediately apparent from these spectra are two profiles: a more intense profile for the even masses and the other (dark profile) corresponding to the odd masses. Peaks at odd masses generally arise due to ^{13}C , N, or fragmentation. Because FIMS does not cause much fragmentation and these spectra have been corrected for natural abundance of ^{13}C , the odd-mass profile arises mainly from compounds containing nitrogen.

At first glance, the FI mass spectra of all the resids look very similar. The similarity is reassuring because several processing requirements tend to provide resids of similar molecular weight range and polarity. Apart from being similar, the spectra also show that the resids are very complex mixtures. The bulk of the material in these samples falls in the 200-1200 molecular weight range and considering coal-origin and heteroatom content of the products, the "average" molecule at, say, m/z 600 would contain one oxygen, one-half nitrogen, and one-quarter sulfur. Therefore, most of the resid molecules are polyfunctional, and not classifiable, even in principle, according to simple chemical type or class. (3) For these reasons, we focused primarily on the overall profiles. We note here that there are a few peaks in the 240 to 340 Da range in each of the spectra that do stand out in all the spectra, and we examined them in some detail. However, before discussing this group of peaks, we first describe our attempt at a semi-quantitative characterization of the overall profiles.

In many instances, the spectra appear to be composed of two partially overlapping clusters of peaks: one such cluster, which we will call Component A, is centered around 350 Da and the other cluster, which we will call Component B, is centered around 600 Da. Relative to Component B, Component A appears to span a relatively narrower MW range. In other work, we had observed the somewhat bi-modal distribution of molecular weights in coal liquefaction resids. However, those observations were with isolated samples, and we were not sure if they were indicative of a general trend. Examination of fifteen closely related samples in this project confirmed the general nature of this distribution, and we felt encouraged to examine this distribution and see if the relative amounts of the two components can be correlated with some process-related parameters.

Several steps are involved in deconvoluting the spectra into Components A and B. First, we have to assign a general functional form to each of the component envelopes; second we perform a least-squares fit on a few selected samples to derive the parameters for the general formula describing the two components; and third we fit the spectra using these expressions while varying only the relative amplitude factors. We chose to express the rising part of each envelope as a power function of the molecular weight (m^α) and the decline as an exponential ($e^{-\beta m}$). The parameters α and β were to be different for each of the two components, but the overall functional form was constrained to be the same. The following expression gives the intensity (I_m) at any mass:

$$I_m = Q_A m^{\alpha_A} e^{-\beta_A m} + Q_B m^{\alpha_B} e^{-\beta_B m}$$

Here Q_A and Q_B are the weighting factors for the two curves. The parameters α_A , β_A , α_B , and β_B were determined by a regression analysis. Rather than fit all of the spectra by regression, we decided that a more meaningful test would be to select for regression five of the most divergent looking spectra. Once the parameters α and β were determined, they were fixed and the remaining spectra were fitted by varying only the Q 's. Figure 2 shows an example of the deconvolution. The dots are the data for the even masses in the FIMS of the recycle oil from the run with the Pittsburgh coal (Run 259). This spectrum was not among the ones used in the least-squares fit to obtain the parameters defining A and B. The continuous line through the data is the fit obtained by varying the amounts of A and B. The contributions of A and B components to the total fit are shown by the two dashed lines. The fit in this case is reasonably good over most of the mass range, except at high masses where the fit gives a lower intensity than the data. The break in the curve around 450 Da is well mimicked by the fit. Those spectra without a distinct break in the curve were not fit quite so well.

To obtain the relative *weight* fractions of the two components, A and B, we integrate the product of mass with the fitted expressions over the mass range. Thus:

$$\%A = \frac{100 \times \int Q_A m^{\alpha_A} e^{-\beta_A m} \cdot m \, dm}{\int Q_A m^{\alpha_A} e^{-\beta_A m} \cdot m \, dm + \int Q_B m^{\alpha_B} e^{-\beta_B m} \cdot m \, dm}$$

The data in Table I show the wt% A in the various samples.

Correlation of Lumped Component Levels with Process Parameters and Yields

Having in hand the deconvolution results summarized in Table I, an attempt can be made to see how the levels of Components A and B correlate with process conditions and product character and yields as previously summarized.⁽⁴⁾ The Illinois No. 6 catalytic-catalytic product oil (Run 257) has a very pronounced low-mass intensity (200-400 Da) as is also reflected in the large A content (32%). This low-mass grouping is somewhat less prominent in the "younger" interstage oil (22%). Evidently, under the catalytic-catalytic conditions, high yields of material that is low molecular weight are produced from the coal or "fresh" resid in the first-stage reactor, and most noticeably, in the second-stage reactor.

In significant contrast to the prominent low-mass intensity in the Run 257 product oil, the recycle oil (which nominally differs from the product oil only in that a portion of the stream has been split off, sent through a vacuum flash separator, and had the ash and insoluble organic matter removed in the ROSE-SR unit) has substantially less of the 200 to 400 Da intensity (13%). Whereas one expects some of the high molecular weight organic material visible with FIMS to be rejected along with the ash, and therefore for the *higher* end of the molecular weight profile to be trimmed in the recycle oil (as compared with the product oil), it is the *lower* end of the profile that has shrunk. This observation suggests significant retrogression between V1067 and V131B; in other words, that significant coupling occurs when the high temperatures are maintained during the "physical" separation process or subsequently in the holding tanks, but catalyst and H₂ pressure are largely absent.

In the case of the Pittsburgh coal, which was also processed in the catalytic-catalytic mode (Run 259), as we move from the interstage oil to the product oil, we see that Component B dominates over Component A. In this case, the fresh resid seems to be much less readily converted (in the second-stage reactor) into A; the net change in fact is for the B to become *more* important as a result of reaction in the second stage. The differences between the Pittsburgh product oil and the recycle oil seem to reflect mainly removal of high molecular weight material, B. This is as would be expected, but is in contrast to the Illinois catalytic-catalytic case, where the effect of putting a side stream through the ROSE-SR unit (and the holding tanks) was curiously to *increase* the amount of B.

The next appropriate comparison is between the Illinois catalytic-catalytic run (Run 257), and the Illinois thermal-catalytic run (Run 250). In Run 250, the level of Component A in the interstage oil is only about half that in Run 257, and passage through the Stage 2 reactor *decreases* Component A still further (rather than increasing it as in Run 257). We conclude (since Stage 2 is catalytic in both cases) that the product of the thermal first stage is less reactive. Apparently the "fresh" resid is more refractory because of the absence of catalyst and/or the slightly higher temperatures used during operation of a thermal first stage.

Moving to the two lower rank coals in this series, also processed in a therm-cat configuration, we see that for both the Wyodak coal and the lignite, second-stage reaction causes a decrease in the percentage of Component A — a change that is qualitatively similar to that seen for the Illinois therm-cat run (Run 250). With respect to changes between the product oil and the recycle stream, there is a slight increase in Component A for both the Wyodak and the lignite, whereas for the Illinois No. 6 coal (Run 250), Component A had decreased. Since we associated the decrease in Component A between the product and recycle streams for the Illinois No. 6 runs with a proclivity for retrogression, we would conclude from the slight *increase* in A that the Wyodak and lignite resids are actually less prone to retrograde reaction than the Illinois No. 6 resids. The observed increase in A supports the conclusion that PCAH species, which are expected to be less abundant in the lower rank coals and their products, are the primary candidates for retrogressive reactions in these highly processed resids. The observed increase in Component A is thus most likely due to a greater rejection of Component B as was observed with the Pittsburgh coal.

To summarize, the attempt to make a straightforward association between the amounts of Components A and B in each resid was surprisingly successful, however some loose ends remain. For instance, a decrease in

Component A as a resid moves through the processing stream can reflect not only regression to the heavier component, B, but also upgrading to distillate. For simplicity, we have simply chosen to try first to rationalize the data in terms of the possibility that is more troublesome in process terms, namely retrogression of Component A to B.

Examination of Prominent Individual Peaks

While a large part of each of the FI-mass spectral profiles is basically quite smooth, with few prominent masses, it is noteworthy that at the low mass end (240 to 350 Da), there is substantial "structure" in the spectra. Moreover, the same peaks appear as prominent in spectra of all the fifteen resids. The six major series apparent in the spectra of these resids begin at m/z 242, 276, 282, 300, 308, and 316. In Figure 1 we have labeled some of these prominent peaks.

Curiously enough, the six major peaks apparent in these resid spectra are either the same as, or closely related to, those recently identified by Sullivan, Boduszynski, and Fetzer (5) as showing substantial increases during hydrotreating of petroleum vacuum gas oil fractions. Based on the evidence presented by Sullivan et al. (5), and the very striking correspondence between the major peaks seen here and some of those identified by them, we consider it to be very likely that most of the prominent peaks noted here are causally related to the difficulty of catalytic/thermal breakdown to smaller species (distillate) and to the buildup of more refractory resid and IOM. At present, it is difficult to make a more quantitative statement regarding the importance of these peaks. However, a few of the trends that emerge from an initial examination are listed below.

- Consistent with the fact that the Pittsburgh resid is the most difficult to upgrade, the intensities for m/z 276, benzo[ghi]perylene, observed for the Pittsburgh coal (Run 259) are generally higher than those for any other sample. However, this relationship appears not to always hold. In the interstage and recycle oils for Run 259, the levels are 2 to 2.5 times higher than the respective samples for Run 257, the catalytic/catalytic Illinois No. 6 run, but for the product oil the levels are essentially equal.
- The cat/cat run with Illinois No. 6 coal (Run 257), produces more of m/z 276 by about a factor of two than the therm/cat run (Run 250), even though the resid produced in 250 was considered to have been more difficult to upgrade. If the large PCAH are produced in significant part by the cracking activity of the alumina-supported catalysts, we might rationalize that without the first stage catalyst, less benzo[ghi]perylene is formed. But if we accept this explanation, we are then forced to say that the difficulty in upgrading the Illinois therm/cat fresh resid is not due to benzoperlylenes, coronenes, etc., but is due instead to the fact that less cracking occurred in the first stage. While this latter rationalization may be correct, it is apparent that the situation is complex and not susceptible to analysis by simple inspection.
- If instead of comparing the absolute levels, we compare the ratios of peaks at m/z 276 and 300, we find that in going from the recycle stream to the interstage oil the relative amount of benzo[ghi]perylene increases in the more difficult-to-process Runs 250 and 259, while it decreases in Run 257.
- Changes in the ratios of hydroaromatic/aromatic pairs as the resid moves through the system provide an additional point for comparison. We find that the hard-to-convert Runs 250 and 259 show distinct decreases in the ratio of hexahydrobenzo[ghi]perylene to benzo[ghi]perylene. On the other hand, the "good" run 257 actually shows an increase in this hydroaromatic/aromatic ratio as a result of addition of coal to the recycle oil and reaction in the first stage reactor. The appearance of high levels of benzoperlylene in Run 259 is presumably related to the fact that the level of cyclic- β -hydrogen (i.e., hydroaromatic hydrogen, as determined by NMR) in the recycle oil was the lowest of these three runs.

These trends do not extend to the entire set of runs. In other words we were not able to construct a consistent set of correlations between the most prominent homologous series and the processing behavior in all five runs. However we believe it is very likely that the difficulty in significant part is that the run-to-run comparisons attempted are anything but all-other-things-being-equal comparisons. A more careful examination of these data is warranted. One correction that ought to be included in this analysis is for the background intensity of all other components that might be present at these specific masses. The background could be adequately represented by the "fit" to the profile described in the previous section. The correction is small for peaks at 242 Da, but probably substantial for those at 300 Da. An alternative strategy would be to perform a

factor analysis on this set of peaks and identify the major trends. We suggest that these tasks be undertaken in a future effort.

SUMMARY

During this research effort we found that FIMS of many of the liquefaction resid samples exhibited a bimodal molecular weight distribution. The relative amounts of the low and high molecular weight components differ significantly from sample to sample, and simple mathematical deconvolution into Components A and B has revealed a correlation between the variations in A and B on the one hand and coal type, process conditions, and process performance on the other. While the correspondence is not perfect, the deconvolution leads to conclusions reasonably in concert with what is already recognized in coal liquefaction. It is satisfying to see so many observations about reactivity reiterated, not on the basis of yields, but on the basis of differences in molecular weight distribution of streams that are already constrained by process conditions and product fractionation to be as similar as possible. The mass spectra consistently showed a same set of few prominent peaks in the low mass end. Interestingly, these masses were identical with those previously associated by Sullivan et al. with increased difficulties in hydrotreating vacuum gas oils. This similarity prompted us to seek correlations between processing variables the intensity of these peaks. Our partial success in finding such correlations warrants a more extensive examination of the variations in these prominent masses, which when coupled with the deconvolution into lumped low and high molecular weight components, is likely to provide substantial independent information for cross-correlation with other resid properties and processing parameters.

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Table 1

PERCENTAGE OF LOW-MOLECULAR WEIGHT COMPONENT A IN RESIDS TAKEN FROM DIFFERENT RUNS AND SAMPLING POINTS

Wt% A in the Sample Determined from Even-Mass Profile

Sample point	255	251-II	250	257	259
	Lignite Therm-Cat	Wyodak Therm-Cat	Illinois Therm-Cat	Illinois Cat-Cat	Pittsburgh Cat-Cat
Interstage oil	21.5	11.4	13.9	22.4	13.7
Product oil	18.2	9.0	10.4	32.0	9.2
Recycle oil	21.6	10.0	8.6	13.1	18.5

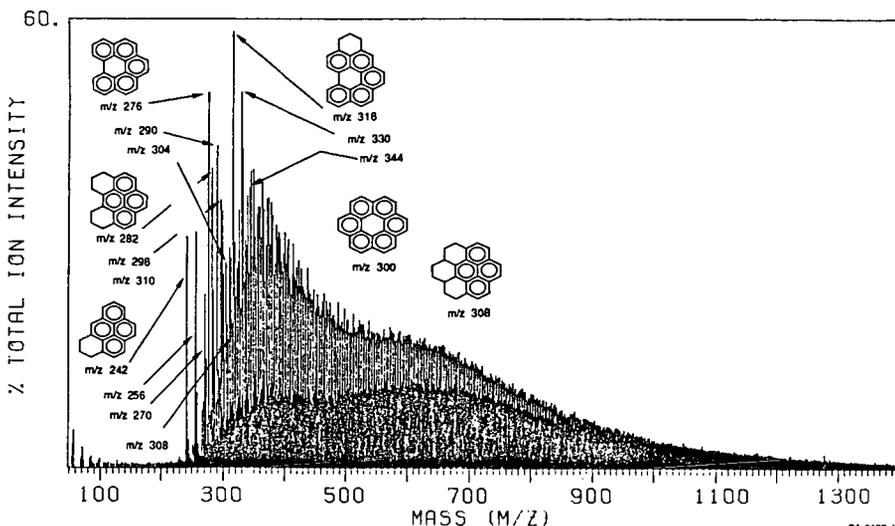


Figure 1. FIMS of the Pittsburgh (Run 259) recycle oil showing the prominent PCAH structures in the 200-350 Da range.

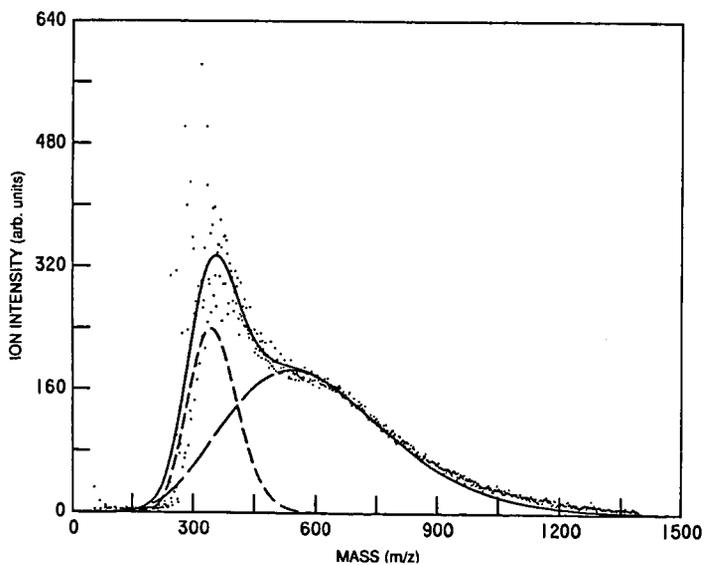


Figure 2. Deconvolution of the FIMS of Pittsburgh (Run 259) recycle oil into Components A and B.