

IV. ANALYTICAL PROCEDURES

As described in Section III, the gaseous and liquid fractions of the reactor products were collected separately for analysis.

A. Gaseous Product

During the first quarter of the contract a modified Carle Model 530 gas chromatograph was purchased for on-line analysis of the non-condensable gaseous product. This instrument is capable of analyzing saturated and unsaturated hydrocarbons through hexane, polar compounds (methanol, water, dimethyl ether) and fixed gases (hydrogen, carbon monoxide, carbon dioxide, nitrogen). Before the Carle instrument was available, product gas samples were collected in 500 cc. cylinders and analyzed off-line by conventional GC methods. The Carle was received in May 1982 and went on-line in June, 1982. The unit performed satisfactorily for the remainder of the contract.

B. Liquid Product

The peculiar nature of the liquid product presented three difficult problems in arriving at a satisfactory analytical procedure. These are discussed below.

1. Aqueous/hydrocarbon phase separation

Because of difficulties encountered in separating the three phases recovered in the product receiver (aqueous product, solid product, liquid hydrocarbon product), the initial results were delayed. The mixture of the phases and the varying amounts of each, which varied widely, made the task more difficult. Ultimately, a centrifugal separation proved workable.

2. Analysis of aqueous phase

Once the liquid phase separation had been accomplished, the aqueous phase was analyzed by standard gas chromatographic methods for methanol, dimethyl ether, and water.

3. Hydrocarbon type analysis

During the first twelve months of the contract, a considerable effort was undertaken, which ultimately proved fruitless, to investigate whether the hydrocarbon group type analysis could be measured more accurately by liquid chromatography than by standard Fluorescent Indicator Analysis (FIA) analysis. The early FIA results indicated that some of the product components had a natural fluorescence under U.V. light. This tended to mask the bands in the FIA test, leading to questionable results.

Liquid chromatography proved capable of separating the group types, but the accuracy was suspect. As a check, samples were submitted to two manufacturers, for the purpose of comparing results with those of FIA analysis on identical samples.

The results from one manufacturer were unacceptable and the other manufacturer reported that they were unable to perform the analysis. Thus, the search for an alternative was abandoned at that time.

However, a new possibility arose in connection with the acquisition (June 1982) of an Envirochem Unacon Model 810B concentrating purge and trap system chromatograph, which was obtained for use in the analysis of the overall liquid product (C5 through C20). Samples were submitted to Perkin-Elmer for separation of group types by liquid chromatography and then to Envirochem for quantification with the Unacon 810B.

The findings were: (a) the saturates fraction was lighter than in the original sample (the higher boiling saturates were missing); (b) some of the mid to heavy saturates were found in the olefin fraction; (c) normal paraffins were also found in the aromatics fraction.

From these results it appears that the highly non-polar Freon type solvent used by Perkin-Elmer could not reliably separate the group types from samples with a wide boiling point range. Perkin-Elmer also tried a pentane solvent, which also proved unacceptable, due to the inability to separate saturates from olefins.

Perkin-Elmer continued to work on the problem and concluded that current state-of-the-art column technology was not capable of making the desired separation. They did succeed in separating saturates and olefins from the aromatics.

IBM also made an attempt to perform this separation. Their results were consistent with earlier attempts and by May 1983 further attempts were abandoned.

Analysis of the liquid samples remained a problem. However, an alternative method had proven to be quite satisfactory albeit tedious. The refractive index (R.I.) and densities were used to estimate the aromatics content. The densities and R.I.'s of paraffins and olefins with the same carbon number are similar. An aromatic with the same boiling point has a very different density and refractive index. First, the simulated distillation curve was used to obtain an

average boiling point of the liquid. The density and refractive index of the methylated aromatic with the same boiling point was also found. Two equations were set up assuming that the density and R.I.'s were additive. Each one was solved separately for the percentage of aromatics. These two percentages were often close in value. When this was so, the fraction of aromatics was considered accurate. When the numbers differed, the number based upon R.I. was used, since this method was considered the most reliable.

4. Analysis of C5 + liquid product

The C5 + portion of each sample was first separated from the the total liquid hydrocarbon sample using the Envirochem Unacon Model 810B concentrating purge and trap system, mentioned above. (This equipment experienced considerable problems, including electrical component failures and valve leaks, which resulted in several months of down-time after the installation.)

The C5 + portion was then analyzed for carbon number content by glass capillary gas chromatography, using a Perkin-Elmer Model 910 gas chromatograph.

C. Other Analytical Tests

Occasionally, when warranted, an extended run was made with an enlarged catalyst charge to produce enough product for further characterizations such as octane

or cetane number or pour point.

D. Reporting

Analytical results for each run, including detailed material balances, were reported in a table which included (a) data relating to the run as a whole, and (b) data for each sample analyzed during the run.

Supplementing each table were four series of displays:

1. Four graphs in which the performance of the catalyst during the duration of the run was plotted against time on stream by the following criteria:

- Conversion of syngas, hydrogen, and carbon monoxide to hydrocarbons.
- Hydrocarbon product selectivity by carbon number groups.
- Isomerization of the pentane fraction.
- Percent olefins in the C4 product.

2. A graph for each sample which plotted the simulated distillation curve (boiling point vs. percent distilled).

3. A graph for each sample which plotted the Schulz-Flory hydrocarbon product distribution.

4. A chromatograph from the simulated distillation of each sample.