THE APPLICATION OF ADVANCED ANALYTICAL TECHNIQUES
TO DIRECT COAL LIQUEFACTION

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INTRODUCTION

Direct coal liquefaction is a complicated and ill-defined chemical process. In order to promote coal liquefaction as a feasible alternative-energy technology, fundamental chemical understanding of the direct liquefaction process must be obtained. There exists, however, a gap between the advanced, modern techniques of the analytical chemist and the application of those techniques by the direct coal liquefaction process developer. There are two major reasons for the existence of this gap: 1) Much research in advanced analytical chemistry concentrates on instrument development and not method application, and 2) appropriate direct coal liquefaction samples for method applications are frequently difficult to obtain.

Consol is coordinating a program designed to bridge the gap, and thus to advance our knowledge of the process chemistry of direct coal liquefaction. The program is designed to provide well-documented samples to researchers who are utilizing techniques potentially useful for the analysis of coal derived samples. The choice of samples and techniques was based on an extensive survey (1) made by Consol of the present status of analytical methodology associated with direct coal liquefaction technology. Sources of information included process developers and analytical chemists.

Identified in the survey are a number of broadly characterizable needs. These categories include a need for:

- a better understanding of the nature of the high molecular weight, non-distillable residual materials (both soluble and insoluble) in the process streams.

- improved techniques for molecular characterization, heteroatom and hydrogen speciation and a knowledge of the hydrocarbon structural changes across coal liquefaction systems.

- better methods for sample separation.

- application of advanced data analysis methods.

- the use of more advanced predictive models.

- on-line analytical techniques.

- better methods for catalyst monitoring.

Various analytical techniques currently in routine use provide a valuable, but incomplete, understanding of direct coal liquefaction process chemistry, and thus cannot fully address these needs. In this program, specific methodologies (or

techniques) potentially relevant to addressing some of these needs have been identified (Table 1). Many of these methods are new only in that they have not been fully demonstrated for their applicability to coal liquids. Other techniques are "cutting edge" and are currently under development for a number of applications, including natural product analyses. Organizations or research groups that are involved in the program are identified, in Table 1, with the method that they are employing.

Methods under consideration in this program are directed towards the characterization of the non-distillable resid portion of liquefaction oils because of the importance of this material to the liquefaction process. In current direct liquefaction technology, the heaviest soluble materials produced from the coal are recycled to near extinction. These heavy soluble materials (850°F+) typically account for 50% of the recycle stream fed to the first reactor stage in current U.S. two-stage liquefaction technology. At a 2:1 recycle stream to coal feed ratio to the first stage, the principal reactor feedstock is recycled resid, not coal. The analysis of this heaviest portion of the direct liquefaction product stream (the resid) is a much more challenging problem than analysis of the lighter materials produced by coal liquefaction. It is believed that by understanding the composition and behavior of this heavy material an improved understanding of the direct coal liquefaction process will be achieved.

PROGRAM STRUCTURE

In order to bridge the gap between the process developer and the analytical chemist and improve our fundamental understanding of the chemistry of coal conversion to liquid products, a program was organized by Consol to coordinate the distribution of well-documented direct coal liquefaction samples to evaluate potentially useful analytical techniques. The results are being evaluated in regard to the usefulness of the analytical information in adding to the chemical knowledge of the direct liquefaction process. The program is structured into two phases. In Phase I, a number of organizations were chosen to participate in the program (Table 1). Eighteen different analytical methods were incorporated into the program for Phase I. These methods are, for the most part, well established analytical techniques which are uncommon in their application to coal-derived materials. Each researcher is responsible for the interpretation of the results of the tests in light of the processing information provided by Consol with each sample. In order to provide the maximum information on any one sample, Phase I of the program was structured to use techniques which both complement and supplement each other. Phase II of the program may include expansion of Phase I tests with methods that appear to be promising, the addition of methods and techniques not considered in Phase I, and a concerted effort to tie together the methods which were chosen in Phase I. Phase II also will be the appropriate point in the program to evaluate the reliability of the analytical information from promising techniques. This may be accomplished, when practical, by round robin tests.

SAMPLES

A key to the success of the program is the proper selection of samples. Evaluation of the analytical methodologies will be based in part on the utility of the method for identifying differences in the samples which can be attributed to differences in the conditions under which the samples were produced. This may include such diverse variables as feed coal rank. reactor temperature, catalyst type, age, or use in one or both reactors (in a two-stage system), sampling point in the direct coal liquefaction plant, and whether or not the feed coal was in some way treated before liquefaction. It is necessary to provide a diverse set of samples to the analytical researcher for testing. In Phase I of the program, sample sets for each method were

chosen with large differences in production variables (Table 2). Analytical methods that cannot only distinguish among the samples, but can provide information useful for predictive purposes will be considered successful techniques.

All samples in the program come from the Conscl sample bank, which includes materials from the Wilsonville, Lummus, HRI, H-Coal Pilot Plant, and UOP lique-faction and coprocessing programs. In addition, Consol continues to obtair and analyze samples from active DOE-sponsored process development programs. All samples distributed in the program were analyzed by Consol. Such analyses include (when appropriate): elemental analysis, ash content, ash elemental analysis, solubility fractionation, phenolic -OH concentration, calorific value, and hydrogen classes by ^{1}H-NMR. In addition, Consol has documented the full history of the samples (plant, process conditions, age, storage conditions, hydrogen consumption, and yield data for the associated run). Kinetic parameters were calculated for a number of the coal liquefaction runs from which samples were selected for the program. All information was supplied to the program participants to aid in the evaluation of the analytical methods.

The sample sets for the entire program were integrated so that the maximum information content can be obtained not only by judicious choice of samples for analysis by any one method, but by the application of as many of the methods as possible to a single sample. A total of eighteen different methods will be utilized in Phase I of the program. Some of there methods, for example Field Ionization Mass Spectrometry and Field Desorption Mass Spectrometry, will be used for identical samples and will yield similar information. In other cases, different analyses will provide a better understanding of the sample, for example: the use of carbonization tests to determine the propensity of the process oil to undergo retrogressive reactions will be supplemented with information on the chemical content of that oil obtained by separation technologies, such as supercritical fluid chromatography. Numerous other examples of integration of the methods exist in the program. These become apparent by examination of Table 1.

ANALYTICAL METHODOLOGIES

The analytical methodologies employed in the program are most easily discussed by categorizing them with the needs that they address. The research groups or organizations that are investigating the use of these techniques are identified in the following text; more detail can be found in Table 1.

Resid Analysis
Resids will be inspected by microscopic techniques. The Pennsylvania State University will study samples with reflectance techniques, the University of Kentucky Center for Applied Energy Research will use fluorescence techniques. Changes in reflectance of certain macerals can indicate if the material has undergone forward reaction (hydrogenation) or retrogressive reaction (condensation). Chemical analysis of resids will include various separation techniques, specifically liquid chromatography (LC), supercritical fluid chromatography (SFC), and solubility fractionation. Supercritical fluid chromatography will be employed by Virginia Polytechnic Institute to study higher molecular weight materials with limited volatility. Coupled with mass spectrometry, SFC is a powerful technique for the examination of materials with molecular weights in excess of 500 Daltons. The National Institute for Petroleum and Energy Research will use a methodology for the separation of resids into more tractable fractions for further analysis by separation based on solubility fractionation, acid/base/neutral separations, and separations based on functionality. Analysis of the resulting fractions will simplify the correlation of the behavior of the material to the process conditions.

Two potential spectroscopic techniques for resid analysis are infrared or Fourier transform infrared (FTIR) spectroscopy and mass spectrometry (both field ionization mass spectrometry (FIMS) and field desorption mass spectrometry (FDMS)). The combination of FTIR with thermogravimetric analyses (TG-FTIR), which will be done by Advanced Fuel Research, allows for the rapid spectral identification of the components of the thermally evolved material. The char remaining in the TG is subsequently burned in oxygen and CO_2, H_2O, and SO_2 are measured. Battelle PNL will employ field desorption mass spectrometry (FDMS) as another technique suitable for the direct analysis of resids. Using ionization modes such as field desorption (FD), high molecular weight samples can be ionized directly from the condensed phase without the need for vaporization by heating. SRI international will utilize FIMS (field ionization mass spectrometry) which has an advantage over other methods of ionization in that it produces molecular ions in high abundance with fragmentation occurring only rarely; thus a molecular weight profile of the material is obtained with reasonable clarity and accuracy.

Heteroatom Speciation

One of the most important problems associated with the analytical work on coal liquids is that of being able to follow and identify the heteroatom species through the process, from the feed coal to the various product streams. Determination of the functional groups important for retrograde reactions and resid reactivity is considered of paramount importance. The most difficult to detect and measure directly are the oxygenated species. A method which will be used by SRI International to attempt to track some of the oxygenated species is trimethyliodosilane derivatization. The method is a wet chemical technique for partial analysis of the oxygen functional groups in coal-derived resids. It involves the reaction of $(CH_3)_3SiI$ with alkyl carbon-oxygen bonds (ROR', ROAr, RCOOR', RCOR', RCOH, and ROH) to produce alkyl carbon-iodine bonds. Sulfoxides also react, though this is not an expected group in coal liquids. Alkyl carbon-oxygen bonds are quantified by measuring reacted iodine. A more direct technique which will be employed by Advanced Fuel Research to determine the concentration of hydroxyl groups is quantitative Fourier transform infrared spectroscopy (FTIR). In addition, qualitative analysis of the resid material by FTIR may yield information on the types of ether linkages present (oxygen linked to aliphatic or aromatic carbon).

Hydrogen Speciation and Hydrocarbon Structure

Tracking of the hydrogen in the coal liquefaction system is a formidable task. One technique which will be examined by Western Research Institute for estimation of the hydrogen consumed in hydrogenation and bond cleavage reactions, and heteroatom removal, is based on both ^1H and ^{13}C solid-state NMR. Solid-state NMR measurements can be made on whole coals, resids, and insoluble fractions obtained at different stages in the liquefaction process, and from different liquefaction processes. Two-dimensional NMR will also be applied to coal samples by Battelle PNL. A second technique which will be applied to both resids and distillates by Advanced Fuel Research is FTIR. Determination can be made of the distribution of aromatic hydrogen (whether 1, 2 or more adjacent hydrogens are on a ring), and the forms of aliphatic hydrogen (methyl, or methylene).

On-line Analyses

Methodologies for on-line analysis of liquefaction process streams are difficult to formulate. Techniques which rely on optical throughput or scattering often are not amenable to materials which are opaque or contain particulate matter. One method with some potential is FTIR. This technique has not yet been applied to coal liquefaction process streams, although it has proven useful for on-line stability measurements of jet fuels. Preliminary scoping studies by Advanced Fuel Research will show if the method is feasible.

Application of Standard Petroleum Feed Tests to Coal Liquefaction Products

A definite analytical need of the processor of coal liquefaction products is to know the refining requirements of the raw liquid products. A correlation drawn between operating variables of the finishing process and net product characteristics (in regard to specification requirements) will be extremely useful. In addition, this knowledge will provide more accurate estimations of upgrading costs to specification fuels. Although it is acknowledged that the standard petroleum feedstock tests are not tailored for the analysis of coal liquids, it is believed that they are at least a starting point for this analysis. Therefore, in a directed attempt to meet this particular analytical need, standard petroleum refinery feed analyses were performed by Conoco, Petroleum Products Research Division, on products of the Wilsonville plant.

CONCLUSION

The goal of this work is to bridge the gap between the analytical chemist and the direct coal liquefaction process developer by identifying, demonstrating, and verifying the usefulness of novel analytical techniques for the analysis of direct coal liquefaction derived materials. As described above, this program successfully matches these analytical needs and the novel analytical technologies.

ACKNOWLEDGEMENTS

REFERENCES

1. Brandes, S.D.; Robbins, G.A.; Winschel, R.A.; . rke, F.P. "Coal Liquefaction Process Streams Characterization and Evaluation - Analytical Needs Assessment, Topical Report"; DOE Contract No. DE-AC22-89PC89883, March 1991.

TABLE 1

ANALYTICAL METHODOLOGIES

Organization Analytical Method	Samples	Variables
SRI International		
Field Ionization Mass Spectrometry (FIMS)	Distillation Resids (850°F⁺)	Coal Rank Reactor Configiguration Sampling Point
Oxygen Speciation by Derivatization	Whole Process Oils	Coal Rank Thermal Pretreatment
Battelle PNL		
2-D NMR spectroscopy	Distillation Resids (850°F⁺) Feed Coals	Coal Rank Sampling Point
Field Desorption Mass Spectrometry (FDMS)	Distillation Resids (850°F⁺)	Coal Rank Reactor Configuration Sampling Point
Supercritical Fluid Chromatography (SFC)	THF-Soluble Portion of Distillate Resids	Coal Rank Reactor Configuration Sampling Point
The Pennsylvania State University		
Gold Tube Carbonization	Distillation Resids (850°F⁺)	Coal Rank Reactor Configuration Sampling Point Thermal Pretreatment
Reflectance Microscopy	THF-Insoluble Resids	Coal Rank Reactor Configuration
Advanced Fuel Research		
FTIR	Distillation Resids (850°F⁺) THF-Soluble Portion of Distillate Resids	Coal Rank Sampling Point Catalyst Age
TG-FTIR	Distillation Resids (850°F⁺) THF-Soluble Portion of Distillate Resids	Coal Rank Sampling Point

TABLE 1 (Cont'd)

ANALYTICAL METHODOLOGIES

Organization Analytical Method	Samples	Variables
University of Kentucky/Center for Applied Energy Research		
Fluorescence Microscopy	Distillation Resids (850°F⁺) THF-Soluble Portion of Distillate Resids	Coal Rank Sampling Point Catalyst Age
Virginia Polytechnic Institute		
LC-FTIR	THF-Soluble Portion of Distillate Resids	Coal Rank Reactor Configuration Ashy/Deashed Streams Sampling Point
SFE-SFC	THF-Soluble Portion of Distillate Resids	Coal Rank Reactor Configuration Ashy/Deashed Streams Sampling Point
Western Research Institute		
Solid State ^{1}H/^{13}C NMR	Distillation Resids (850°F⁺)	Coal Rank Sampling Point
^{13}C NMR	Process Oils	Coal Rank Sampling Point
National Institute for Petroleum and Energy Research		
Acid/Base/Neutral Separation	Distillation Resids (850°F⁺)	Coal Rank Sampling Point
High-Performance Liquid Chromatography (HPLC)	Filter Liquids Process Oils	Pretreatment Coal Cleaning
2-D NMR	Distillation Resids (850°F⁺) Process Oils	Coal Rank Sampling Point
Conoco Inc., Petroleum Products Research Division		
ASTM Crude Oil Analyses	Net Product Oil	Coal Rank

TABLE 2

PROGRAM SAMPLE SET

Wilsonville Pilot Plant Samples

850°F⁺ Distillation Resid Samples
>   Runs: 250, 251, 257, 259, 255, 256, 257
>   Sample Streams: Recycle, Interstage, Second Stage Product

Tetrahydrofuran-Insoluble Portion of 850°F⁺ Distillation Resids
>   Runs: 250, 251, 257, 259
>   Sample Streams: Recycle, Interstage

Tetrahydrofuran-Soluble Portion of 850°F⁺ Distillation Resids
>   Runs: 250, 251, 256, 257, 259, 260
>   Sample Streams: Recycle, Interstage. Second Stage Product

Whole Oil Samples
>   Runs: 251, 255, 257, 259
>   Sample Streams: Recycle, Interstage, Second Stage Product,
>   Net Overhead Products

Tetrahydrofuran-Soluble Portion of Whole Oil Samples
>   Run: 259
>   Sample Stream: Recycle

HRI Bench Unit Samples

850°F⁺ Distillation Resid Samples
>   Runs: 1-27, CC-2, CC-5
>   Sample Streams: Pressure Filter Liquid, First Stage Process Oil

Tetrahydrofuran-Soluble Portion of 850°F⁺ Distillation Resids
>   Runs: CC-2, CC-5
>   Sample Streams: Pressure Filter Liquid, First Stage Process Oil

Whole Oil Samples
>   Runs: CC-1, CC-2, CC-5
>   Sample Streams: Pressure Filter Liquid, First Stage Process Oil,
>   Separator Process Overhead Distillate

Lummus Process Development Unit

850°F⁺ Distillation Resid Samples
>   Run: 3LCF10
>   Sample Stream: Feed to LC-Finer

Tetrahydrofuran Soluble Portion of 850°F⁺ Distillation Resids
>   Run: 3LCF10
>   Sample Stream: Feed to LC-Finer