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EXISTING TECHNOLOGY TRANSFER REPORT ANALYTICAL CAPABILITIES

By
K. C. Tewari

June 1984

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Air Products and Chemicals, Inc.
Allentown, Pennsylvania

and

International Coal Refining Company
Allentown, Pennsylvania

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Prepared by
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Edited by
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Air Products and Chemicals, Inc.
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From 1974 to 1980, Air Products and Chemicals, Inc. conducted a broad spectrum of internal research projects on coal, coal liquefaction processing, and coal liquids analysis. These projects are individually reported to the United States Department of Energy by a set of five "Existing Technology Transfer Reports" as follows:

1. Liquefaction Process and Product Studies, DOE/OR/03054-109
2. Filtration and Deashing Technology, DOE/OR/03054-118
3. Dissolver Cold-Flow Modelling, DOE/OR/03054-108
4. Second-Stage Support, DOE/OR/03054-117
5. Analytical Capabilities, DOE/OR/03054-116

Summarizing the information in these reports is a publication titled "Technology Transfer Reports Summary," DOE/OR/03054-119, which provides an overview of the five reports listed above by highlighting the program objectives/results and listing the documents in which the original experimental data are contained.

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INTRODUCTION AND BACKGROUND

Air Products and Chemicals (APCI) began research on Solvent Refined Coal (SRC-I) in 1974 with the startup of 6T/D Wilsonville pilot plant, which was designed, built and operated by Catalytic. In the same year bench-scale research was initiated by APCI Corporate R&D at Trexlertown, Pa. This research effort continued at a relatively low level until mid 1979. At that time the research staff, facilities and development efforts were significantly expanded as a result of obtaining three research contracts with the Department of Energy. These continuing research efforts in support of SRC-I process technology required accurate and timely analytical characterization of the feed, intermediates and products for choosing processing and refining parameters and evaluating the adaptability of SRC-I products to ultimate uses. A major deterrent to the analysis of coal and coal-derived products was that the so-called standard methods developed primarily for the petroleum industry were not usually directly applicable to coal-derived fuels and required modification and reinterpretation. In addition, the new approaches usually based on sophisticated state-of-the-art instrumentation, required methods development and a thorough evaluation with regard to accuracy, reproducibility and reliability of the analysis technique as applied to coal-derived products. Recognizing the requirement of analytical support for coal research programs and need of an in-house coal analysis laboratory, APCI initiated a continuing analytical development program with the following objectives:

- Review and identify current test methods
- Purchase and evaluate analytical equipment for the coal analysis laboratory.
- Select and train the analytical laboratory personnel.
- Validate or modify existing methods.
- Provide routine analytical support to coal research and development program.
- Develop new methods as required.
- Identify problem areas and future needs.

This report summarizes the direction and progress of the analytical development efforts during the period 1974 to 1980 under APCI project numbers 87-05845, 87-0-8884 and 87-1-X023. The analytical development efforts summarized here though preliminary and historic in nature, led to the identification of analytical problems associated with each of the analysis technique as applied to coal-derived products and initiation of two major research programs; (1) Program 26.1 - "SRC Demonstration Plant Analytical Laboratory," (2) Program 12.1.10 - "Development of SRC-I Product Analysis", designed to develop and document analytical procedures for characterizing the feed, intermediates and products of the proposed SRC-I Demonstration Plant.

SUMMARY OF WORK PERFORMED

The overall objective of the on-going analytical efforts was to develop in-house expertise and analytical capability for the analysis of coal and coal-derived products in support of SRC-I process technology. The approach taken and work accomplished involved:

- Identification of test methods and associated equipment.
- Review and implementation of analytical facility plan.
- Evaluation of existing instrumentation.
- Evaluation and purchase of new instruments.
- Training of laboratory personnel.
- Validation or development of analytical methods.
- Development of standard product work-up methods.
- Development of analytical protocol for detailed characterization of SRC-I solid and liquid products.

Expertise in analytical chemistry was developed by organizing historical knowledge and assimilating new knowledge as it became available from inside and outside research facilities and the chemical literature. The data were then used to define analytical methods, instrumentation, space, staff needed to create a functional coal analysis laboratory.

The analytical techniques identified were: ultimate analysis, solvent separation, capillary gas chromatography, capillary gas-mass spectrometry, high performance liquid chromatography, thermogravimetric analysis, infrared, near infrared, nuclear magnetic resonance, vapor pressure osmometry, distillation, x-ray fluorescence and atomic absorption.

Major instruments evaluated and installed in the coal analysis laboratory were Perkin-Elmer 240 elemental analyzer, Leco SC-132 sulfur analyzer, Dohrmann MCTS-30 low level sulfur analyzer, Perkin-Elmer TGS-1 thermal analyzer and DSC-1B differential scanning calorimetry, Perkin-Elmer Model 3920 gas chromatograph with flame ionization detector, Finnigan 4021 GC/MS system, Beckman 5270 UV/VIS/NIR spectrophotometer, and a Waters ALC/201 and a Beckman/Altex high performance liquid chromatography systems.

The methods development and validation efforts led to the documentation of the following procedures:

- o Method CHN-4: for simultaneous determination of carbon, hydrogen and nitrogen.
- o Method Oxygen-6: for total organic oxygen analysis
- o Method Nitrogen-8: for the determination of low level nitrogen (0.2%-1.0%) in solid and liquid organic samples.
- o Method Sulfur-10: a coulometric procedure for the determination of total sulfur in the range of 0.1 ppm to 10,000 ppm.
- o Method TGA-3: a thermogravimetric analysis procedure for SRC liquid products.
- o Method DSC-5: differential scanning calorimetric procedure for the measurements of glass transition temperature. An ideal technique for direct determination of heat capacity as a function of temperature.
- o Method GC-1: a gas chromatographic procedure for the qualitative identification of normal paraffins and olefins.
- o Method GC-2: a gas chromatographic procedure for qualitative identification of polynuclear hydrocarbons in coal-distillate liquids.

- Method #1160: a near-infrared procedure for quantitative determination of oxygen as OH and nitrogen as NH and NH_2.
- X-ray diffraction procedure for the determination of the orientation tendency in calcined coke.

The area of critical need identified was the development of standard analytical work-up methods for SRC-I products and intermediates that could provide effectively and efficiently input data for material balance, measuring recycle solvent quality for plant operation and control, and assessing product chemical compositional changes as a function of processing parameters. The analytical efforts led to the development and documentation of the following methods:

- Column Chromatographic Separation: a silica/alumina column chromatographic procedure for the separation of coal-derived distillate liquids into function-group enriched fractions (saturates, aromatics, phenols and nitrogen bases).

- Capillary Gas Chromatographic Separation: a procedure to characterize coal-liquids at molecular level. The high efficiency column can separate individual molecular species if their boiling points are within a half degree Fahrenheit.

- High Performance Liquid Chromatographic Procedure: a reverse phase column chromatographic procedure to quantitatively profile the hydrocarbon neutral fraction of a coal-liquefaction recycle solvent. The method used to determine aromatic ring size distribution and to evaluate solvent quality.

- Solvent Separation Procedures: These analytical procedures, marked as Procedure A, D and W, were developed to separate a total coal-derived product liquid into five operationally defined fractions - oils/distillate, asphaltenes, preasphaltenes, SRC-Oils and residue. The procedures were selected on the basis that the fractions best simulate the separation of the Wilsonville pilot plant product stream, i.e., distillation to recover recycle solvent and solvent extraction to recover solvent refined coal from residue.

A major analytical effort was to characterize individual fractions from each procedure. In comparing the similar fractions from each procedure we found differences both on the molecular level and the overall fraction level, which were attributed to the solvent composition and the order of analysis used to isolate them.

RESULTS AND DISCUSSION

The results of individual analytical effort are summarized below:

A. Coal Analysis Laboratory: Instrumentation and Methods Development

Expertise in analytical chemistry was developed by organizing historical knowledge and assimilating new knowledge as it became available from inside and outside research facilities and the chemical literature. The data were then used to define analytical methods, instrumentation, space and staff needed to create a functional coal analysis laboratory. The analytical techniques identified and the nature of the information anticipated from each test are given below:

- Ultimate Analysis: Quantification of carbon, hydrogen, nitrogen, oxygen, sulfur and ash content required for product characterization and completion of mass and material balances.

- Capillary Gas Chromatography (GC): Separation of individual molecular species and characterization of SRC liquids at molecular level.

- Capillary Gas Chromatography-Mass Spectrometry (GC-MS): Direct profile of molecular species, isolation of specific compound types and rapid evaluation of the changes in distillation liquid fractions.

- Thermogravimetric Analysis (TGA): Proximate analysis and rapid evaluation of boiling range, volatility and thermal stability of coal-derived materials.

- High Performance Liquid Chromatography (HPLC): Rapid separation and quantification of coal liquids for compound types-saturates/aromatics/polars.

- Infrared (IR): Function group identification.

- Near Infrared (NIR): Rapid measurement of the hydroxyl content of SRC-I liquids and SRC-I components.

- Nuclear Magnetic Resonance (NMR): Proton distribution, aromaticity and average structural information.

- Vapor Pressure Osmometry (VPO): Number average molecular weight.

- Distillation (Simulated via Gas Chromatography): Boiling point distribution.

- X-ray Fluorescence and Atomic Absorption: Major, minor and trace element distribution.

- X-ray Diffraction: Orientation tendency in calcined coke.

The major instruments evaluated and installed in the coal analysis laboratory, and associated methods development efforts are summarized below:

- Elemental Analysis:

  Perkin-Elmer Model 240 elemental analyzer was evaluated for the simultaneous determination of carbon, hydrogen and nitrogen in SRC and SRC-related products. Method CHN-4 (see Appendix A, attachment 1) details the principle, analysis procedure and precision and accuracy statements on the test method. A major problem in the analysis encountered was the variation of combustion characteristics from one SRC-I product to another. The SRC-I products contain certain specific classes of materials such as polynuclear aromatics, heterocyclic nitrogen derivatives, organic- metallic compounds and inorganic compounds which are difficult to analyze. Either they are refractory, or they contain elements or functional groups which prohibit the proper and complete combustion of the product or interfere with the detection system . Inhomogeneity of the solid sample and volatility of liquid samples effect the analysis precision and require specific sample handling techniques.

  Method Oxygen-6 (see Appendix A, attachment 2) describes the organic oxygen analysis procedure using a Perkin-Elmer 240 elemental analyzer equipped with an oxygen analysis kit, P-E Part No.

240-0124. The standard deviation of analytical precision of the method as applied to various SRC solid and liquid products found to vary in the range 0.1 to 0.26%.

Method Nitrogen-8 (see Appendix A, attachment 3) describes the procedure for the determination of low level nitrogen (0.2%-1.0%) in solid and liquid organic samples. The procedure is the same as described in Method CHN-4 except it uses larger sample weight, and encapsulated hydrocarbon blank. More accurate results are obtained with the hydrocarbon blank because the amount of air in the encapsulated blank and the encapsulated sample is kept consistent.

Evaluation of the performance of a Leco SC-132 sulfur analyzer showed it is capable of excellent analytical precision and can be applied to analyze SRC-I related products with a standard deviation of less than ±0.04%, in the range 0.2 to 5 wt%.

Method Sulfur-10 (see Appendix A, attachment 4) describes microcoulometric titration procedure using Dohrmann MCTS-30 system for the determination of total sulfur in the range of 0.1 ppm to 10,000 ppm for the samples having an organic matrix. The method is applicable for trace sulfur analysis in hydrotreated SRC distillate liquids having a chlorine level less than 10 times the sulfur content and heavy metal concentration less than 500 ppm. The method provides an acceptable precision, ±3.0% at more than 500 ppm sulfur level.

o Thermal Analysis:

The instruments evaluated were Perkin-Elmer TGS-1 thermal analyzer and a Perkin-Elmer DSC-1B Differential Scanning Calorimeter.

Method TGA-3 (see Appendix A, attachment 5) describes the thermogravimetric analysis procedure for SRC-I liquid products. The method determines the weight loss as a function of temperature in a controlled atmosphere. The data can be used to approximate the boiling point ranges and amount of residue present in the sample. The method is general can also be applied to SRC-I solid samples.

Method DSC-5 (see Appendix A, attachment 6) describes the procedure for the determination of the glass transition temperature of polymers, by differential scanning calorimetry (DSC). Since DSC measures heat capacity directly it is an ideal technique for the determination of heat capacity as function of temperature of coal and SRC-I solid products.

o Gas Chromatograph (GC) Analysis

A Perkin-Elmer Model 3920 Gas Chromatograph with Flame Ionization Detector (FID), Perkin-Elmer PEP-2 Data System for peak integration and SCOT OV-101 50' x 0.02" ID column, was used to develop Method GC-1 and Method GC-2 (see Appendix A attachment 7). Method GC-1 describes the GC analysis procedure for the qualitative identification of normal paraffins (C_5-C_{28}) and olefins in Fischer-Tropsch reaction products. the column efficiency and resolution however is not sufficient to distinguish olefins from paraffins of the same carbon numbers. Method GC-2 describes the procedure for the qualitative identification of polynuclear hydrocarbons in coal-derived distillate liquids. In spite of the poor resolution the method provides identification of Pyrene, fluoranthrene, 9-methylanthracene, anthracene, dibenzothiophene, fluorene, dibenzofuran, acenaphthene, biphenyl, 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, tetralin and Indan.

Another developed method for the analysis of coal-distillate liquids is described under "Products Work-Up Procedures" of this report.

A newly developed capillary column gas chromatographic method using a glass SE-52 column for the analysis of coal-derived liquids is described in reference 2. The method provides excellent resolution of most components along with the ability to program temperature necessary for eluting 4 to 6-ring species.

NIR Analysis

A Beckman 5270 UV/VIS/NIR Spectrophotometer with wavelength range of 19-3000 nm was evaluated for a near-infrared analysis of oxygen and nitrogen functionality in coal-derived materials. The method quantitatively determines oxygen as OH and nitrogen as NH and NH_2

in a sample of material soluble in methylene chloride. The method is used in conjunction with direct elemental analysis data of oxygen and nitrogen to define the functional group distribution of a methylene chloride soluble fraction. The details of the method are described in analytical method #1160 (see Appendix A, attachment 8).

- HPLC Analysis

Two HPLC systems, a waters ALC/201 with Perkin-Elmer LC-55 variable wavelength UV detector and a Beckman/Altex system with variable wavelength Hitachi UV detector were used to characterize heavy SRC-I liquid fractions. Procedures were developed to separate samples according to organic classes and to determine fused-ring distribution. The description and application of the developed procedures are given under the subtitle "Product Work-Up Procedures" of this report.

- X-Ray Diffraction Analysis of Coke

A Philips X-ray Diffractometer was used to develop method for the determination of the orientation tendency in calcined coke (see Appendix A, attachment 9). The object of the method was to provide a measure of the shape characteristics of calcined coke particles which have been shown to be directly relatable to the characteristics in graphitized carbon particles.

- Gas Chromatography/Mass Spectroscopy (GC/MS)

To resolve compound types found in coal-derived liquids, the mass spectrometric analysis requirement was an instrument which could scan with adequate sensitivity to 600 AMU when operating at a maximum resolution ($M/\Delta M$) of 10,000. To develop such a capability needed to characterize SRC-I distillate liquids, initial efforts were to evaluate the then available Perkin-Elmer RMU-6E Mass Spectrometer at Lehigh University. The manufacturer's specifications of the instrument were consistent with the analysis needs. A study was undertaken to determine if the RMU-6E could obtain the specified resolution ($M/\Delta M = 10{,}000$), and, if not, to determine maximum resolution obtainable. It was found that the instrument cannot resolve all the compound types needed since it can achieve a maximum spectral resolution of only 5,000 in both single and double focusing mode. For example, the instrument could not resolve a biphenyl with a molecular weight of 224 from dibenzofuran with the same molecular weight (resolution required 6,000). It could, however, resolve a phenol and a phenanthrene having molecular weight of 200 or less (for details see Appendix A, attachment 10).

The greatest difficulty in the mass spectrometric analysis was to resolve molecular ions of the oxygen containing structural types from molecular ions of the aromatic structural types. It was, however, recognized that it was possible to characterize coal-derived distillate liquids by medium resolution mass spectrometric analysis using a column chromatographic separation into functional-group enriched fractions prior to mass spectrometric analysis. Further evaluation efforts showed that capillary column gas chromatography, combined with medium resolution mass spectrometry, flame ionization detector (FID), or element-selective detection systems was a valuable technique for qualitative analysis of coal-derived liquid products and led to the purchase of Finnigan 4021 GC/MS system equipped with negative ion capability and 96 megabyte disc storage (see Appendix A, attachment 10). See reference 2 for the developed GC/MS coal liquid analysis method.

B. Product Work-Up Procedures and Analysis of Distillate Liquids

The objective of the analytical efforts was to establish standard work-up procedures to effectively and efficiently analyze and characterize coal-derived materials from process studies at Trexlertown and to support SRC-I Demonstration Plant program.

The analytical work-up procedures developed are listed below:

1. Solvent Separation

a. Procedure A: This procedure was designed to characterize coal liquefaction products by separation into fractions based on the solubility behavior in pyridine, benzene and pentane. The sample can be solid, liquid or a mixture thereof, with less than 1% material boiling below 300°F. Coal liquefaction products are separated by sequential solvent extraction into fractions operationally defined as:

- Oils: pentane soluble
- Asphaltenes: pentane insoluble and benzene soluble
- Preasphaltenes: pyridine soluble and benzene insoluble
- Residue: pyridine insoluble

The separation is carried out at room temperature under nitrogen using high-quality solvents (pesticide or HPLC grade). The procedure reflects a more efficient and direct measure of the coal conversion processes. Figure 1 outlines the procedure, and Appendix B attachment 1, details the laboratory work-up, and associated development efforts. In general, 5-8 gm of the total product is frozen in liquid nitrogen to achieve a homogeneous sample that can be crushed to a fine powder in the inert atmosphere. Pentane is added to solubilize the oils and ultrasonic agitation is used to extract the oils from the solid matrix. The pentane solubles are filtered using a five micron Millipore filter unit. Extraction and sonication with the addition of pentane are continued in 500 mL portions until the filtrate is clear, 2-3 liter. Once the oils have been removed benzene is used to extract the asphaltenes. Pyridine is subsequently used to extract preasphaltenes in a similar fashion. Solvents are removed under nitrogen and fractions weighed for direct material recovery.

The reproducibility of the solvent separation procedure A on a coal derived total product liquid (see Appendix B, attachment 1) is exemplified by the following data:

	Mean (%)	Standard Deviation[a]
Oils	63.3	1.06
Asphaltenes	8.7	0.94
Preasphaltenes	9.7	1.23
Residue	18.2	0.31

[a] The result of five trials.

b. Procedure D (Distillation/Separation)

In the operation at the Wilsonville pilot plant samples taken at plantsite V110 (distillation feed) are first batch distilled at high vacuum (0.5 mm Hg) to remove the liquid products. The resulting bottoms are extracted with cresol to isolate unconverted residue/minerals (cresol insolubles) from the converted product, SRC. SRC is then solvent separated to isolate SRC-oils, asphaltene and preasphaltenes by Soxhlet extraction. The solvent separation procedure as performed at Wilsonville is given in Appendix B, attachment 2. As performed at Wilsonville the entire procedure takes 4-5 days and a material balance is achieved by calculating the preasphaltenes by difference.

We modified the Wilsonville procedures to achieve a direct measure of each fraction for material balance and decreased the laboratory time by using ultrafiltration and sonication in place of Soxhlet extraction. The procedure adopted involves a flash distillation of 300g of the total product liquid taking cuts IBP-420°F and 420-550°F under 100 mm Hg, and 550 to ~850°F end point at 0.5 mm Hg. The bottoms are pyridine extracted to give the soluble SRC with rejection of the insoluble organic matter and mineral matter. The SRC is freed from pyridine and extracted with benzene by ultrasonic agitation and filtered through a 5 micron Millipore filter. Benzene insolubles on the filter are recovered as preasphaltenes. Asphaltenes are obtained by precipitating them from 50 mL of benzene in 500 mL n-pentanes. The oils are therefore the n-pentane:benzene (10:1) solubles that are recovered by removing the solvent mixture by rotovap under nitrogen at 70°C. As described in Figure 2 and detailed in Appendix B, attachments 3 and 4, the distillation/separation procedure requires a total of 22 man-hours.

c. Procedure W (Modified Wilsonville Method)

The solvent separation procedure practiced at Wilsonville (Appendix B, attachment 2) requires that the starting sample be a distillation bottoms free of cresol insoluble material. Because the procedure involves extensive Soxhlet extraction and not all materials are directly recovered and weighed, we modified the method as outlined in Figure 3 and detailed in Appendix B, attachment 4. The method uses total product as starting material and substitutes ultrasonic extraction/microfiltration in place of Soxhlet extraction. Since the procedure uses benzene to solubilize the material and then precipitates the asphaltenes from a mixture of n-pentane-benzene (10:1) the chemical composition of the oils and asphaltenes may show significant differences when compared to the similar fraction of Procedure A.

Procedures A, D and W describe above each provide, depending on the order of analysis used, operationally defined fractions that may be different in their chemical compositions as well as the quantity of fraction recovered. The detailed analytical characterization of the fractions from each separation procedure is described in Appendix B, attachment 5. In comparing the fractions from each procedure we find many more differences than similarities. Differences were apparent both on the molecular level and the overall fraction level. We observed that the number average molecular weight for the distillate was less than that for solvent separated oils, and that the pentane soluble oils from Procedure A had a smaller molecular weight than Procedure W oils which were soluble in n-pentane: benzene (10:1). This can be attributed to larger molecular species being co-solubilized with the addition of benzene. Increase of refractive index measurements confirmed that the oils/distillate from each procedure are different and also confirmed the observed increase in molecular weight. The preasphaltene fraction recovered from the distillation procedure had a higher molecular weight than the preasphaltenes recovered from the solvent fractionation procedures. We can attribute this to possible repolymerization of oils-asphaltenes-preasphaltenes during the prolonged (3-6 hours) heating of the toal sample.

In general, the distillation procedure gave a reproducible distillate yield, but a bottoms (850°F+) that may have undergone repolymerization as evident from our analytical characterization. The distillation procedure can produce an oil product that nearly resembles a Wilsonville recycle solvent, if special heating conditions are used.

The solvent separated preasphaltenes and residues were similar giving nearly identical yield and ash content, while the oils and asphaltenes exhibited different chemical and physical properties. The differences, as discussed, are attributed to the solvent composition used to isolate them.

2. Column Chromatographic Separation

A column chromatographic method was developed for semiquantitative separation of coal-derived distillate liquids into functional-group enrich fractions. Figure 4 outlines the procedure and Appendix B, attachment 6 describes the development efforts. The distillate is treated with HCl (g) while in benzene solution to remove N-base components as HCl-adducts. The benzene solubles remaining (acid/neutrals) are subjected to silica gel/alumina column chromatography to give three subfractions: saturates, aromatics and phenols. The base components are reclaimed by passing NH_3 through a mixture of the HCl-adduct in benzene.

3. Gas Chromatography

A gas chromatographic separation method was developed to characterize coal liquids at the molecular level. The separation was performed using the conditions

Detector	Hydrogen Flame Ionization
Liquid Phase	8% SP-2100
Solid Phase	Gas-chrom Q
Column Temperature	Programmed at +50°C for 10 min. then 5°C/min to 300°C
Sample Induction Temperature	150°C
Carrier Gas	Helium
Flow Rate	30 mL/min
Column Length/Diameter	4.07 m x 4.8 mm OD (10 ft x 3/16")
Sample Size	0.9 μL (microliter)
Detector Temperature	310°C
Calculated Theor. Plates	2668 per meter

A model compound mixture was used for peak identification and relative retention time measurements. The retention times were related to the boiling point of the respective compounds. Figure 5 gives a relationship between boiling point and structure of the compounds typically found in recycle solvents. See Appendix B, attachment 6 for the application of GC method to characterize Wilsonville recycle solvent and its column chromatographic separated subfractions.

4. High Performance Liquid Chromatographic (HPLC) Procedure

A HPLC procedure was developed to quantitatively profile the hydrocarbon neutral fraction of a coal-liquefaction recycle solvent. The recycle solvent was separated into polar and nonpolar fractions by silica/alumina column chromatographic procedure described previously. The nonpolar fraction, composed of saturates, aromatics and hydroaromatics was used for chromatographic analysis. Optimum chromatographic conditions were found using a reversed phase column C-18 (ODS) and acetonitrile as the mobil phase. Maximum UV-response was found at 295 mm on the variable wavelength UV-detector. The sample concentration of 3 mg/ml in CH_2Cl_2 using a 20 µL sample loop and a flow rate of 5 mL/min were found to be optimum. Four standard components; naphthalene, phenanthrene, 2,3-dimethylnaphthalene and pyrene were used to assess reproducibility of retention times. Reproducibility was found to be ±0.1 minute of a 15 minute chromatogram. The response of the differential refractometer provided a relative measure of component concentration while the UV-detector at 295 mm, due to the variability of molar adsorptivity, was selected to enhance the absorption of 2-3 ring component.

The chromatographic procedure was used to demonstrate the differences in ring size distribution in the neutral fractions of two Wilsonville recycle solvents characterized by the microautoclave test to be different in solvent quality. For details see Appendix B, attachment 7.

SUBSEQUENT TASKS AND STUDIES

In developing the SRC-I process, International Coal Refining Company (ICRC) recognized the need of an analytical laboratory for sound analytical characterization of the feed, intermediate and products of the proposed demonstration plant at Newman, Kentucky. To accomplish this objective, two major programs were defined.

1. Program Area 26.1--SRC-I Demonstration Plant Analytical Laboratory
2. Program Area 12.1.10--Development of SRC-I Product Analysis

Under Program 26.1, expertise in analytical chemistry was developed by organizing historical knowledge and assimilating new knowledge as it became available from ICRC's contractors and the chemical literature. the data were then used to define samples, analytical methods, instrumentation, space, and staff needed to create a functional analytical laboratory.

Specific major accomplishments were: (1) definition of the performing areas, instruments, waste-solvent management, and staff qualifications for >4,300 ft^2 of laboratory space; (2) documentation of a sophisticated capillary gas chromatography/mass spectrometry method for identifying coal-derived saturates, aromatics, phenols, nitrogen bases; (3) development of a comprehensive X-ray method to profile and semiquantitatively measure major, minor, and trace elements in SRC, anode cokes, coal, and KMAC; and, most significantly, (4) a detailed Analytical Methods Manual listing over 70 laboratory procedures that can provide the most precise data base possible with current (1982) technology.

Program 12.1.10 was designed to define, quantify, document, and develop laboratory procedures that would correlate the analytical data bases (historical and future) from the Advanced Coal Liquefaction Facility in Wilsonville, Alabama with those from ICRC's 100-lb/day process development units in Trexlertown, Pennsylvania.

Major accomplishments were: (1) a comprehensive audit of Wilsonville's material-balance and daily sampling sites, along with the analytical procedures used in 1982; (2) a detailed precision/reproducibility study of five key analytical procedures to establish correlations between ICRC's and Wilsonville data bases; (3) establishment interlaboratory round-robin testing that resulted in development of standard analytical methods for coal conversion [cresol solubility (precision, ±1%), solvent fraction (±5%), vacuum distillation (±3%), simulated distillation by gas chromatography (±4%), and elemental analysis (±2%)]; (4) a comprehensive four-year historical review of the value of the microautoclave solvent-quality test (kinetic) used at Wilsonville and its impact on "next-day" process performance, which showed not direct correlation of the method as a predictive tool; (5) the finding that coal pyrite content (>1.2%) and its distribution had an impact on daily Wilsonville plant performance; (6) the finding that for each change of coal type at Wilsonville, more than 30 days is required in order for gas production and solvent molecular composition to reach a steady state; and (7) development of a solvent quality test that uses the "feed" coal with or without hydrogen as measure of "next-day" performance.

Reference 1 and 2 provide summarized accomplishments under the program 26.1 and 12.1.10 and collated analytical procedures required to operate SRC-I plant.

REFERENCES

1. Schweighardt, F. K., July 1983, Internal R&D Task Summary Report: Analytical Methods Development, DOE/OR/03054-21, International Coal Refining Co., Allentown, Pa.

2. Klusaritz, M. L., et al., March 1983. Final Technical Report: SRC-I Demonstration Plant Analytical Laboratory Methods Manual. DOE/OR/03054-14. International Coal Refining Co., Allentown, Pa.

FIGURE 1
PRODUCT LIQUID SEPARATION
PROCEDURE A

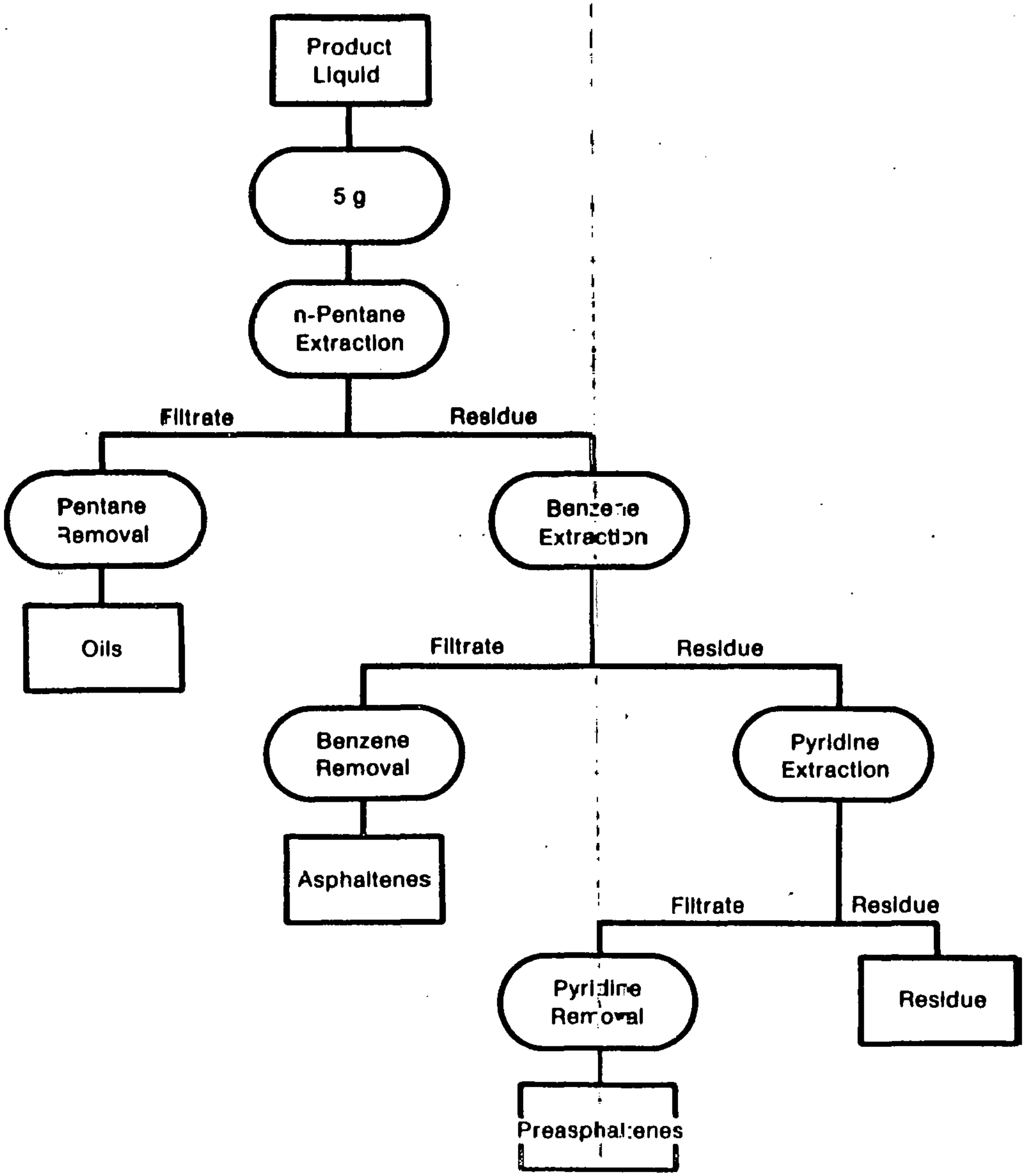


FIGURE 2
PRODUCT LIQUID SEPARATION
PROCEDURE D

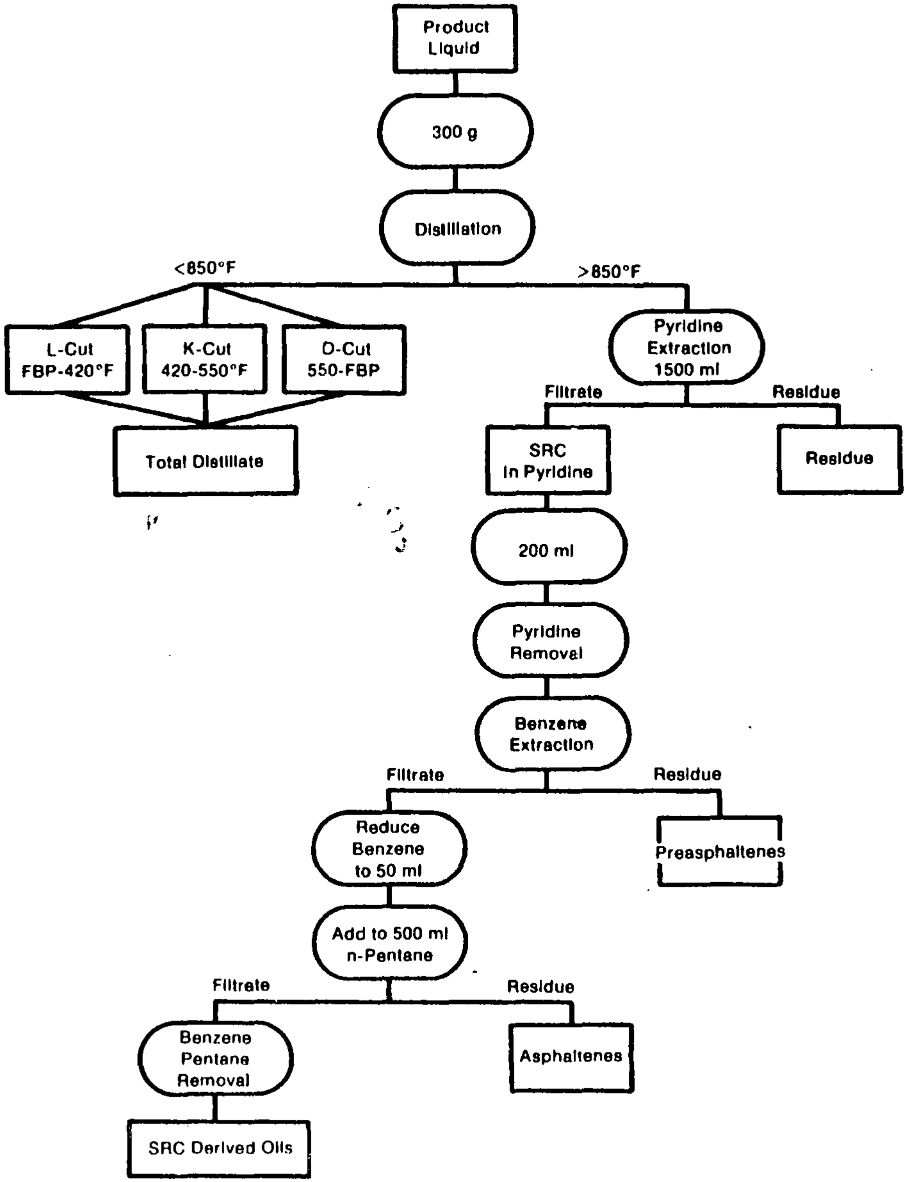


FIGURE 3
PRODUCT LIQUID SEPARATION
PROCEDURE W

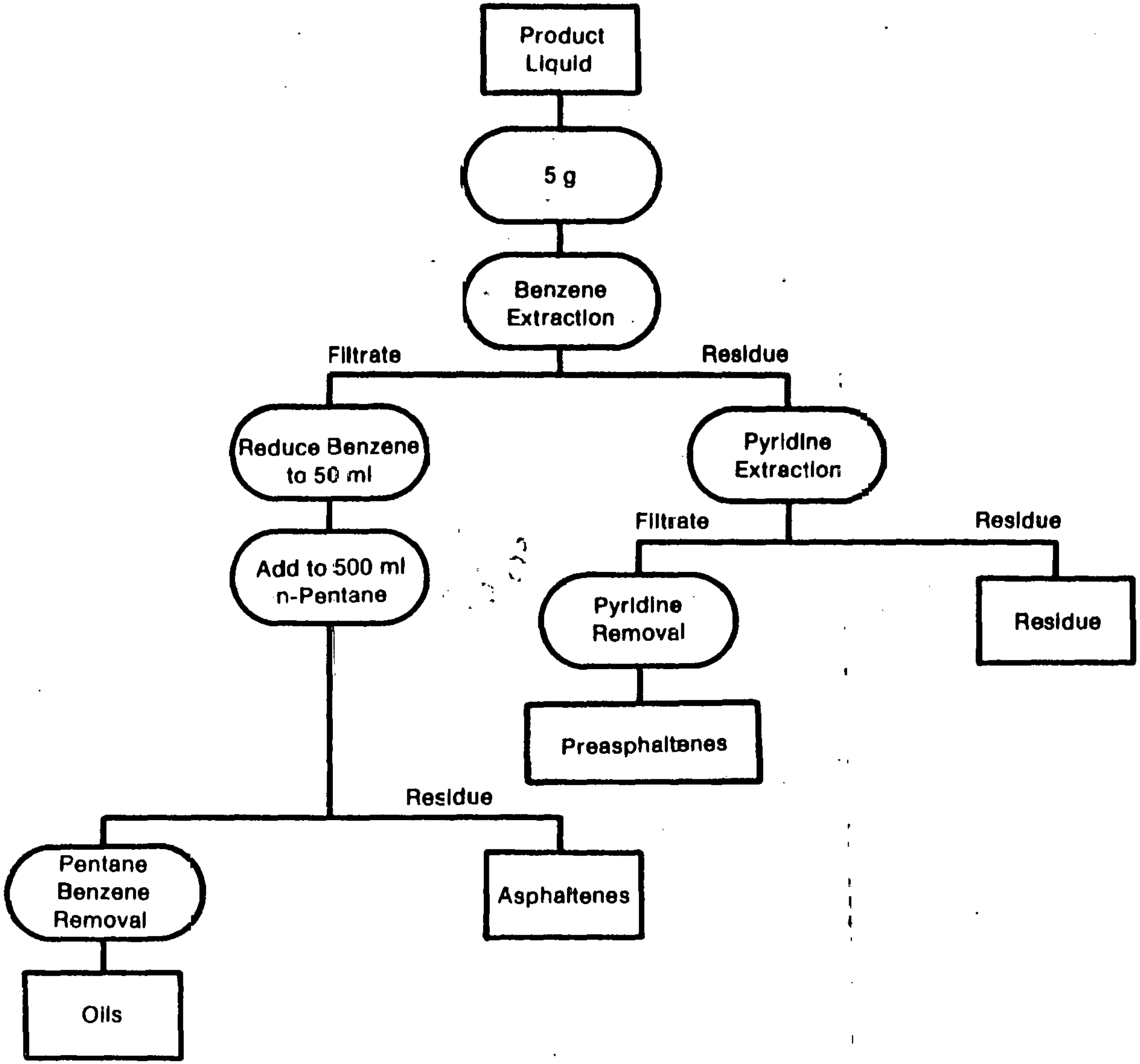


FIGURE 4
COLUMN SEPARATION
OF A PROCESS SOLVENT

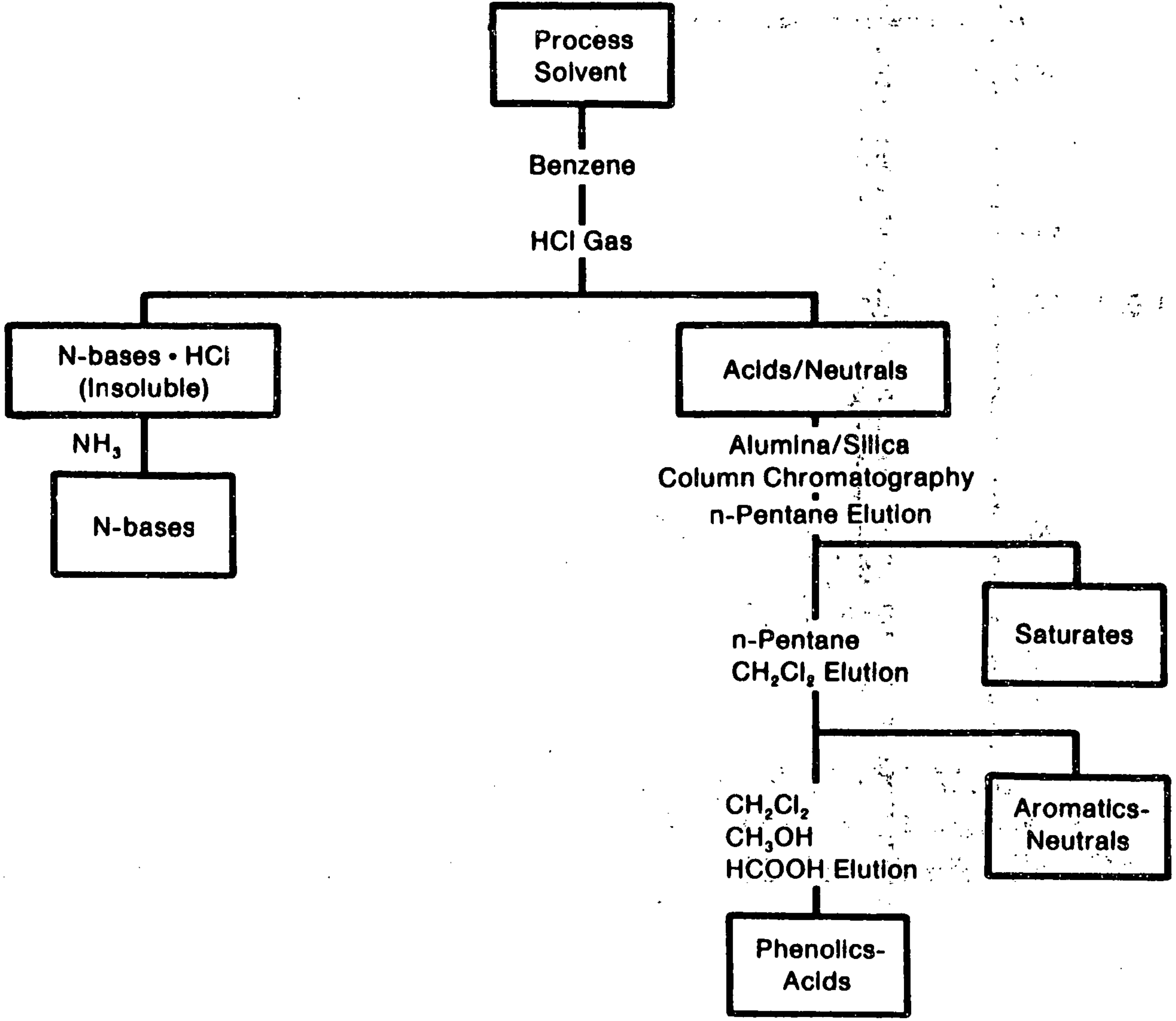
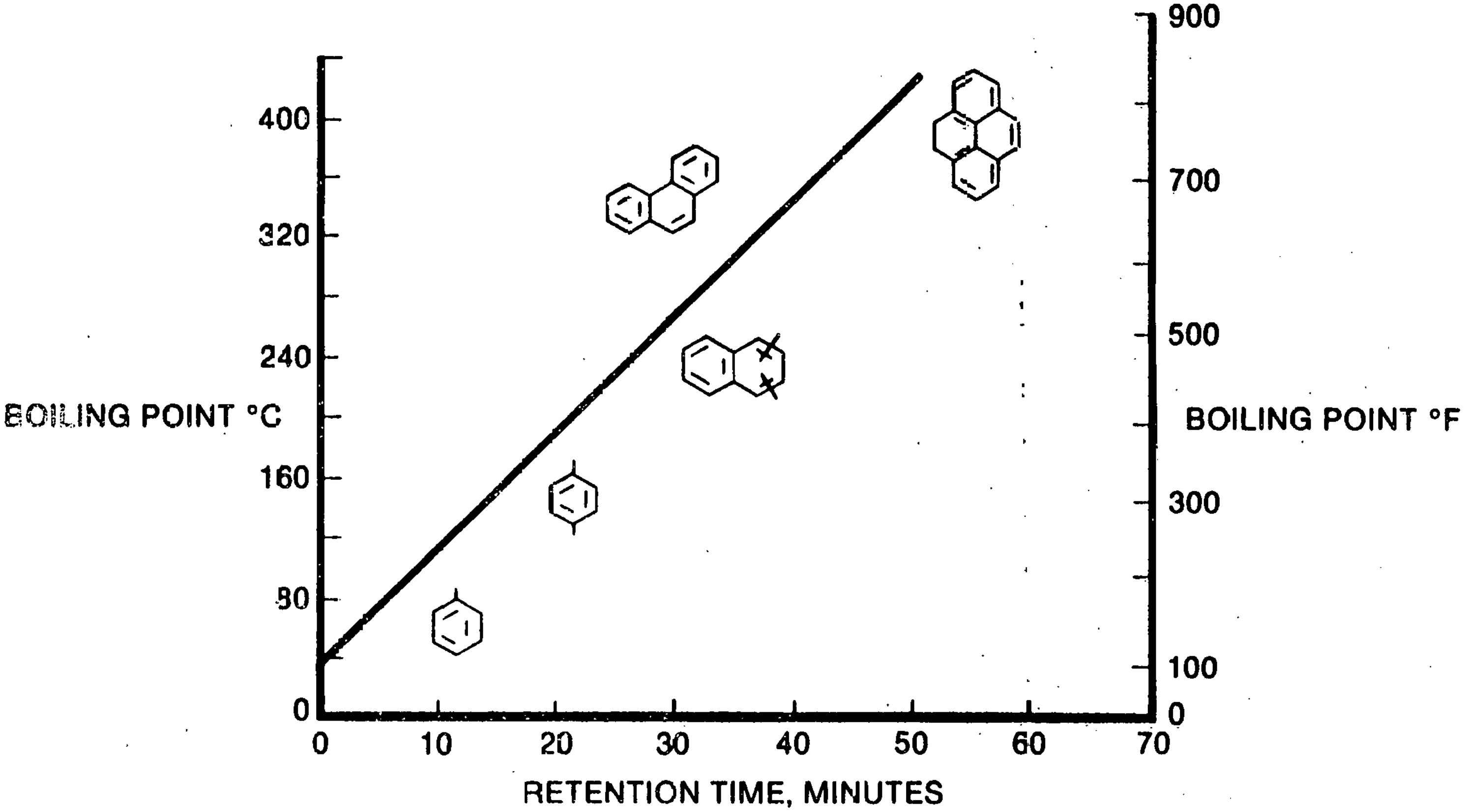


FIGURE 5
STANDARD CURVE OF GAS-CHROMATOGRAPHIC RETENTION TIME VERSUS BOILING POINT OF POLYNUCLEAR AROMATIC HYDROCARBONS FOUND IN COAL LIQUIDS.



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