Correlation of Recycle Solvent Quality to Coal Liquefaction

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INTRODUCTION

"Solvent quality" is a contrived solvent property used in coal liquefaction. It is assumed to be an important guide for expressing how well a recycle solvent will convert coal to products soluble in tetrahydrofuran (THF) or pyridine. Over the past 40-50 years, much has been written about the solvents used to prepare coal slurries, yet few solvent quality parameters have been quantified and related to process conditions or feedstocks.

For this report, solvent quality was measured by kinetic microautoclave test as used at the Wilsonville Advanced Coal Liquefaction Facility (1). The microautoclave method, originally developed by the Conoco Coal Development Company, has been used to quantify solvent quality at Wilsonville since 1978. This method (Note 1) defines solvent quality as the weight percent tetrahydrofuran solubles generated, based on weight percent moisture- and ash-free (MAF) coal. Traditionally, a solvent quality test result in the lower range (≈65) warned of potential preheater coking problems. More recently, solvent quality has been used to monitor the effects of adding light solvent refined coal (LSRC) and distillates to the solvent stream to enhance coal liquefaction and maintain solvent balance.

This study attempts to identify important independent and dependent variables associated with the solvent refining of coal (SRC) by relating plant operation to coal feedstock and product slate and by correlating the impact to changes in the results from the microautoclave solvent quality test.

PROPERTIES AND CHARACTERISTICS OF COAL LIQUEFACTION SOLVENTS

In SRC liquefaction, an effective process solvent should be (a) coal-derived to permit continuous plant operation; (b) a distillate with a nominal boiling range of 450-850°F; (c) able to sustain a 10-40 wt % coal slurry through feed pumps; (d) able to rapidly accept coal dissolution products in solution or suspension; (e) able to act as a hydrogen donor or shuttling agent for hydrogen transfer under a predominantly free-radical mechanism; and (f) capable of carrying the liquefaction product stream through solid/liquid separation processes and ultimately of being recycled to continue the process.

The chemical properties of recycle solvents have been well-documented by Whitehurst et al. (2), Burke et al.,(3) and Neavel (4). A recycle solvent generated under SRC-I process conditions exhibits a complex molecular composition. The solvent is composed of a mixture of alkyl (C_1-C_4)-substituted polynuclear hetero- and hydroaromatic compounds. Gas chromatography/mass spectrometry (GC/MS) data have revealed that 40 individual components comprise almost 60 wt % of the solvent. The remaining 40 wt % may include hundreds to thousands of individual compounds (5). The major molecular species are (5-30%) substituted naphthalenes and (5-10%) phenanthrenes.

During SRC-I liquefaction, each time the solvent/coal mixture passed through the reactor 0-30 wt% new solvent material is generated, on an MAF feed coal basis. Therefore, the molecular composition would be expected to constantly change and shift in response to processing conditions and feed slurry composition. At Wilsonville, the virgin distillate solvent exits the process at vacuum tower T102, trays 3 and 8 (see Figure 1 for a process flow scheme). The solvent is then held briefly in a holding tank (V178), from which daily samples are taken for solvent quality testing.

Recently, the solvent in V178 (originally V131A) has been mixed with LSRC or other product streams in tank V131B just before it is recycled into the process at V101A as a new coal slurry. The LSRC, a product stream from the critical solvent deasher, is added to the distillate solvent for several reasons. Most important to the overall process is that LSRC appears to enhance solvent quality by adding high-boiling compounds (6), and somehow promotes distillate yield so that solvent balance is maintained. Handling the LSRC in material balance calculations is a problem. If the LSRC is inert, it can simply be subtracted. However, if the LSRC is a reactant, its degree of conversion must be quantified before an oil yield can be computed (7). Because the addition of LSRC to the distillate solvent has not been continous for all coal types, solvent quality values from V131B samples are not included throughout this report.

Anthracene oil is sometimes added to the system at V178 to maintain solvent balance. For this study, data points were eliminated if more than 5% by volume anthracene oil was added to the V178 solvent within 5 days of a material balance period.

THE ROLE OF SOLVENT IN SRC-I LIQUEFACTION

Our current understanding of coal liquefaction is that bituminous coal, when mixed with solvent at 200-250°F begins to dissolve, but that most of the coal matrix is in suspension. The primary dissolution products are believed to be small molecules already trapped within the coal (8). Depending on coal type and rank, these compounds may represent 5-20% of the coal.

At Wilsonville, the feed slurry is held at 150-250°F (depending on the percent LSRC added) for 8-12 hr without hydrogen before it enters the preheater (B102) under partial hydrogen pressure. Under these holding conditions in tanks V101A and V101B, the recycle solvent must exhibit good dissolving power. That way, the solvent can extract and exchange with the small molecules trapped in the coal and fill other voids created by loss of water and swelling.

Thermal reactions, in which sissile bonds (9) break and initiate actual coal matrix liquefaction, do not occur until ~600°F. Such temperatures are first reached in the preheater (B102) under ~2,000 psi hydrogen pressure. At liquefaction temperatures, the nascent free radicals apparently rapidly combine with labile hydrogen from the feed coal during the first .1-5 min, forming a cresol- (or pyridine-) soluble product (4). When temperatures in the preheater reach 780°F, the recycle solvent appears to rapidly solvate the primary liquefaction product. After the process slurry stream enters the reactor, the exothermic reaction drives the temperature to almost 840°F during a residence time of 30-60 min. In the reactor the original recycle solvent and the new coal product components shuttle hydrogen to free-radical sites generated from splitting and cracking at reaction temperature (840°F).

The solvent, which is now modified in molecular composition by the addition of cracking and splitting products from 0-30 wt % MAF coal, can itself be rehydrogenated. This newly available, "donatable" hydrogen can be shuttled to more recently generated active sites formed in reactor R101 to further stabilize the system.

That portion of the solvent that is active in shuttling hydrogen to free-radical sites has been associated with the hydroaromatic content. Other hydrogen-transfer species have been suggested (2) to be active when hydroaromatic species were absent or depleted, including aromatic hydroxyl (e.g., β-naphthol) and alkyl (methyl) side chains like those found on 2-methylnaphthalene. Curran et al. (10) concluded that the liquefaction solvent needs sufficient donatable hydrogen to promote greater distillate yield and reduce coking, and that the hydrogen can come from many sources.

Correlation of Solvent Quality to Process Operation

A review of past operating reports from Wilsonville and interviews with Wilsonville staff resulted in an assemblage of 48 primary parameters that define a pilot plant run under the SRC-I first-stage regime (Note 2). Fifty-seven data points analyzed for these 48 variables span from 1978 (run 133) to 1982 (run 234). During this period, five major coal types were processed for 3-58 days on stream, per run. Usually one to three data points from each run were selected to represent a material balance at nominal steady-state conditions. These material balance points form the data base of this report.

In analyzing these data, we assumed that each coal type can be viewed independently, and that data for each coal type can be averaged. The reason for this assumption was that we believe the variability in coal reactivity changes the demand on the operating conditions, generates a coal-specific recycle solvent after line out, and would promote a unique product distribution. All coals or similar coal types are combined only when deemed necessary for general comparison purposes. The objective of this study is therefore to relate the microautoclave solvent quality test result to process factors that cause or are affected by a change in the solvent's role in SRC-I liquefaction.

The objectives of first-stage SRC-I liquefaction are assumed to be:

- Maximum conversion of coal to cresol (or pyridine) solubles
- Minimum hydrogen consumption based on MAF coal conversion
- Maintenance of process solvent in solvent balance
- Minimum hydrocarbon and maximum heteroatom gas production
- Minimum preasphaltene content in the vacuum tower (T102) bottoms

The major process variables considered are coal type, dissolver (R101) temperature and pressure, and coal space rate in the dissolver.

Reaction severity, i.e., the degree of coal conversion to distillate and gas, can be assessed from yield structure information, such as hydrocarbon and heteroatom gas production (total gas minus H_2O) and net hydrogen consumption.

Although total gas production may not seem to relate to the recycle solvent's physical or chemical properties, it is presumed to be affected by "solvent quality." Solvent quality in this case refers to the solvent's ability to shuttle hydrogen to those coal species that have split into large components and to minimize hydrocarbon cracking that forms C_1-C_4 gases.

The benzene solubles (SRC oils and asphaltenes) of the vacuum tower bottoms (T102) and the total SRC (pyridine solubles) of this same stream may be the best analyzed samples to quantify both product distribution and reaction severity. This T102 bottoms stream is "process-normalized" in that minor process excursions are averaged by the volume and throughput of the tower.

Process solvent is not measured, but it is determined by difference when calculating a material balance from laboratory distillation (450-end point) and subsequent gas chromatography results (450-850°F). We believe process solvent yield is neither a precise nor an accurate parameter to consider for correlation.

The light oils (C_5-450°F), which are quantified by gas chromatography data, provide another measure of liquefaction severity and solvent breakdown independent of total gas production.

Table 1 lists typical process parameters with the limits of the values accepted as equivalent in this study.

Table 1

Wilsonville SRC Process Conditions

Dissolver pressure	1,700 ± 100 psig
Dissolver temperature	825 ± 10°F
Dissolver volume in use	75%
Coal space rate	38 ± 3 lb/hr-ft^3
H_2 partial pressure (heater inlet)	1,470 ± 75 psi

Representative solvent quality test results for V178 (holding tank) solvent collected over the past 4 years are plotted as a function of time and coal type in Figure 2. Day-to-day variation can be as great as 10 units on the solvent quality scale. As an analytical test, solvent quality may be considered to have a precision of ±2.

RESULTS

Total Gas Production

Figure 3 plots the entire data set for total hydrocarbon and heteroatom gas production (MAF coal) vs. solvent quality for all coals. The distribution is clustered at 8 ± 2% total gas and 75 ± 6 solvent quality. Replotting total gas production from Kentucky #9 coal only gives four distribution curves, one for each mine. Figure 4 shows that each plot has distinct clusters and a few outlying data points. In Figure 4, the data points are coded to define common dissolver conditions (pressure, temperature, and volume used). Only in the Fies Mine Kentucky #9 coal is there an apparent shift to greater gas production at higher dissolver temperature and pressure. Figure 5 provides a different perspective by plotting total gas production data as a function of days on stream over 4 years. Note that because all data points are presented, process conditions varied more than the accepted limits given in (Table 1) for any one common preheater/reactor condition. Note that high gas production usually follows a change in coal type. This trend is apparently independent of reactor pressure, coal space rate, and almost independent of temperature (825-840°F).

Gas production is graphed as a function of total elemental hydrogen consumption in Figure 6; all data points are presented. If a total gas production range of 5-10% and a hydrogen consumption of 1.5-3% on MAF coal are arbitrarily set as lower and upper limits, the points outside these limits are mainly those from the material balance periods taken within 30 days after a change in coal type for SRC-I processing. These same points are the outlying data points in Figure 4.

Product Correlation to Solvent Quality

In order to analyze the data meaningfully and objectively, we related solvent qualities to product distribution by coal type at the selected material balance periods. Process variables such as preheater temperature and reactor pressure, temperature, and volume are documented in the discussion.

Dotiki Kentucky #9 Coal. The major differences in processing Dotiki coal occurred between Runs 202/203 and 204/206/208. The first set of runs was conducted at a lower dissolver temperature (825 vs. 840°F). Also, the pyrite content of the coal in runs 206B and 208 was less than 1.1%, whereas in run 203 it was 1.3%.

Figures 7A-7D plot solvent quality vs. specific product components. Figure 7A (pyrite content vs. solvent quality) identifies each point by run/ material balance number and can be used as a guide to identify the equivalent run in Figures 7B-7D.

Solvent quality does not appear to affect product yield. However, the percent pyrite in the feed coal appears to affect solvent quality; that is, if the percent pyrite is below 1.1 wt %, the solvent quality value deviates from the major distribution cluster. The operating conditions during runs 206 and 207 were upset because the high-pressure separator failed and nearly 70 vol % of the unit was filled with cresol-insoluble material. Run 208, which was short, however, had the highest solvent quality (70) and lowest (1.1%) pyrite content. This solvent quality value is unusually high; its cause is unknown and only one material balance (MB) sample was taken for this run. Daily solvent qualities measured before and after the 208AB MB were between 64 and 66.

Lafayette Kentucky #9 Coal. Runs 163 to 201 were conducted with Lafayette coal. Runs 163, 166, and 201 were at 75% dissolver volume at 1,700 psi and 825°F; dissolver pressure in runs 167, 168, 171, and 172 increased to 2,100 psi with only 50 vol % of the dissolver in use; and run 190 was performed at 2,100 psi, 825°F, and 75% dissolver volume. The largest volumes of anthracene oil were added to the system between runs 170 and 182. Solvent quality increased from 65 to 75, but fell to 68 after run 182 and remained there until the next coal type (Dotiki) was used. Figures 8A-8D illustrate the relationship for Lafayette coal. Note that most Lafayette feed coals had a pyrite content of less than 1.2 wt %.

Pyro Kentucky #9 Coal. Pyro Mine coal was run under dissolver conditions of 1,700 psi and 825°F for runs 151, 159, 160, and 161, and at 2,100 psi and 825°F for run 162. These process conditions are the most constant for the coals tested. Because run 151 was conducted with Indiana V solvent and processed 3 months before run 159, run 151 can be eliminated from each solvent quality correlation. Figures 9A-9D show the relationship between Pyro coal solvent quality and product distribution. Product yield ranged widely (±8%), but solvent quality changed only slightly (± 2). The range of product distribution is no less than that for other coal types that experienced solvent quality changes of more than ±10 from the average.

Fies Kentucky #9 Coal. Fies Mine coal was processed under the most varied conditions of all coal types (Note 2). Most Fies Mine coal was run at dissolver conditions of 2,100 psi, 840°F, and 75 vol %. Only three feed coals (229A, 229B, and 210AB) had a pyrite content below 1.1%. Anthracene oil was added only once, after run 210. Solvent quality was 75 and was not greatly affected (±2). The reason for this is not clear, but the optimum activity of hydrogenated anthracene oil may be 75 ± 2 as measured by the solvent quality test. Solvent quality and product distribution for Fies Mine coal are compared in Figures 10A-10D. In general, only total gas production (depicted earlier in Figure 4) shows any apparent correlation between solvent quality and dissolver temperature: lower dissolver temperature and higher solvent quality yield the lowest gas production.

Effect of Solvent Quality on the Attainment of Liquefaction Objectives

We assume solvents are primary products of the feed coals, therefore their compositions are affected first by the coal's structure, second by processing conditions, and third by addition of external material (LSRC), control of distillate boiling point distribution, or modification by chemical means.

Once a new steady-state process condition is reached and the solvent lined out, the solvent's new properties apparently allow a different product yield distribution to be maintained. The preheater and reactor temperatures have their greatest impact on the rate of formation of primary liquefaction products that place a demand on the solvent for rapid coal dissolution and hydrogen donation.

If the solvent is returned to the front end without addition from another stream (LSRC or distillate), we can at best anticipate an apparent steady-state solvent because the feed coal is constantly changing. Most importantly, the coal's pyrite content and distribution is more variable than the organic macromolecular structure. Figure 11 shows the range in solvent quality as a function

of coal type with and without LSRC addition, independent of process conditions, for all material balance periods. Circles represent average results, and the bars define the upper and lower limits of the solvent quality.

Next, we considered only those solvent quality results obtained from material balances more than 30 days after a change in feed coal type and more than 5 days after addition of anthracene oil. All data points were averaged by coal type with respect to their pyrite concentration (Figure 12).

Figure 12 shows that the Fies, Pyro, and Indiana V coals with >1.2% pyrite generated solvents with average SQ values above 72. The trend of Fies, Pyro, and Indiana coal data clustering together and Dotiki and Lafayette coal data clustering together was also observed for nearly all average product distributions (e.g., Figures 7-11) as well as other variables not included in this report.

Measurement of Liquefaction Behavior

Based on these observations, a logical approach to defining coal-derived recycle solvent quality is to react samples of the solvent, or the modified solvent, in the microautoclave test with the daily feed coal. This solvent quality test would involve comparison of the daily microautoclave product distribution (residue, preasphaltenes, and total benzene solubles) with the product distribution for a well-maintained standard coal of the same type. The primary liquefaction activity of the solvent would be determined under hydrogen-starved, solvent-rich conditions, to mimic the slurry tanks and the rapid coal dissolution process in the preheater at 750 ± 2°F. The secondary liquefaction activity of the solvent would be determined from a similar product distribution under hydrogen-rich conditions (2,000 psi), to quantify the sustaining hydrogen-transfer reactions in the reactor.

These two tests would be made within the same sand bath; at the same time, a third test microautoclave would be run. In this third bomb, the standard coal type would be reacted with a standard model compound solvent mixture. Together, all three results would provide internal checks on the reliability of the test (standard coal vs. standard solvent); optimum continued dissolution of process coal (feed coal vs. recycle solvent/no H_2); and optimum continued conversion to the desired product slate (feed coal vs. recycle solvent/ H_2).

Figure 13 summarize how this approach to measuring solvent quality could be used to predict liquefaction behavior of the next day's operation. Over a 3-month period in our laboratories, we have demonstrated that solvents from holding tank V178 yield different SQ values depending on whether they are tested with the feed coal that they will be slurried within the next run or a standard Indiana V coal. The greatest difference is the relative distribution of benzene solubles to preasphaltenes. Silver and Miller (11) were first to note similar coal conversion differences when using a solvent generated from Wyodak coal and reacting it with Kentucky #9 coal.

SUMMARY

The concept of quantifying solvent quality by a microautoclave test does have merit if the test is run with the same coal-type used for coal liquefaction. Correlation of the solvent quality result to preheater chemistry (rapid coal dissolution with minimum hydrogen shuttling) and reactor chemistry (rapid and sustaining hydrogen donation/shuttling) is apparently possible. As used at Wilsonville during runs 133-234, the microautoclave SQ result was of tangential significance for absolute day-to-day pilot plant operation. However, during the past 4 years the Wilsonville staff has collected SQ data under the most varied of conditions, e.g., changes in feed coal, addition of LSRC to the solvent, redefinition of solvent boiling range, and most recently, addition of hydrotreated material to the solvent. These SQ results do provide us with a relative measure of coal conversion behavior to solvent composition under pilot plant conditions to consider for future process design. The Wilsonville staff has prepared a topical report on solvent activity covering this subject (12).

From our SQ study of Wilsonville it is our opinion that bench-scale experiments comparing different coals with solvents of questionable parentage for single pass conversion are at best of limited relative value, and result in conflicting interpretations from lab to lab. Such experiments do define the kind of solvent composition that provides specific results. If such results or such solvents can be produced in situ is another question. Laboratory liquefaction experiments that may be the most meaningful (although the most time-consuming and expensive) are full recycle of the solvent for attaining apparent steady-state operation. We estimate 5-12 solvent passes are required for line-out depending on process conditions.

Note 1

Wilsonville Solvent Quality Test (#43080-60): Into a 30 mL bomb, add 1.5 g of standard Indiana V coal, 12 g of solvent, and a 1-in. steel rod. Place in sandbath (750°F) for 10 min and shake at 1,000 spm over 1.5 in. Extract the reaction products with tetrahydrofuran (THF) to determine THF insolubles. Calculate percent conversion on MAF coal. See Reference 12 for details.

Note 2

The full data base is available upon request from the author.

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FIGURE 1

WILSONVILLE PILOT PLANT PROCESS FLOW DIAGRAM

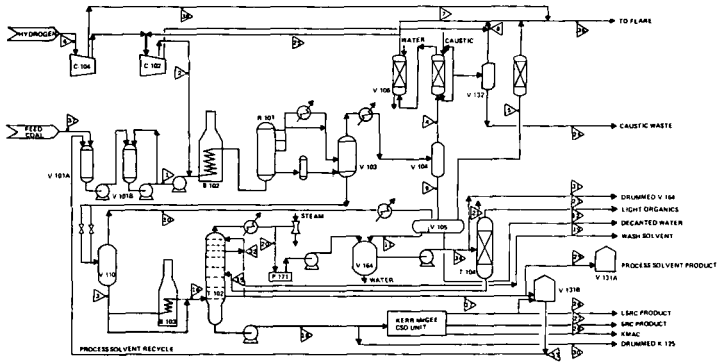


FIGURE 2

WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

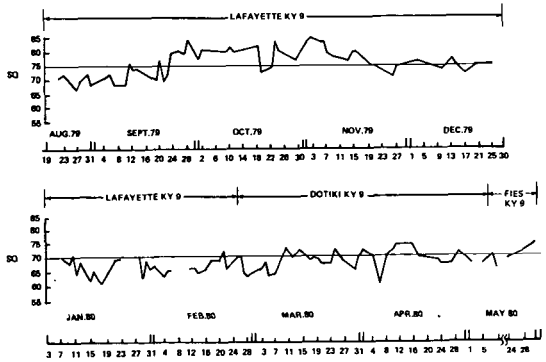


FIGURE 3

TOTAL GASES VS. SOLVENT QUALITY
ALL DATA POINTS

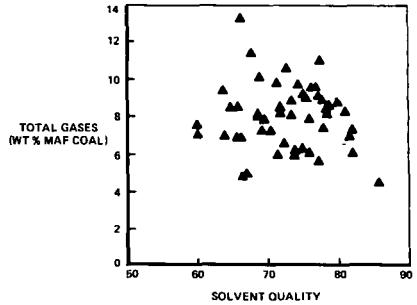


FIGURE 4

SOLVENT QUALITY VS. TOTAL GAS (WT % MAF COAL)

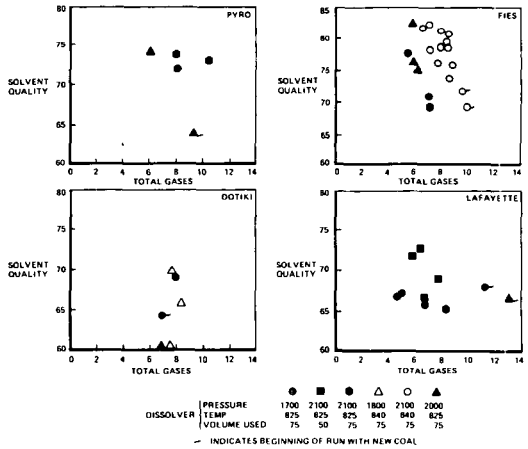


FIGURE 5

TOTAL GAS (HYDROCARBON + HETEROATOM)
AS A FUNCTION OF TIME

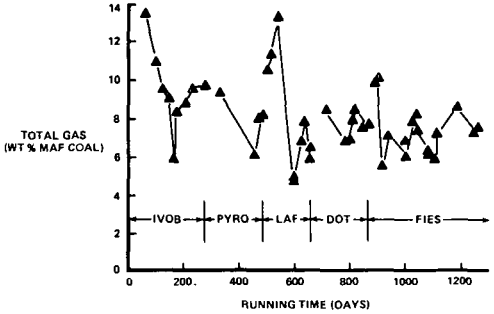


FIGURE 6

HYDROGEN CONSUMPTION VS.
TOTAL GAS PRODUCTION
ALL DATA POINTS

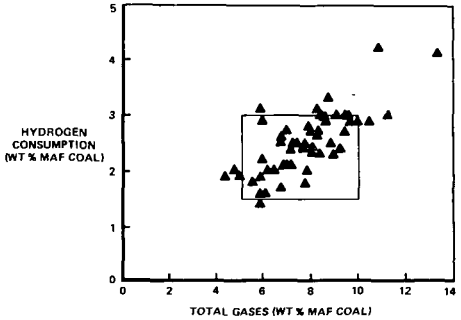


FIGURE 7

SOLVENT QUALITY VS.
PRODUCT YIELDS FOR DOTIKI COAL

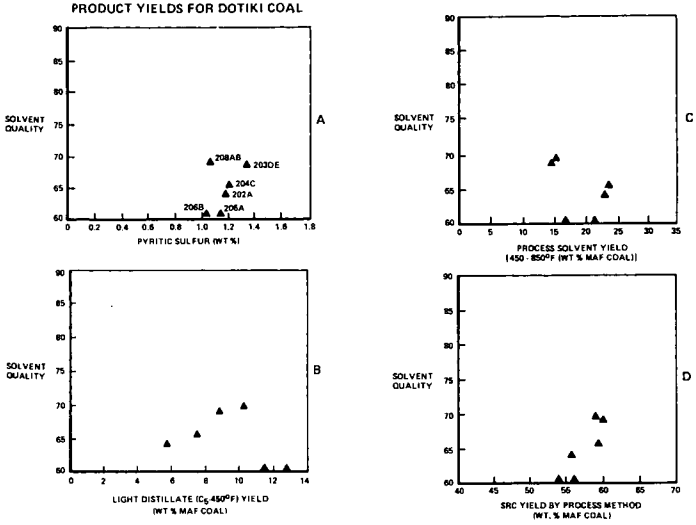


FIGURE 8

SOLVENT QUALITY VS.
PRODUCT YIELDS FOR LAFAYETTE COAL

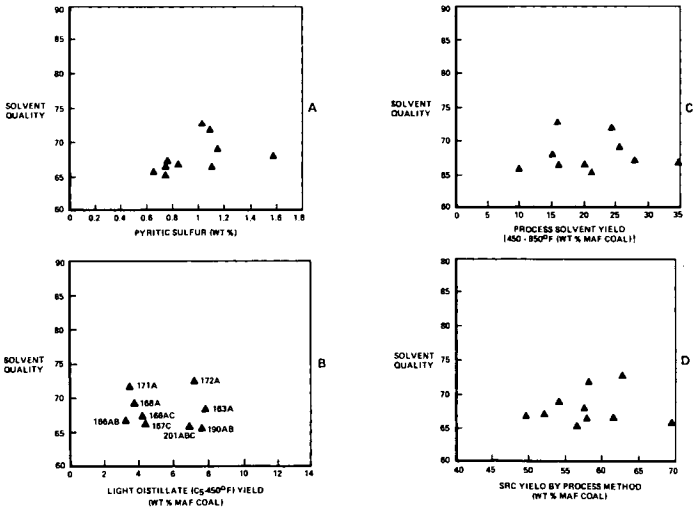


FIGURE 9

SOLVENT QUALITY VS.
PRODUCT YIELDS FOR PYRO COAL

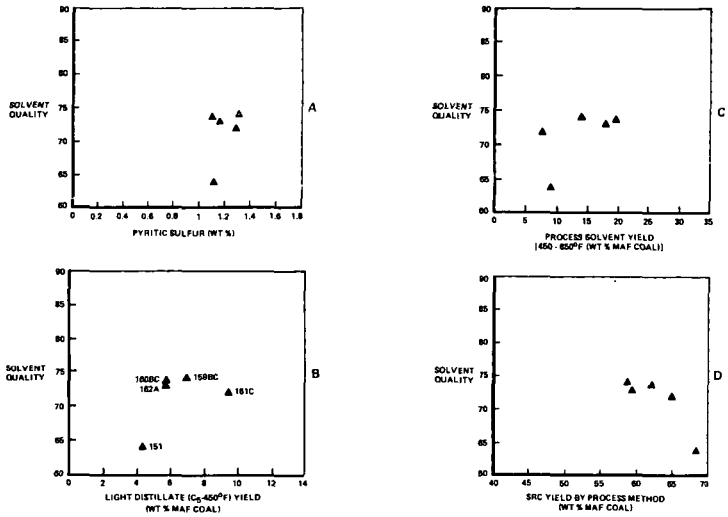


FIGURE 10

SOLVENT QUALITY VS.
PRODUCT YIELDS FOR FIES COAL

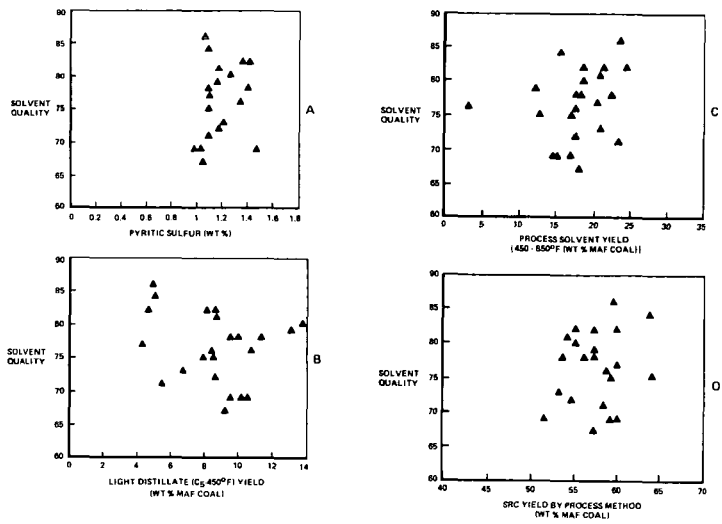
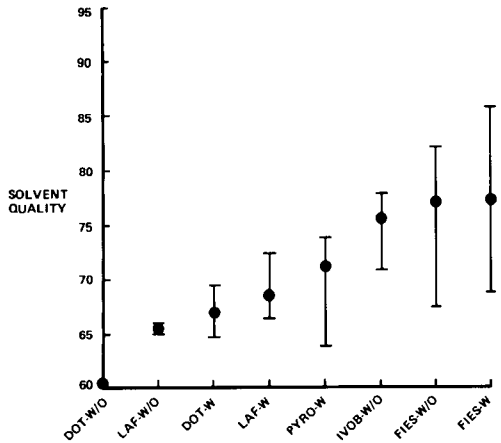


FIGURE 11

WILSONVILLE SOLVENT QUALITY (SQ) VS. COAL TYPE



W : WITH LSRC ADDITION
W/O : WITHOUT LSRC ADDITION

FIGURE 12

COAL PYRITE VS. SOLVENT QUALITY BY COAL TYPE

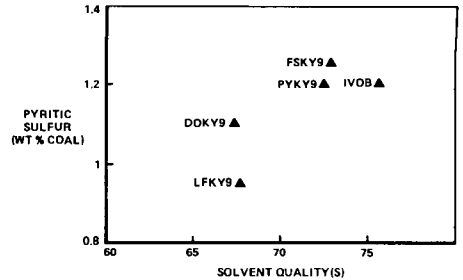


FIGURE 13

PROPOSED SRC-I SOLVENT QUALITY TEST

SOLVENT \ COAL	STO PROCESS COAL-TYPE (1)	DAILY TOTE-BIN NO H_2 (1)	DAILY TOTE-BIN H_2 (2)
STD SOLVENT TET/MN	QUALITY ASSURANCE TEST		
DAILY RECYCLE SOLVENT		PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT - DISTRIBUTION
DAILY RECYCLE SOLVENT & ADDITIVE		PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT DISTRIBUTION

(1) MICROAUTOCLAVE S/C (8/1); 10 MINUTES AT 750°F
DETERMINE: RESIDUE (THR) – PREASPHALTENES – BENZENE SOLUBLES

(2) TEST CONDITIONS TO BE DETERMINED