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EXPLORATORY RESEARCH ON SOLVENT REFINED COAL LIQUEFACTION

Annual Technical Progress Report, January 1—December 31, 1979

September 1980

Work Performed Under Contract No. AC01-79ET14800

The Pittsburg and Midway Coal Mining Co.
Shawnee Mission, Kansas

U. S. DEPARTMENT OF ENERGY

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EXPLORATORY RESEARCH
ON
SOLVENT REFINED COAL LIQUEFACTION

ANNUAL TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JANUARY 1, 1979 THROUGH DECEMBER 31, 1979

THE PITTSBURG & MIDWAY COAL MINING CO.
P. O. BOX 2970
SHAWNEE MISSION, KANSAS 66201

September 1980

PREPARED FOR THE
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DIVISION OF COAL CONVERSION AND UTILIZATION
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ABSTRACT

This report summarizes the progress of the "Exploratory Research on Solvent Refined Coal Liquefaction" project by The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory during 1979. In a series of experiments with varying feed gas composition, low levels (5-10 mole %) of carbon monoxide had little effect on the SRC II processing of Pittsburgh Seam coal (Powhatan No. 5 Mine) while higher levels (20-40 mole %) resulted in a general degradation of operability and reduced oil yields. Addition of finely divided (~1 μm) pyrite to the reactive Powhatan coal had little effect on oil yields although the molecular weight of the distillation residue was apparently decreased. When finely divided pyrite and magnetite were added to the less reactive coals from the Loveridge and Blacksville No. 1 Mines (also Pittsburgh Seam), however, substantial increases in oil yields and product quality were obtained. In a comparison of upflow and downflow dissolver configurations with Powhatan coal in the SRC II mode, there was no difference in yields or product quality. A study characterizing specific reactors revealed a significantly higher conversion in the SRC I mode with a reactor approximating plug flow conditions compared to a completely backmixed reactor. In the SRC II mode there was only a slightly higher oil yield with the plug flow reactor.

I. SUMMARY

The activities of the Merriam Laboratory during 1979 were focused in four major areas:

1. Evaluation of the effect of adding iron compounds in both the SRC I and SRC II processes.
2. Exploration of the effects of utilizing synthesis gas in the SRC II processing of a Pittsburgh Seam coal.
3. Evaluation of the potential usefulness of novel reactor configurations and determination of the effect of backmixing in the reactor.
4. Investigation of short residence time coal liquefaction*.

Beginning March 1, 1979, the Merriam activities were carried out under a separate contract with the Department of Energy. Prior to that time, the work was reported in conjunction with activities at the Fort Lewis Pilot Plant. The second quarter 1979 progress report**, therefore, included a summary of the various reports describing previous work at Merriam along with a description of the new contract objectives and a history of the Merriam Laboratory in solvent refining of coal.

A. Addition of Iron Compounds

The first series of runs (DOE 288-295) investigating the effect of adding iron compounds (pyrite [FeS_2], magnetite [Fe_3O_4], ferrous sulfide [FeS] and pyrite in combination with molecular sieve) was in the SRC I mode with Pittsburgh Seam coals from the Blacksville No. 1 and Loveridge Mines. The pyrite and magnetite were finely divided (particle size ~1 μm) whereas the ferrous sulfide and molecular sieve were ground to pass 150 mesh. Slightly improved oil yields were obtained with all of the iron compounds although pyrite was apparently the most effective. There was a slight increase in hydrogenation level with the added pyrite and a very slight improvement in desulfurization with the magnetite addition. The details of this study are found in the first quarter 1979 progress report†.

In the second series of experiments investigating additives (runs DOE 333R-339R), finely divided pyrite was added to Pittsburgh Seam

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* Discussion of the short residence time coal liquefaction studies will be delayed until a later report.

** Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980, FE/14800-10.

† Solvent Refined Coal, Quarterly Technical Report for the period January 1, 1979 through March 31, 1979; February 1980, FE/496-172.

coal from the Powhatan No. 5 Mine and finely divided pyrite and magnetite were added to Pittsburgh Seam coal from the Loveridge Mine. There was little change in total oil yield from Powhatan coal with added pyrite, apparently due to the already high iron content and reactivity of the coal. Heavy distillate quality was also unchanged, except for decreased desulfurization with pyrite addition. The fusion point of the distillation residue was reduced by 40°C with pyrite in the feed, however, and its solubility in hexane and benzene increased. In contrast, total oil yield from the less reactive Loveridge coal was increased 8-11% (absolute) by pyrite addition and to a lesser extent by adding magnetite. A corresponding decrease in SRC and IOM yields was observed. Desulfurization and denitrogenation of the heavy distillate product were also enhanced by the addition of iron containing compounds. Although operability was satisfactory while processing Loveridge coal with additives, it became impossible to run when the additives were removed. A complete description of this work was given in the third quarter 1979 progress report*.

As part of the additives work, a four-run series (DOE 301-304) was conducted with solvent received from the Wilsonville Pilot Plant, coal from either the Pyro Mine or Colonial Mine (KY 9/14), and with or without added pyrite. One of the objectives of this work was to investigate the decline in solvent quality experienced by the Wilsonville Pilot Plant during runs in support of the SRC I Demonstration Plant. No problems related to solvent quality or coking were apparent in the Merriam runs. The solvent received from Wilsonville was found to contain an unusually high hydrogen content (9.0 wt %). This level decreased substantially during the two initial Merriam runs which were made under Wilsonville conditions. There was an increase of about 5% (absolute) in recycle solvent and total oil yields with pyrite addition and a decrease in SRC yield of 3%. After the supply of Pyro Mine coal was exhausted, the feed was changed to Kentucky 9/14 coal from the Colonial Mine with little apparent change in results. In the final run in this series, the operating temperature was increased from the Wilsonville temperature of 441°C (826°F) to a temperature more typical of Merriam SRC I operations, 455°C (851°F). There was a further decline in hydrogen content of the recycle solvent and SRC and an improvement in desulfurization. This work is described in the second quarter 1979 progress report**.

B. Synthesis Gas Utilization

Two series of experiments were conducted to investigate the effect of carbon monoxide in the feed gas on the SRC II processing of Pittsburgh Seam coal from the Powhatan No. 5 Mine. In the first series (runs DOE 296R-298R) low levels (5-10 mole %) of carbon

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period July 1, 1979 through September 30, 1979; July 1980, FE/14800-11.

** Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980, FE/14800-10.

monoxide had no apparent effect on oil or SRC yields, but did result in the formation of ammonium carbonate (bicarbonate) deposits in vapor-liquid separation vessels. In the second series (runs DOE 331RB-332RB), high carbon monoxide levels (20-40 mole %) were found to contribute to a general degradation of unit operability as evidenced by increased unfiltered coal solution (UFCS) viscosity and plugging of the slurry feed and dissolver systems. Oil yields were substantially below those found in earlier work at 5-10 percent concentrations. SRC and insoluble organic matter (IOM) yields were increased and total hydrogen consumption decreased. Carbon monoxide consumption and carbon dioxide production were consistent with the shift reaction at all levels of CO addition. The low level carbon monoxide addition was reported in the first quarter 1979 progress report* and the higher level addition in the second quarter 1979 progress report**.

C. Reactor Behavior

In work reported this quarter, two aspects of reactor behavior were analyzed. In the first study (comprised of three series of runs), the use of novel reactor configurations (3-pass† and downflow reactors) was explored. In the second study, the effect of backmixing in the reactor was investigated.

1. Three-Pass Reactor

The yields obtained with the 3-pass dissolver (run DOE 340) were consistent with the residence time that would result if slurry bypassed the second and third tubes of the dissolver.

2. Downflow Reactor, Kentucky 9/14 Coal

The experiments with the downflow dissolver and Kentucky 9/14 coal (runs DOE 341 and 342R) were confounded by an increased severity in the preheater which was dictated by operating difficulties. There was a 2 percent (absolute) decrease in overall coal conversion in the SRC I mode with the downflow configuration based on insoluble organic matter (IOM) yields even though the residence time in the dissolver was at least twice as long. In the SRC II mode, there was apparently a 1% decrease in conversion with the downflow configuration although the comparison was hindered by a somewhat different preheater outlet temperature in the control run. In the SRC I mode, conversion of SRC to oil was increased by the combination of higher preheater severity, longer residence time in the

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* Solvent Refined Coal, Quarterly Technical Progress Report for the Period January 1, 1979 through March 31, 1979; Feb. 1980, FE/496-172.

** Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980, FE/14800-10.

† The 3-pass dissolver was upflow, downflow, upflow in slurry with corresponding cocurrent, countercurrent, cocurrent hydrogen flow.

dissolver and downflow dissolver configuration. In the SRC II mode, however, higher severity in just the preheater plus the downflow configuration resulted in decreased conversion of SRC to oil. The data also suggest that product quality was slightly worse in the downflow configuration.

3. Comparison of Upflow and Downflow Reactors, Powhatan Coal

Runs DOE 343R-344R involved a comparison of upflow and downflow dissolver configurations in the SRC II processing of Pittsburgh Seam coal from the Powhatan No. 5 Mine. The effects of small changes in preheater temperature and total pressure were also investigated.

Operability in the downflow configuration was considerably better than in the runs with Kentucky 9/14 coal reported above. This was due to reduced plugging by the Powhatan coal and improved methods for monitoring and controlling slurry level.

There was no difference in yields between upflow and downflow dissolver configurations. In addition, no difference was found in yields between operation at 2000 and 1800 psig with either upflow or downflow configurations. Operating the preheater at 425°C rather than the usual 400°C had no effect on yields with the downflow configuration but shifted the products to lighter molecular weight ranges with the upflow dissolver. The dissolver L/D also had no effect in the range of 27 to 54 with the upflow configuration.

There was no difference in product quality between upflow and downflow dissolvers, between operation at 1800 and 2000 psig or due to a change in preheater temperature except for heavy distillate (HD) sulfur level. There was significantly greater desulfurization of the HD product with the upflow dissolver configuration (sulfur level of 0.37% compared to 0.49%).

4. Determination of the Effect of Backmixing

Four experiments (runs DOE 345-348R) were conducted to determine the effect of backmixing in the reactor on yields, hydrogen consumption and product quality. Two experiments were conducted in each mode, SRC I and SRC II. In each mode, one experiment was made with a continuous stirred tank reactor (CSTR) and the other with a reactor employing a high length/diameter ratio to approximate plug flow.

The total oil yield in the SRC I mode was 8.2% (absolute) higher with the plug flow reactor. This increase was accompanied by a 2.5% (absolute) lower SRC yield and a 4.5% (absolute) lower insoluble organic matter (IOM) yield. The recycle solvent production was within 2% (absolute) of the break-even level with the plug flow reactor compared to a 6% deficit with the CSTR. The hydrogen consumption was 0.8% absolute (62% relative) higher with the plug flow reactor.

In the SRC II mode there was a slightly higher total oil yield, 2.8% absolute, with the plug flow reactor accompanied by a 2.9% (absolute) lower SRC yield and a 0.4% lower IOM yield. Hydrogen consumption was apparently slightly higher with the plug flow reactor, 0.6% absolute or 15% relative.

Desulfurization was generally greater with the plug flow reactor and the molecular weight of the distillation residue was less.

Residence time distribution measurements indicated that the continuous stirred tank reactor had essentially complete backmixing. There was also considerable backmixing in the tubular reactors which had Peclet Numbers ranging from about 2 to 4.

II. INTRODUCTION

This report covers work at The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory on the Solvent Refined Coal (SRC) process during the period January 1, 1979 through December 31, 1979 with emphasis on work performed during the period October 1, 1979 through December 31, 1979. Details of the work performed during the first nine months of 1979 are available in quarterly reports.

A. Reports of Previous Work

Previous work at this laboratory has been described in interim, final, monthly, quarterly and annual reports to the Office of Coal Research, the Energy Research and Development Administration and the Department of Energy. A summary of these documents appears in the second quarter 1979 report* along with a description of the current contract objectives and a history of the Merriam Laboratory in solvent refining of coal.

B. Currently Reported Work

During the fourth quarter of 1979, activities at the Merriam Laboratory included:

- Investigation of novel reactor configurations in both the SRC I and SRC II modes with Kentucky 9/14 and Pittsburgh Seam (Powhatan No. 5 Mine) coals.
- A comparison of plug flow and completely backmixed reactors with Kentucky 9/14 coal in the SRC I mode and Pittsburgh Seam coal from the Powhatan No. 5 Mine in the SRC II mode.
- Characterization of solvent extracts from distillation residues, determination of volatile material in the extracts, and a detailed study on the repeatability of the solvent extraction method.

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980, FE/14800-10.

- A residence time distribution study to characterize the macromixing in various reactor configurations.

The run conditions and results for all runs reported this quarter are shown in Table I.

III. DISCUSSION

A. Investigation of Novel Reactor Configurations

1. Background

Three series of runs were conducted in this study. In the first series, with Kentucky 9/14 coal, one 4-part experiment was carried out in the SRC I mode with a 3-pass (upflow, downflow, upflow) dissolver. In the next series, also with Kentucky 9/14 coal, two experiments were conducted in a downflow dissolver, one each in the SRC I and SRC II modes. In the last series of experiments, upflow and downflow dissolvers were compared with Powhatan coal in the SRC II mode. The run conditions for all runs are summarized in Table I and the various reactor configurations are described in Section III-F, Maintenance and Modifications.

The results of previous experiments at the Merriam Laboratory involving downward flow of slurry have generally been inconclusive.

Investigation of an upflow/downflow design was reported in the third quarter 1978 progress report*. In this configuration, the advantage of countercurrent hydrogen flow was apparently more than offset by the lack of mineral matter accumulation in the downflow section of the dissolver. There was a significant decrease in conversion of SRC to distillate oil in both the SRC I and SRC II modes compared to the upflow configuration. It is possible, however, that slurry was flowing out the top of the dissolver, bypassing the downflow section.

Investigation of a downflow, countercurrent hydrogen dissolver was reported in the first quarter 1977 progress report**. It was found that in the SRC I mode the downflow dissolver resulted in lower oil yields and reduced product quality. In the SRC II mode, product quality was also reduced in the downflow dissolver although there was little change in oil yields. There was an increase in C_1-C_4 yield in both SRC I and SRC II modes with the downflow configuration. In light of the current work, it is not certain that all of the slurry was leaving the dissolver through the bottom, so these results are questionable.

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* Solvent Refined Coal, Quarterly Technical Report for the Period July 1, 1978 through September 30, 1978; August 1979, FE-496-160.

** Solvent Refined Coal, Quarterly Technical Report for the Period January 1, 1977 through March 31, 1977; July 1977, FE-496-134.

2. Three-Pass Dissolver Runs

a. Experimental

The conditions selected for run DOE 340 were those used to compare SRC I yields with different reactor configurations in the past. A 3-pass dissolver (see section III-F, Maintenance and Modifications) with cocurrent, countercurrent, cocurrent hydrogen flow was employed to remove product gases part way through the reaction and expose the slurry to fresh hydrogen. This configuration represents a potential improvement over the upflow/downflow dissolver tested previously in that there is a high concentration of solids in two upflow sections of the dissolver, both early and late in the reaction.

In the first part of the run, the total hydrogen flow was proportioned to deliver one third to the preheater and one third each to the second and third dissolver passes. The hydrogen flows to the preheater and second dissolver passes were varied during the run as discussed below.

b. Operation

Poor oil yields during the first part of the run led to speculation that slurry was largely bypassing the second and third tubes of the dissolver. Thirty-six hours into the run, hydrogen flow into the second tube was reduced from 8.7 to 2.8 moles/hour to determine if the gas flow was lifting the slurry overhead and out the gas exit line. Shortly thereafter, a soft plug apparently formed near the entrance to the second tube and the slurry level in the second tube dropped to almost zero. By 61 hours on stream the oil yield had not improved and the hydrogen flow to the second tube was increased to the original 8.7 moles per hour. The plug immediately broke free and the slurry level came back up. At 86 hours on stream the hydrogen feed to the preheater was doubled to determine if the reaction there was starved for hydrogen. The yield remained poor, and at 116 hours on stream a plug formed somewhere between the preheater hydrogen inlet and the second tube of the reactor, forcing a shutdown.

c. Yields

The yields for the 3-pass dissolver run, DOE 340, are compared to those from a similar upflow run below. The conditions are identical, except for the hydrogen flow rate.

Conditions*	DOE 235	DOE 340-1	DOE 340-2	DOE 340-3	DOE 340-4
Dissolver	Upflow	3-pass	3-pass	3-pass	3-pass
H_2 Feed, moles/hr					
Preheater	23.9	8.8	8.8	8.8	18.0
Countercurrent Reactor (second pass)	--	8.7	2.8	8.7	8.7
Cocurrent Reactor (third pass)	--	8.4	8.4	8.4	8.4
Total, moles/hr	23.9	25.9	20.0	25.9	35.1
Total, wt % based on slurry	4.3	4.5	3.5	4.4	6.0
Yields**, wt % MF Coal					
C_1-C_4	10.1	7.8	5.6	5.7	5.8
Recycle Solvent	12.3	1.7	0.5	(1.2)	2.4
Total Oil	28.9	18.9	16.4	13.2	16.7
SRC	38.2	50.9	56.6	57.2	54.6
IOM	4.6	5.5	6.1	6.3	5.6

* All at 1 hr residence time, 455°C, 2000 psi, 45% Ky 9/14 coal/55% reycle solvent.

** Based on dist. of filtrate.

The yields for each part of run DOE 340 are based on only one or two distillations and there is considerable scatter in the data. These results should, therefore, be considered qualitative. Although the differences between the yields in the various segments of run DOE 340 are probably within the experimental error, there is a significant difference between the standard upflow dissolver and the 3-pass dissolver. Recycle solvent yield dropped from about 12% to essentially breakeven levels, total oil was reduced by at least 10% (absolute), SRC was increased by 12-18%, IOM was increased by 0.9-1.5% and C_1-C_4 yields dropped 2.3-5.5% with the 3-pass dissolver. The yields for the 3-pass dissolver are near what would be expected for an upflow dissolver with about 20 minutes residence time, other conditions being the same. This suggests that the slurry was exiting through the vapor exit line, bypassing the second and third tubes of the dissolver.

d. Product Quality

There was little difference in product quality between a previous upflow run at similar conditions and the 3-pass dissolver run, except for sulfur level. It was lower by about 0.1-0.3 percent (absolute) in both the recycle solvent and SRC for the upflow run:

	DOE 235 Upflow	DOE 340 3-Pass
Recycle Solvent*		
% S	0.4 (.34-.37)	0.6 (0.5-0.6)
% N	1.1 (NA)	1.0 (.93-1.01)
SRC*		
% S	0.5 (.54-.55)	0.8 (0.7-0.9)
% N	2.3 (NA)	2.2 (2.2-2.3)

* Average and range for available analyses.

The viscosities of the unfiltered coal solutions for run DOE 340 are shown in Table II and Figure 1. The viscosities of the feed slurries are shown in Table III and Figure 2. Due to a lack of viscosity data for experiments in a standard reactor at the same conditions, it is not possible to attribute changes in viscosity to reactor configuration.

The solubilities of the distillation residues in hexane, benzene, toluene and pyridine are shown in Table IV. Due to erratic operation during this run, it is difficult to draw conclusions based on the solubilities.

3. Downflow Dissolver Runs, Kentucky 9/14 Coal

a. Experimental

The 3-pass dissolver was to be used for all of the Kentucky 9/14 coal runs. Difficulties with level control in the second, downflow, pass during run DOE 340, however, led to substitution of a single pass downflow dissolver for runs DOE 341 and DOE 342R to study flow control specifically.

Run DOE 341 was to be conducted under the conditions used by the Fort Lewis Pilot Plant in material balance runs 4 and 8. This would have been a "base point" run; i.e., one designed to produce an optimum amount of SRC fuel consistent with known system constraints. These conditions were later modified to improve operability, however, so a direct comparison with a previous upflow experiment cannot be made.

Run DOE 342R was to be made at 455°C, 1800 psig and 1 hour residence time. The average residence time turned out to be about 20% higher than planned due to difficulties in operation.

b. Operation

Operation was erratic during runs DOE 341 and 342 due to a settling of soft solids in the bottom of the downflow dissolver which plugged the slurry exit line. These plugs were broken by closing the vapor exit line. This caused a slight increase in dissolver pressure forcing the slurry out the bottom. This procedure was repeated as necessary to maintain the level in the dissolver within a rather broad, but measurable, range. Since this procedure was necessary in runs DOE 341 and 342R with the downflow dissolver, it is suspected that some or all of slurry was leaving the 3-pass dissolver through the vapor line during run DOE 340, bypassing the second and third tubes.

The differential pressure indicator, which was to be used to measure the level in the dissolver, was found to be of insufficient range, so the slurry level was monitored by watching the thermocouple readings in the top half (vapor space) of the downflow dissolver. When the liquid level reached the first thermocouple position in the vapor space (nine inches above the inlet), a sharp increase in the temperature reading was observed. The vapor exit line was then closed until slurry spilled over into the high temperature separator indicating that the plug was broken. In this manner the slurry level was controlled between the slurry inlet and the thermocouple position, resulting in a nominal slurry residence time of 48±6 minutes for run DOE 341. In run DOE 342R, an attempt was made to obtain better control over the level by moving the thermocouples in the vapor space closer to the slurry inlet (to two inches apart). This was unsuccessful, however, because due to conditions in the dissolver, all of these thermocouples read nearly the same. The residence time in DOE 342RB was therefore controlled to only 69±9 minutes.

During run DOE 341, plug material from the bottom of the dissolver was analyzed. It was found to contain 40-50% pyridine insolubles with 28% ash in the insolubles. Since the plug material was primarily unconverted coal, the severity in the preheater was increased to alleviate the plugging in the dissolver.

There appears to be a significant difference in solids residence time distribution (RTD) between upflow and downflow operation. In upflow, dense particles or agglomerations of particles would tend to settle out in the dissolver until they have become small enough through reaction to be swept out with the liquid. In downflow, these same particles could block the slurry exit line. This may not be a problem in larger dissolvers since the extent of reaction of solid particles depends in part on the length of time it takes to fall from the dissolver inlet to the outlet. This is a function of the size of the unit as well as nominal slurry residence time. In addition, the size of the particles relative to the diameter of the exit port will have an effect on the tendency of the particles to form a plug.

The outlet temperature of the preheater was increased to 425°C during run DOE 341 and the pump rate was cut in half (residence time doubled). This resulted in an average temperature of 435°C* and a residence time of

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* Due to an endothermic reaction and/or heat transfer characteristics in the preheater, it was necessary to run the middle of the preheater at about 440°C to obtain an outlet temperature of 425°C.

about 42 minutes in the preheater so that a significant portion of the total reaction took place there. This increase in preheater severity greatly reduced the plugging in the bottom of the dissolver.

c. Yields

The yields for the SRC I downflow run with Kentucky 9/14 coal, DOE 341D, are compared to those for an upflow experiment below:

Conditions*	GU 127	DOE 341D
Dissolver	Upflow	Downflow
Nominal Slurry Residence Time, min.	21	48±6
Preheater outlet temperature, °C	400	425
Hydrogen feed, wt %	4.6	7.7
Yields,** Wt % MF Coal		
C_1-C_4	3.3	10.9
Recycle Solvent	5.2	(6.4)
Total Oil	13.1	12.0
SRC	61.4	50.9
IOM	5.5	7.5

* For both, dissolver temperature was 450°C, pressure 1410 psig, 39% Kentucky 9/14 coal in slurry.

** Based on dist. of filtrate.

It is difficult to draw conclusions on the differences between upflow and downflow configurations due to operating difficulties, but it appears that conversion of coal was lower in the downflow dissolver based on the 2% higher IOM yield. There is also a significant shift to lighter products in the downflow run which is largely a consequence of the higher temperature and longer residence time in the preheater (29 minutes at an average temperature of about 435°C) and longer residence time in the dissolver.

The yields for the SRC II downflow experiment with Kentucky 9/14 coal, run DOE 342RB, are compared to those for a similar upflow run below:

Conditions*	DOE 237R	DOE 342RB
Dissolver	Upflow	Downflow
Preheater outlet temperature, °C	400	425
Residence time, hr	1.07	1.2±0.2
Pressure, psig	2000	1800
Yields, Wt % MF Coal		
C_1-C_4	14.6	17.8
Heavy Distillate	24.6	4.8
Total Oil	39.5	30.8
SRC	22.5	32.2
IOM	4.6	5.4

* For both, 30% Kentucky 9/14 coal in slurry, 455°C dissolver temperature.

The yields for DOE 342RB are based on only one UFCS distillation so the information should be considered qualitative. Again, there was an increase in IOM and a significant shift from heavy distillate to light oils and gases with the downflow dissolver and high severity preheater. Conversion of SRC to oil was also less in the downflow configuration.

d. Product Quality

In the SRC I downflow experiment (DOE 341), product hydrogenation was somewhat less than in a similar upflow run:

	GU 127 SRC I Upflow	DOE 341D SRC I Downflow
Recycle Solvent*		
% H	7.8 (7.7-7.9)	7.2 (7.1-7.5)
% S	0.5 (0.46-0.46)	0.5 (0.50-0.57)
SRC*		
% H	5.8 (5.7-5.9)	5.4 (5.3-5.4)
% S	0.8 (0.82-0.86)	0.7 (0.64-0.66)
Fusion Point	190 (181-197)	150 (147-152)

* Average and range for available analyses.

The sulfur level of the recycle solvent was slightly higher in the downflow run, but the level in the SRC was slightly less. The fusion point of the SRC was about 40°C lower in the downflow configuration, although this was probably the result of the longer residence time.

The product analyses in the SRC II run (DOE 342R) show about the same deviations between different products for the same run as between upflow and downflow experiments:

	DOE 237R SRC II Upflow	DOE 342RB SRC II Downflow
Heavy Distillate**		
% S	0.4 (0.3-0.4)	0.5 (0.45-0.53)
% H	7.7 (7.6-7.8)	7.5 (7.4-7.6)
Distillation Residue*		
% S	2.3 (1.8-3.1)	2.6 (2.5-2.7)
Fusion Pt, °C	117 (106-132)	133 (125-150)

* Average and range for available analyses.
** Boiling range for DOE 237 >249°C; and for DOE 342RB >288°C

In general, however, the product quality was slightly higher in the upflow run than in downflow.

The viscosities of unfiltered coal solutions (UFCS) for runs DOE 341 and 342R are shown in Table II and Figure 1. The viscosities of feed slurries are shown in Table III and Figure 2. Due to a lack of viscosity data for upflow experiments at the same conditions, it is not possible to attribute changes in viscosity to direction of flow in the dissolver.

The solubilities of the distillation residues from runs DOE 341 and 342 in hexane, benzene, toluene and pyridine are shown in Table IV. Due to erratic operation during this series of runs, it is difficult to draw conclusions based on the solubility behavior.

4. Comparison of Upflow and Downflow Dissolver Configurations with Powhatan Coal

a. Experimental

In the work described above, direct comparisons with upflow experiments were not possible due to changes made in run conditions because of operability problems. In addition, data on the processing of Pittsburgh seam coal from the Powhatan No. 5 Mine with alternate dissolver configurations were desired. One three-part experiment, run DOE 343R, was therefore conducted with Powhatan coal and a downflow dissolver configuration and one three-part experiment, run DOE 344R, with an upflow dissolver configuration.

Runs DOE 343R and 344R were made at 455°C, 1800 psig and 1 hour residence time. The hydrogen flow rate was increased to 6 percent based on slurry, from the 4 percent used previously, to eliminate any effects due to a difference in hydrogen availability between upflow and downflow. Two percent was delivered to the preheater and 4 percent to the dissolver. Previous work has shown that lowering the flow of hydrogen to the dissolver below 4 percent affects performance, whereas increasing the flow from 4 to 6 percent has little effect.

In the initial part of each run, the preheater outlet temperature was kept at 425°C, a condition which improved downflow operability in the Kentucky coal runs. In addition, the pressure was initially maintained at 2000 psig to provide the best opportunity for a successful run until the operability with Powhatan coal could be determined. These conditions were later relaxed, first by dropping the preheater outlet temperature to the normal Merriam level of 400°C followed by a reduction in pressure to 1800 psig.

b. Operation

Operation during runs DOE 343R and 344R was improved substantially over that with Kentucky 9/14 coal reported above. This was due, in part, to the switch to Powhatan coal which created less plugging in the bottom of the downflow dissolver. In addition, an improved system was used for monitoring the slurry level in the dissolver.

The slurry level was monitored primarily by use of a differential pressure gauge with additional indication from a series of thermocouples (see Section III-F).

The valve on the vapor exit line was closed about once an hour during run DOE 343R to force slurry out the bottom of the dissolver. The resulting fluctuations in slurry level were much less than in runs DOE 341 and 342R reported above. A typical operating cycle involved a decrease in dissolver slurry level of about 6 1/2 inches while the vapor line was closed for 0.8 minutes. This would be followed by a 10 minute rise in slurry level to the normal position where slurry would begin to spill over into the high temperature, high pressure separator from the slurry exit line. Over the next 50 minutes the slurry level would rise about another 1-2 inches until the valve on the vapor line was closed again. The exact residence time in this system would be difficult to compute because the slurry level was varying, the slurry was flowing out the bottom of the dissolver during only part of each cycle, and the "cycles" were of varying length. The actual value is close to the nominal slurry residence time, however.

Operation of the upflow experiment, DOE 344R, was carried out in the conventional manner (except for hydrogen injection in the bottom of the dissolver, dissolver L/D and slurry level monitoring) and was generally uneventful.

c. Yields

A comparison of the yields with upflow and downflow dissolver configurations in the SRC II mode with Powhatan coal is shown in Table V.

There was no significant difference in yields between the upflow and downflow dissolver configurations. An averaging of the yields for the three parts of each run is shown below:

Yields, wt % MF Coal	Downflow (DOE 343R)	Upflow (DOE 344R)
C_1-C_4	14.9	15.0
Total Oil	39.4	39.5
SRC	26.5	26.3
IOM	4.9	4.8

The 0.1-0.2 percent differences are well within experimental error.

In addition, there was no significant difference in yields between operation at 2000 psig and 1800 psig in either upflow or downflow configurations (Table I).

Operating the preheater at 425°C instead of 400°C had no discernable effect on yields in the downflow configuration but did shift the products to lighter molecular weight ranges in the upflow configuration. C_1-C_4 and middle distillate yields were higher while heavy distillate and SRC were lower with the higher preheater temperature. Total conversion (based on IOM yield) was not affected by preheater temperature.

There also was no effect of dissolver L/D in the range 27 to 54 as shown by a comparison of the yields for upflow runs in the full DOE 1 dissolver (run DOE 278R) or 1/2 dissolver (run DOE 344RD).

The naphtha, middle distillate and heavy distillate yields were fairly constant during these runs and the small variations that did occur may be due, in part, to slight differences in slurry formulation.

d. Product Quality

In the Powhatan coal runs in the SRC II mode there was no significant difference in heavy distillate or distillation residue product quality (Table I) between upflow and downflow except for sulfur level in the heavy distillate. The heavy distillate sulfur level was 0.49%±0.01% with the downflow configuration and 0.37%±0.02% with the upflow configuration.

There were no significant effects on product quality apparent from changes in the preheater temperature or total pressure.

The viscosities of unfiltered coal solutions (UFCS) are presented in Table VI and Figure 3. The UFCS viscosities were higher with the downflow dissolver configuration (DOE 343R) than with the upflow configuration (DOE 344R), implying higher molecular weight materials in the nondistillable products. In addition, the viscosity increased slightly when the preheater temperature was lowered, from run DOE 343RA to 343RD and 344RB to 344RC, and when the pressure was lowered from run DOE 344RC to 344RD.

The feed slurry viscosities for runs DOE 343R and 344R are presented in Table VII and Figures 4, 5 and 6. The feed slurries generally had higher viscosities with the downflow dissolver configuration than with upflow, as did the unfiltered coal solutions. The slurries from the downflow runs (DOE 343R) exhibited the typical minimum with temperature around 230-250°F, whereas the lower viscosity slurries from the upflow run (DOE 344R) generally did not. As usual, the viscosities decreased with an increase in shear rate.

The solubilities of the distillation residues in hexane, benzene, toluene and pyridine are shown in Table VIII. Any differences in solubilities due to changes in run conditions are of about the same order as differences between replicate extractions.

B. Comparison of Plug Flow and Completely Backmixed Reactors

1. Background

The objective of this study was to determine the effect of backmixing in the reactor on yields, product quality and hydrogen consumption. This is the first time that reactors designed specifically to be completely backmixed or plug flow have been compared at the Merriam Laboratory. The residence time distributions have been measured in the reactors employed and are discussed in Section III-E and Appendix B.

2. Experimental

Runs DOE 345B and 346 were both conducted with the continuous stirred tank reactor (CSTR) described in Section III-F. A low-volume (short residence time) preheater was employed to provide the maximum sensitivity to chanqes in reactor configuration.

The run conditions are shown in Table I. DOE 345B was in the SRC I mode with Kentucky 9/14 coal at the conditions used by Fort Lewis in material balance runs 4 and 8. Run DOE 346R was in the SRC II mode with Pittsburgh Seam coal from the Powhatan No. 5 Mine at 455°C, 1800 psig and 1 hour residence time.

Runs DOE 347 and 348R were conducted in tubular reactors to provide a comparison to the CSTR runs. Run DOE 347 was in the SRC I mode with Kentucky 9/14 coal at the same conditions used in run DOE 346R. A long, thin tube (see Section III-F) was used as a reactor to approximate plug flow conditions in the liquid phase. Run DOE 348R was at the same conditions used in run DOE 346R. The single tube reactor used in run DOE 347R had a volume too small to provide convenient flow rates at the residence time used in the SRC II work. The modified GU 5 reactor (see Section III-F) was therefore used to provide a larger reactor volume in which plug flow conditions were approximated. The same low-volume preheater used in the CSTR experiments was employed to provide the maximum sensitivity to changes in reactor configuration.

Although the reactors were designed to be as close as practical to either completely backmixed (stirred autoclave) or plug flow (single tube and modified GU 5), deviations from ideality occurred. These deviations are discussed in terms of residence time distributions in Section III-E and Appendix B.

3. Operation

Operation was generally satisfactory during runs DOE 345 and 346 in the CSTR.

Some difficulty was encountered in heating the reactor up to temperature while running on flush oil, particularly at the relatively high liquid flow rate used in run DOE 345. This was due to the design of the CSTR. An air space between the autoclave itself and a steel jacket, used for introduction of cooling air, restricted heat transfer from the strip heaters located on the outside of the jacket. In addition, the apparatus was difficult to insulate and large heat losses occurred from the exterior components of the equipment. Satisfactory temperatures were generally achieved after coal was added to the feed and the exothermic reactions were underway.

The stirrer drive on the autoclave also stalled occasionally. This occurred in spite of the fact that the stirrer bearings were purged with about 5 grams/hr of recycle solvent or heavy distillate in runs DOE 345 and 346R, respectively.

Operation was also satisfactory during runs DOE 347 and 348R in the tubular reactors. Temperature control during run DOE 348R was generally better than in earlier experiments with the modified GU 5 reactor due to dual temperature control system (see Section III-F).

4. Yields and Hydrogen Consumptions

The yields and hydrogen consumptions for all four runs are shown in Table I.

a. SRC I Mode

The yields and hydrogen consumptions obtained with the continuous stirred tank reactor (CSTR) and plug flow reactor in the SRC I mode are compared below:

Reactor	DOE 345B CSTR	DOE 347 Plug Flow
Yields, Wt % based on MF Coal		
C_1-C_4	3.9	4.2
Naphtha	3.7	5.0
Wash Solvent	6.2	8.7
Recycle Solvent (loss)	(6.3)	(1.9)
Total Oil	3.6	11.8
SRC	64.4	61.9
IOM	10.1	5.6
Hydrogen Consumption, Wt % based on MF Coal	1.3	2.1

The total oil yield was 8.2% (absolute) higher with the plug flow reactor. This increase was accompanied by a 2.5% (absolute) lower SRC yield and a 4.5% (absolute) lower IOM yield. The recycle solvent production was within 2% (absolute) of the break-even level with the plug flow reactor compared to a 6% deficit with the CSTR. The 45% (relative) lower IOM yield with the plug flow reactor, in particular, illustrates the profound effect of reactor configuration in the SRC I mode.

The hydrogen consumption was 0.8% absolute (62% relative) higher with the plug flow reactor although gas yields were nearly the same. This indicates that the additional hydrogen was consumed in producing oil from nondistillable hydrocarbons and increasing the hydrogen content of the recycle solvent and SRC.

The results with the plug flow reactor are similar to those obtained in previous experiments at conditions used by Fort Lewis in material balance runs 4 and 8.

b. SRC II Mode

The yields and hydrogen consumptions obtained with the two reactor types in the SRC II mode are compared below:

Reactor	DOE 346R CSTR	DOE 348R Plug Flow
Yields, Wt % based on MF Coal		
C_1-C_4	13.5	14.4
Naphtha	9.6	10.3
Middle Distillate	14.2	15.9
Heavy Distillate	12.2	12.6
Total Oil	36.0	38.8
SRC	30.7	27.8
IOM	5.1	4.7
Hydrogen Consumption, Wt % based on MF Coal	4.1	4.7

There was a slightly higher total oil yield, 2.8% absolute, with the plug flow reactor accompanied by a 2.9% (absolute) lower SRC yield and a 0.4% lower IOM yield. There was also a small increase in gas yield.

Hydrogen consumption was also slightly higher with the plug flow reactor, 0.6% absolute or 15% relative.

The results with the plug flow reactor are similar to those in earlier runs with the DOE 1 reactor* at the same conditions.

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* A tubular reactor with a lower L/D ratio; 1.55 m (61") long with a 27.9 mm (1.10") I.D.

5. Product Quality

The product analyses for all four runs are shown in Table I.

a. SRC I Mode

The compositions of the recycle solvents and SRC's obtained with the CSTR and plug flow reactor in the SRC I mode are compared below:

Reactor	DOE 345B CSTR	DOE 347 Plug Flow
Recycle Solvent Analyses		
% C	88.6	87.8
% H	7.0	7.6
% S	0.64	0.52
% N	0.81	0.88
% O	2.9	3.2
SRC Analyses		
% C	86.8	86.9
% H	5.2	5.6
% S	1.08	0.90
% N	2.00	2.14
Fusion Point, °C	207	154

The hydrogen levels in both the recycle solvent and SRC were about 8% (relative) higher with the plug flow reactor and the sulfur concentrations were 17-19% (relative) less. In addition, the fusion point of the SRC was 53°C lower with the plug flow reactor.

The viscosities of the unfiltered coals solutions for runs DOE 345B and DOE 347 are shown in Table IX. The UFCS viscosities with the CSTR and plug flow reactor in the SRC I mode are compared on Figure 7. The UFCS viscosity from the plug flow experiment was much less than that from the CSTR which reflects the lower conversion in the latter. In the CSTR experiment, run DOE 345B, the solids (IOM plus ash) level in the UFCS was about 8.3% whereas in the plug flow run, DOE 347, the solids level was 6.5%.

The solubility of the distillation residues (SRC products) in the SRC I mode, shown as a fraction of the solubility in pyridine, with the CSTR and plug flow reactors are compared below:

Reactor	DOE 345 CSTR	DOE 347 Plug Flow
Ratio of Average Solubilities*		
Hexane/Pyridine	0.043	0.092
Toluene/Pyridine	0.493	0.617

* Averaged for one or two trials and three different products in each case.

The solubilities of the distillation residues in both hexane and toluene were significantly higher with the plug flow reactor. This apparently lower molecular weight was also reflected in the fusion points of the residues (154°C versus 207°C) and the UFCS viscosities.

b. SRC II Mode

The heavy distillate and distillation residue analyses obtained with the two reactor types are summarized below:

Reactor	DOE 346R CSTR	DOE 348R Plug Flow
Heavy Distillate Analyses		
% C	88.6	88.7
% H	7.6	7.7
% S	0.36	0.28
% N	1.13	1.14
% O	2.3	2.2
Distillation Residue Analyses		
% C	69.3	68.1
% H	4.1	4.1
% S	2.52	2.72
% N	1.43	1.40
% Ash	21.9	23.1
Fusion Point, °C	115	121

The desulfurization of the heavy distillate was significantly greater with the plug flow reactor resulting in 22% (relative) less sulfur in the product. The other heavy distillate analyses are the same.

The distillation residue analyses are essentially the same with the CSTR and plug flow reactors except for sulfur concentration which was about 8% higher (relative) with the plug flow reactor. The higher sulfur level is probably due to the slightly higher ash content.

The viscosities of the unfiltered coal solutions for runs DOE 346R and 348R are shown in Table X.

The UFCS viscosities for the CSTR and plug flow experiments in the SRC II mode are compared on Figure 8. Again the UFCS from the plug flow run, DOE 348R, had a lower viscosity than in the CSTR run, DOE 346R, although the difference was not as pronounced as in the SRC I experiments. The solids level was essentially the same (5.1%) in the UFCS from the two runs indicating that the liquid part of the UFCS from the plug flow run had a molecular weight which was lower than from the CSTR run.

These data suggest that the UFCS viscosity is affected by both the solids level and molecular weight of the liquid.

The viscosities of the feed slurries from runs DOE 346R and 348R are shown in Table XI.

The ways in which reactor configuration and shear rate affect feed slurry viscosities are shown on Figure 9. The feed slurry viscosity was significantly lower with the plug flow reactor than with the CSTR. Since the slurry blend composition was essentially the same in each case, the lower viscosity with the plug flow reactor again reflects a lower molecular weight in the liquid part of the UFCS. The feed slurries also show the normal decrease in viscosity as shear rate is increased. The minimum in viscosity, typical of coal feed slurries, occurs at about 250°F for the slurry with the highest viscosity and shifts to higher temperature while becoming less pronounced for slurries of lower viscosity.

The solubilities of the distillation residues for the SRC II experiments are compared for the CSTR and plug flow reactors below:

Reactor	DOE 346R CSTR	DOE 348R Plug Flow
Ratio of Average Solubilities*		
Hexane/Pyridine	0.381	0.422
Toluene/Pyridine	0.836	0.873

* Average of two trials and two or three different products in each case.

The solubilities of the distillation residues in hexane and toluene were also greater with the plug flow reactor in the SRC II mode, although the relative changes were not as great as in the SRC I mode. Even though the solubility and viscosity data indicate a distillation residue with a lower molecular weight when using the plug flow reactor, the fusion point was nearly the same with the two reactor types.

C. Simulated Distillation

A procedure for simulated distillation by gas chromatography was presented in the first quarter 1979 progress report*. Since then, simulated distillation has been used to provide the boiling point distributions of all product oils. A summary of recent activities in the development of this technology is provided below.

1. Normal Paraffin versus Aromatic Calibration Standard

The temperature distribution curve for the simulated distillation presented in the first quarter 1979 report for the SRC II

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* Solvent Refined Coal, Quarterly Technical Report for the Period January 1, 1979 through March 31, 1979; February 1980, FE/496-172.

P99-36-7 aliquot product blend was based on a calibration curve generated from retention time data of normal paraffins (reproduced here as Figure 10). Due to the aromatic nature of coal liquids, a question arose as to the reason for using normal paraffins as the calibration standard as opposed to using an aromatic hydrocarbon mixture as the calibration standard.

A sample of an aromatic hydrocarbon standardization mixture was obtained from the Wilsonville Pilot Plant. Retention time data and a calibration curve were generated from this sample and the aliquot blend oil sample was again analyzed using this standard to generate the temperature distribution data. These data are shown graphically in Figure 11. The comparison is again to the true boiling point data. The discrepancy between the two curves when using the aromatic standard is much greater than when using the normal paraffin standard. The normal paraffin mixture will therefore be used for all calibrations at Merriam.

2. Simulated Distillation of P99 Debutanizer Bottoms

Although comparison of the temperature distribution curves produced by simulated distillation (n-paraffin standard) and the true boiling point methods on the aliquot blend oil sample used above show excellent agreement, the simulated distillation method was further substantiated by comparing another sample for which true boiling point temperature distribution data were available. For this reason a sample of debutanizer bottoms from Harmarville run P99-36-7 was obtained and a simulated distillation analysis was performed. The results of this comparison are presented graphically in Figure 12.

Again, the curves generated from the simulated distillation and the true boiling point methods show excellent agreement.

D. Solvent Extraction of Distillation Residues

A complete description of the solvent extraction procedure was given in the third quarter 1979 progress report*.

Work has continued to study the repeatability of the method by completing at least eight separate extractions on nine separate samples from run DOE 344R, a total of 77 trials in all. This allows determination of the variations between distillations for a particular "lined-out" period and changes in solubility brought about by relatively small changes in run conditions. It was found that the precision of replicate determinations was better with good solvents than with poor solvents; pyridine giving the best results and hexane the worst. Replicate trials on individual samples extracted with pyridine resulted in solubilities which frequently

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period July 1, 1979 through September 30, 1979; July 1980, FE/14800-11.

agreed within a range 0.1 to 0.2% (absolute), even allowing for a 24 hour difference in extraction times. It was also found that the solubility of the distillation residues had a predictable response to changes in reaction conditions, mode of operation (SRC I or SRC II) and to the effect of catalysis.

The amount of volatile material in SRC II distillation residues was also estimated using results for each of the solvents by employing the simulated distillation gas chromatograph technique:

Extraction Solvent	% Volatile in Extract	% Volatile in Distillation Residue
Hexane	33.8	7.7
Benzene	21.1	10.9
Toluene	16.3	0.7
Pyridine	12.5	7.9

In general, the volatile material had a boiling range of 400-600°C while heavy distillate boils below about 450°C.

An elemental analysis of benzene, toluene and pyridine extracts (corrected for imbibed solvent) from run DOE 344-51 distillation residue showed that the heteroatom content was higher in materials which were less soluble:

Extraction Solvent	Analysis of Extract		
	% Sulfur	% Nitrogen	% Oxygen
Benzene	0.36	1.85	1.44
Toluene	0.42	1.87	1.60
Pyridine	0.43	2.32	2.52

A complete discussion of this work is included in Appendix A.

E. Residence Time Distribution Studies

Residence time distribution (RTD) measurements were used to characterize the macromixing in five reactor configurations:

1. Modified GU 5
2. Single tube
3. DOE 1
4. CSTR without baffles
5. CSTR with baffles

Two mathematical models were used to correlate the RTD measurements and the results are presented in terms of Holdback Numbers for all reactors and Peclet Numbers for the tubular reactors.

It was found that the two CSTR configurations both had essentially complete backmixing. They both also had a small amount of bypassing (dead space) which was more pronounced in the CSTR without baffles.

The tubular reactors also had a considerable amount of backmixing, particularly the DOE 1 reactor. The modified GU 5 reactor was the most plug flow with a Peclet Number (N_{Pe})* of 4.4 followed by the single tube reactor with a Peclet Number of 2.0. With the DOE 1 reactor the Peclet Number was only 1.1.

The details of this study are given in Appendix B.

F. Maintenance and Modifications

1. Maintenance

a. The "o" rings previously in use on the Pressure Products Industries (PPI) hydrogen compressor were made from an ethylene/proplene copolymer which was apparently incompatable with the hydraulic oil in the compressor. These have been replaced with a set made from Viton and there have been no problems with gas leakage or ring decomposition since.

2. Modifications

a. Mini-Computer

A Digital Equipment Corporation Model PDP 11 minicomputer has been installed in the laboratory and software development is underway. The computer will be used to process data for material balances from the Fluke data logger, on-line gas chromatograph, simulated distillation chromatograph, and three user's terminals.

b. Reactor Configurations and Related Modifications

Run DOE 340 was made using a 3-tube dissolver as shown in Figure 13. Slurry was introduced to the bottom of the first tube and passed up the first tube, down the second, and up the third. Hydrogen was introduced at the bottom of the second and third tubes as well as in the preheater. Hydrogen flow was cocurrent to slurry in the first tube, countercurrent in the second and cocurrent in the third. A vapor/liquid separator, operated at reaction conditions, was located on top of the second tube to allow product gases to be removed from the slurry.

Due to problems associated with operation of the 3-pass dissolver, it was replaced with a downflow dissolver to

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* For completcly plug flow $N_{Pe} = \infty$; for completely backmixed $N_{Pe} = 0$.

isolate and correct those problems related to the downflow section. Runs DOE 341 and 342R were made using the DOE 1 dissolver in a downflow configuration as shown on Figure 14. The slurry was fed to the middle of the dissolver and flowed downwards, countercurrent to a hydrogen stream. The top half of the dissolver, therefore, served as a vapor/liquid disengaging section.

The unit was shut down twice during run DOE 341 to modify the slurry exit line from the downflow dissolver. The first time a straight, air-cooled, 9.5 mm (3/8") line was installed. The second time a 14.3 mm (9/16"), air-cooled line was installed.

The primary means of determining the slurry level in the dissolver during runs DOE 341 and 342 was by measuring the liquid head with a differential pressure gauge. A large amount of noise was introduced into this signal because the low pressure tap was located on the top of the high temperature, high pressure (HTHP) separator. In order to supplement this indicator during run DOE 342, a series of thermocouples was placed near the slurry entrance to detect the gas/liquid interface.

Run DOE 343R was also made with the downflow dissolver configuration shown in Figure 14. The height of the slurry exit line to the high temperature, high pressure separator was adjusted, however, to raise the level in the dissolver about 22.9 cm (9"). In addition, the low pressure tap for the differential pressure gauge indicating reactor liquid level was moved to the vapor transfer line. Run DOE 344R was made with the upflow dissolver shown in Figure 15.

In runs DOE 343R and 344R about one-third of the hydrogen feed was delivered to the preheater and two-thirds to the dissolver. Hydrogen flow was countercurrent to slurry in the downflow configuration and cocurrent in the upflow configuration.

Slurry level was monitored during runs DOE 343R and 344R primarily by a differential pressure gauge. To keep the differential pressure reading on scale, the shunt resistor in the strip chart recorder was changed. The recorder reading was, therefore, calibrated indirectly by observing changes in the high temperature, high pressure separator level.

Slurry level indication was also provided by a series of thermocouples. In order to improve the sensitivity of the thermocouple indication during run DOE 343R, the slurry level was raised as mentioned above. This level corresponded to the point where a baffle separated zones 4 and 5 in the air furnace. The dissolver zone above the slurry level was maintained at 400°C to further accentuate the temperature difference at the slurry/vapor interface.

The continuous stirred tank reactor (CSTR) used in runs DOE 345B and 346R consisted of a 1-liter stirred autoclave depicted in Figure 16. A new, short-residence time, preheater was installed which was constructed from a 1.43 cm (9/16") I.D. tube, 167 cm (65.7") long with a volume of 240 cm^3.*

The agitator used in run DOE 345B was a 5.08 cm (2") diameter, 6 element, paddle wheel mixer (turbine). A 3-element baffle was installed in the autoclave.

During run DOE 346R, two propeller-type, 6-element mixers were placed on the top part of the stirring rod in addition to the 5.08 cm (2") paddle wheel mixer which was left at the bottom.

Two different reactors were used to approximate plug flow conditions during runs DOE 347 and 348R.

For run DOE 347, the reactor was fabricated from a single 17.5 mm (11/16") I.D. tube 1.83 m (72") long with a volume of 408 cm^3 as shown on Figure 17.

For run DOE 348R, the modified GU 5 reactor, shown on Figure 18, was used. Strip heaters and insulation were placed on the first tube of the two-tube configuration in an attempt to correct a temperature imbalance between the tubes experienced in earlier runs. The entire assembly was placed inside the 6-zone air furnace. The preheater was the same as in the CSTR experiments.

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* The preheater used prior to DOE 345 had an I.D. of 1.75 cm (11/16") and was 137 cm (53.9") long with a volume of 310 cm^3.

TABLE I

Summary of Process Conditions, Yields and Product Analyses

Conditions	DOE 340-1	DOE 340-2	DOE 340-3	DOE 340-4	DOE 341D	DOE 342RB
Coal	Kentucky 9/14					
Dissolver	3-Pass				Downflow	
Nominal Slurry Residence Time, hr.	1.03	1.03	1.01	1.02	0.8±0.1	1.2±0.2
(min.)	(61.9)	(61.6)	(60.7)	(61.0)	(48±6)	(69±9)
Coal Feed Rate, lb/hr/ft^3	31.3	31.5	32.0	31.8	39.7	21.2
Average Dissolver Temperature, °C	451	449	448	448	455	455
°F	844	840	839	839	851	851
Dissolver Pressure, psig	2000	2000	2000	2000	1410	1800
Hydrogen Feed						
Wt % based on slurry	4.51	3.47	4.42	6.03	5.93	6.25
MSCF/ton of coal	38.0	29.2	37.2	50.8	57.5	78.8
% to preheater	34	44	34	51	50	35
% to countercurrent dissolver (2nd pass or downflow)	34	14	34	25	50	65
% to cocurrent dissolver (3rd pass)	32	42	32	24	--	--
Slurry Formulation, wt %						
Coal	45.0				39.0	30.0
Recycled Coal Solution	55.0				61.0	8.5
Recycled Solvent	--	--	--	--	--	61.5
Slurry Blend Composition, wt %						
Coal						30.0
Middle Distillate (193-288°C, 380-550°F)						1.9
Heavy Distillate (>288°C, >550°F)						27.5
SRC						26.2
Ash (from recycle coal solution)						9.1
Insoluble Organic Matter (from recycle coal solution)						5.3
Total Solids						44.4
Yields, Wt % based on MF Coal						
H_2O	7.0	6.2	6.5	6.8	7.4	6.0
CO	0.3	0.1	0.2	0.3	0.2	0.2
CO_2	1.5	1.3	1.5	1.2	1.2	1.2
H_2S	1.5	1.2	1.5	1.5	2.2	1.9
NH_3	0.2	0.2	0.1	0.2	0.2	0.5
C_1	3.4	2.5	2.5	2.5	4.9	7.0
C_2	2.2	1.5	1.6	1.6	3.0	4.7
C_3	1.5	1.1	1.1	1.2	2.0	3.9
C_4	0.7	0.5	.5	0.5	1.0	2.2
Total C_1-C_4	7.8	5.6	5.7	5.8	10.9	17.8
Naphtha, C_5-193°C (380°F)	7.9	7.0	6.2	6.0	7.4	9.6
Wash Solvent, 193-249°C (380-480°F)^b	9.3	8.9	8.2	8.3	11.0	16.6
Recycle Solvent, >249°C (480°F)^c(loss)	1.7	0.5	(1.2)	2.4	(6.4)	4.8
Total Oil	18.9	16.4	13.2	16.7	12.0	30.9
SRC	50.9	56.6	57.2	54.6	50.9	30.2
Insoluble Organic Matter	5.5	6.1	6.3	5.6	7.5	6.1
Ash	10.1	10.1	10.1	10.1	10.2	10.4
Total	103.7	103.8	102.3	102.8	102.7	105.2
H_2 Reacted (gas balance)	3.7	3.8	2.3	2.8	2.7	5.2
Lineout Index	--	--	--	--	--	1.12
Product Analyses						
Recycle Solvent Analyses^c						
% C	88.08	88.11	87.97	88.21	88.87	89.33
% H	7.84	7.89	7.74	7.68	7.23	7.36
% S	0.47	0.60	0.61	0.57	0.52	0.50
% N	0.96	0.99	0.97	1.00	1.02	1.33
% O (by difference)	2.65	2.41	2.71	2.30	2.36	1.98
Specific Gravity	1.0489	1.0657	1.0616	1.0609	1.0703	1.0835
SRC Analyses^d						
% C	88.31	87.71	87.43	87.23	89.24	69.47
% H	5.50	5.28	5.57	5.51	5.36	4.09
% S	0.70	0.88	0.85	0.80	0.65	2.58
% N	2.23	2.26	2.21	2.19	2.26	1.70
% Ash	0.06	0.08	0.55	0.99	0.34	22.26
Fusion Point, °C	162	180	175	154	150	133

a) Kentucky Nos. 9 & 14, Colonial Mine; b) Middle Distillate, 193-288°C (380-550°F) for run DOE 342RB; c) Heavy Distillate, >288°C (550°F) for run DOE 342RB; d) Distillation Residue for run DOE 342RB.

TABLE I (Continued)

Conditions	DOE 343RA	DOE 343RB	DOE 343RC	DOE 344RB	DOE 344RC	DOE 344RD
Coal	Pittsburgh Seam[a]					
Dissolver	Downflow			Upflow		
Nominal Slurry Residence Time, hr	1.00	1.04	1.02	0.99	1.01	1.02
Coal Feed Rate, lb/hr/ft^3	21.5	20.7	21.2	21.8	21.3	21.2
Average Dissolver Temperature, °C	454					
°F	849					
Dissolver Pressure, psig	2000	2000	1800	2000	2000	1800
Hydrogen Feed						
Wt % based on slurry	6.01	6.24	6.10	5.92	6.05	6.17
MSCF/ton of coal	75.9	78.8	77.1	74.8	76.4	78.0
% to preheater	33	33	33	34	34	33
% to dissolver	67	67	67	66	66	67
Slurry Formulation, wt %						
Coal	30.0					
Recycled Coal Solution	61.5					
Recycled Solvent	8.5					
Slurry Blend Composition, wt %						
Coal	30.0	30.0	30.0	30.0	30.0	30.0
Middle Distillate (193-288°C, 380-550°F)	2.4	1.8	1.6	2.3	2.2	1.4
Heavy Distillate (>288°C, >550°F)	27.7	29.0	28.7	30.2	30.8	30.6
SRC	26.1	26.0	25.5	23.7	23.8	25.0
Ash (from recycle coal solution)	9.0	8.6	9.3	9.2	8.8	8.6
Insoluble Organic Matter (from recycle coal solution)	4.8	4.6	4.9	4.6	4.4	4.4
Total Solids	43.8	43.2	44.2	43.8	43.2	43.0
Yields, wt % based on MF Coal						
H_2O	5.41	5.56	5.46	5.09	5.24	5.18
CO	0.22	0.21	0.20	0.42	0.40	0.36
CO_2	0.90	0.84	0.91	1.00	0.88	0.90
H_2S	2.42	2.58	2.76	2.99	2.44	2.52
NH_3	0.47	0.43	0.41	0.47	0.46	0.41
C_1	5.79	5.66	5.69	6.41	5.34	5.36
C_2	3.99	3.91	3.90	4.47	3.79	3.76
C_3	3.44	3.37	3.28	3.87	3.30	3.18
C_4	1.96	1.87	1.80	2.05	1.78	1.70
Total C_1-C_4	15.18	14.81	14.67	16.80	14.21	14.00
Naphtha, C_5-193°C (380°F)	11.12	10.40	10.99	9.86	10.86	9.66
Middle Distillate, 193-288°C (380-550°F)	18.53	18.35	19.18	18.76	17.58	17.74
Heavy Distillate, >288°C, (550°F)	9.55	10.58	9.52	9.60	11.80	12.65
Total Oil	39.20	39.33	39.70	38.22	40.24	40.05
SRC	26.69	27.25	25.65	25.08	26.32	27.36
Insoluble Organic Matter	4.89	4.80	4.97	4.94	4.82	4.81
Ash	9.15	8.99	9.38	9.71	9.70	9.45
Total	104.53	104.80	104.10	104.72	104.71	105.04
H_2 Reacted (gas balance)	4.53	4.80	4.10	4.72	4.71	5.04
Lineout Index	1.08	1.06	0.96	1.04	1.03	1.03
Product Analyses						
Heavy Distillate Analyses						
% C	89.26	88.96	89.09	89.16	89.10	89.14
% H	7.38	7.95	7.62	7.80	7.51	7.45
% S	0.49	0.48	0.49	0.35	0.36	0.39
% N	1.25	1.16	1.22	1.15	1.23	1.26
% O (by difference)	1.62	1.45	1.58	1.54	1.80	1.79
Specific Gravity	1.0801	1.0594	1.0797	1.0617	1.0770	1.0822
Distillation Residue Analyses						
% C	67.56	68.53	68.80	66.51	67.28	67.78
% H	3.93	4.10	4.05	3.86	4.10	4.09
% S	2.75	2.48	2.49	2.82	2.76	2.46
% N	1.38	1.43	1.46	1.33	1.36	1.40
% Ash	23.81	22.88	22.93	25.15	23.96	23.72
Fusion Point, °C	134	122	120	115	132	112

a) Powhatan Mine No. 5

TABLE I (Continued)

Conditions	DOE 345B	DOE 346R	DOE 347	DOE 348R
Coal	Ky 9/14[a]	Pitt Seam[b]	Ky 9/14[a]	Pitt Seam[b]
Dissolver	CSTR		Plug Flow	
Nominal Slurry Residence Time, hr.	0.36	1.01	0.36	1.03
(min.)	(21.6)	(60.9)	(21.5)	(62.0)
Coal Feed Rate, lb/hr/ft^3	77.6	21.2	78.3	20.8
Average Dissolver Temperature, °C	449	454	448	453
°F	840	849	838	847
Dissolver Pressure, psig	1410	1800	1410	1800
Hydrogen Feed				
Wt % based on slurry	1.86	4.03	1.89	4.13
MSCF/ton of coal	18.1	50.9	18.4	52.3
Slurry Formulation, wt %				
Coal	39.0	30.0	39.0	30.0
Recycled Coal Solution	--	61.5	--	61.5
Recycled Solvent	61.0	8.5	61.0	8.5
Slurry Blend Composition, wt %				
Coal		30.0		30.0
Middle Distillate (193-288°C, 380-550°F)		3.0		3.3
Heavy Distillate (>288°C, >550°F)		31.8		32.0
SRC		23.9		23.0
Ash (from recycle coal solution)		7.4		7.8
Insoluble Organic Matter (from recycle coal solution)		3.9		3.9
Total Solids		41.3		41.7
Yields, Wt % based on MF Coal				
H_2O	6.9	5.2	6.3	5.6
CO	0.2	0.5	0.3	0.5
CO_2	1.4	0.8	1.2	0.8
H_2S	1.5	2.4	1.4	2.3
NH_3	0.1	0.4	0.1	0.4
C_1	1.8	5.3	1.9	5.5
C_2	1.1	3.7	1.2	3.9
C_3	0.7	3.0	0.8	3.4
C_4	0.3	1.5	0.3	1.6
Total C_1-C_4	3.9	13.5	4.2	14.4
Naphtha, C_5-193°C (380°F)	3.7	9.6	5.0	10.3
Wash Solvent, 193-249°C (380-480°F)[c]	6.2	14.2	8.7	15.9
Recycle Solvent, >249°C (480°F) (loss)[d]	(6.3)	12.2	(1.9)	12.6
Total Oil	3.6	36.0	11.8	38.8
SRC	64.4	30.7	61.9	27.0
Insoluble Organic Matter	10.1	5.1	5.6	4.7
Ash	9.2	9.5	9.3	9.4
Total	101.3	104.1	102.1	104.7
H_2 Reacted (Gas Balance)	1.3	4.1	2.1	4.7
Lineout Index		1.04		1.04
Product Analyses				
Recycle Solvent Analyses[d]				
% C	88.62	88.61	87.84	88.67
% H	7.01	7.63	7.56	7.69
% S	0.64	0.36	0.52	0.28
% N	0.81	1.05	0.88	1.14
% O (by difference)	2.92	2.35	3.20	2.22
Specific Gravity	1.0733	1.0619	1.0600	1.0656
SRC Analyses[e]				
% C	86.81	69.28	86.94	68.12
% H	5.24	4.14	5.62	4.06
% S	1.08	2.52	0.90	2.72
% N	2.00	1.43	2.14	1.40
% Ash	0.37	21.88	0.16	23.11
Fusion Point, °C	207	115	154	121

a) Kentucky 9 & 14, Colonial Mine; b) Powhatan Mine No. 5; c) Middle Distillate, 193-288°C (380-550°F) for runs DOE 346R and 348R; d) Heavy Distillate, >288°C (550°F) for runs DOE 346R and 348R; e) Distillation Residue for runs DOE 346R and 348R.

TABLE II

Unfiltered Coal Solution Viscosities[a]
Runs DOE 340, 341 and 342R

Run No. DOE-	Temperature °F	Shear Rate Sec^{-1}	Viscosity cP
340-1 P17	210	7.93	46.0
	210	15.86	39.0
	210	39.64	33.4
	210	79.28	31.7
	230	7.93	34.5
	230	15.86	26.0
	230	39.64	22.8
	230	79.28	21.2
	270	15.86	15.8
	270	39.64	13.2
	270	79.28	11.5
340-2 P29	210	7.93	70.0
	210	15.86	65.3
	210	39.64	62.0
	230	7.93	46.0
	230	15.86	41.0
	230	39.64	37.3
	230	79.28	35.6
	270	15.86	21.3
	270	39.64	18.7
	270	79.28	17.1
340-4 P49	210	3.96	93.0
	210	7.93	86.0
	210	15.86	82.8
	210	39.64	78.9
	230	7.93	55.5
	230	15.86	50.5
	230	39.64	47.1
	230	79.28	45.7
	270	15.86	25.0
	270	39.64	22.1
	270	79.28	20.6

TABLE II (Continued)

Run No. DOE-	Temperature °F	Shear Rate Sec^{-1}	Viscosity cP
	210	15.86	31.5
	210	39.64	28.1
	210	79.28	27.2
341D P23	230	15.86	23.0
	230	39.64	19.4
	230	79.28	18.6
	270	39.64	11.7
	270	79.28	10.4
	210	0.083	$26.0X10^3$
	210	0.166	$26.2X10^3$
	210	0.415	$23.8X10^3$
342RB P26	230	0.166	$8.41X10^3$
	230	0.415	$7.49X10^3$
	230	0.830	$7.01X10^3$
	230	1.66	$6.39X10^3$
	270	0.830	$1.73X10^3$
	270	1.66	$1.53X10^3$
	270	3.32	$1.30X10^3$
	270	8.30	$1.09X10^3$

a) Brookfield Model LV viscometer,
spindle No. 18 for DOE 340 & 341D
spindle No. 28 for DOE 342RB
Procedure: 45 min. initial warmup and equilibration;
20-30 min. equilibration after temperature change;
10 min. equilibration after shear rate change.

TABLE III

Feed Slurry Viscosities[a]
Runs DOE 340, 341 and 342R

Run No. DOE-	Temperature °F	Shear Rate Sec^{-1}	Viscosity 10^2 cP
340-4 P49	210	0.830	21.6
	210	1.66	17.8
	210	3.32	12.0
	210	8.30	8.18
	230	1.66	11.8
	230	3.32	9.75
	230	8.30	7.01
	230	16.61	5.32
	270	0.830	31.1
	270	1.66	19.3
	270	3.32	10.9
	270	8.30	8.12
341D[b] P18	210	1.98	2.30
	210	3.96	2.07
	210	7.93	2.08
	210[c]	15.86	1.95
342RB P25	210	0.415	73.9
	210	0.830	68.7
	210	1.66	55.6
	230	0.415	95.5
	230	0.830	69.0
	230	1.66	49.2
	270	0.166	231
	270	0.415	138
	270	0.830	91.2

a) Brookfield Model LV viscometer,
  spindle No. 28 for DOE 340-4 and 342RB
  spindle No. 18 for DOE 341D
Procedure:
  45 min. initial warmup and equilibration;
  20-30 min. equilibration after temperature change;
  10 min. equilibration after shear rate change.

b) The viscosity reading tended to drift with this material.

c) It was not possible to get a stable reading under these conditions. It was found that the sample had separated into two layers, solids rich and oil rich.

TABLE IV

Solvent Extraction of Distillation Residue
Runs DOE 340, 341 and 342R

	DOE 340-3	DOE 341D	DOE 342RB
Dissolver Mode	3-Pass SRC I	Downflow SRC I	Downflow SRC II
Solubility of Distillation Residue			
Wt % in			
Hexane	16.6	21.1	13.1
Benzene	54.7	55.1	36.4
Toluene	63.7	68.5	50.0
Pyridine	98.4	99.5	64.7
Ratio of Solubilities			
Hexane/Pyridine	0.169	0.212	0.202
Benzene/Pyridine	0.556	0.554	0.563
Toluene/Pyridine	0.647	0.688	0.773
Distillation Residue Properties			
% Ash	1.13	0.18	22.53
Fusion Point, °C	164	147	150

TABLE V

Comparison of Yields and Hydrogen Consumption with Upflow and Downflow Reactors; Powhatan Coal, SRC II

	DOE 343RA	DOE 343RB	DOE 343RC	DOE 344RB	DOE 344RC	DOE 344RD	DOE[a] 278R
Conditions							
Dissolver	Downflow			Upflow			
L/D	35			27			54
Preheater Outlet, °C	425	401	401	425	400	401	400
Pressure, psig	2000	2000	1800	2000	2000	1800	1800
Yields[b]							
C_1-C_4	15.2	14.8	14.7	16.8	14.2	14.0	15.0
Naphtha	11.1	10.4	11.0	9.9	10.9	9.7	11.9
Middle Distillate	18.5	18.3	19.2	18.7	17.6	17.7	20.4
Heavy Distillate	9.6	10.6	9.5	9.6	11.8	12.6	8.0
Total Oil	39.2	39.3	39.7	38.2	40.3	40.0	40.3
SRC	26.7	27.2	25.6	25.1	26.3	27.4	25.1
IOM	4.9	4.8	5.0	4.9	4.8	4.8	4.6
H_2 Reacted	4.5	4.8	4.1	4.7	4.7	5.0	4.8

a) From first quarter 1979 progress report.

b) Weight percent based on MF coal.

TABLE VI

Unfiltered Coal Solution Viscosities[a]
Runs DOE 343R and 344R

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^2 cP
343RA P-59	210	0.830	17.6
	210	1.66	15.1
	210	3.32	13.3
	210	8.30	12.2
	230	1.66	8.72
	230	3.32	7.34
	230	8.30	6.11
	230	16.61	5.70
	270	3.32	3.61
	270	8.30	2.66
	270	16.61	2.21
343RB P-88	210	0.830	19.7
	210	1.66	16.1
	210	3.32	13.9
	210	8.30	12.7
	230	1.66	10.1
	230	3.32	8.09
	230	8.30	6.30
	230	16.61	5.54
	270	8.30	2.97
	270	16.61	2.70
344RB P-74	210	3.32	6.11
	210	8.30	5.25
	210	16.61	4.82
	230	3.32	3.77
	230	8.30	2.87
	230	16.61	2.51
	270	3.32	2.44
	270	8.30	1.59
	270	16.61	1.35

TABLE VI (Continued)

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^2 cP
344RC P-116	210	1.66	7.22
	210	3.32	6.50
	210	8.30	5.66
	210	16.61	5.20
	230	3.32	3.69
	230	8.30	3.11
	230	16.61	2.81
	270	8.30	1.62
	270	16.61	1.37
344RD P-157	210	0.830	15.4
	210	1.66	11.8
	210	3.32	10.2
	210	8.30	8.95
	230	1.66	7.06
	230	3.32	5.47
	230	8.30	4.62
	230	16.61	4.12
	270	3.32	2.89
	270	8.30	1.97
	270	16.61	1.63

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 min. initial warmup and equilibration
20-30 min. equilibration after temperature change
10 min. equilibration after shear rate change

TABLE VII

Feed Slurry Viscosities[a]
Runs DOE 343R and 344R

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^2 cP
343RA[b] P-59	230	0.083	541
	230	0.166	287
	230	0.415	167
	230	0.830	108
	270	0.083	574
	270	0.166	361
	270	0.415	211
343RB P-88	210	0.083	874
	210	0.166	550
	230	0.083	504
	230	0.166	390
	230	0.415	173
	230	0.830	123
	270	0.083	463
	270	0.166	426
	270	0.415	214
	270	0.830	119
343RC P-109	210	0.083	706
	210	0.166	385
	210	0.415	196
	230	0.166	327
	230	0.415	167
	230	0.830	111
	270	0.166	343
	270	0.415	190
	270	0.830	113

TABLE VII (Continued)

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^2 cP
344RB P-74	210	0.083	373
	210	0.166	201
	210	0.415	150
	210	0.830	115
	230	0.166	152
	230	0.415	111
	230	0.830	82.5
	230	1.66	57.5
	270	0.166	134
	270	0.415	85.6
	270	0.830	59.5
	270	1.66	39.1
	270	3.32	25.1
344RC P-116	210	0.083	281
	210	0.166	185
	210	0.415	109
	210	0.830	77.9
	210	1.66	58.0
	230	0.166	153
	230	0.415	85.3
	230	0.830	56.6
	230	1.66	39.7
	230	3.32	29.5
	270	0.415	86.6
	270	0.830	61.2
	270	1.66	37.0

TABLE VII (Continued)

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^2 cP
344RD P-149	210	0.083	393
	210	0.166	275
	210	0.415	100
	210	0.830	67.1
	210	1.66	43.1
	230	0.166	138
	230	0.415	76.7
	230	0.830	54.4
	230	1.66	38.2
	230	3.32	26.4
	270	0.415	82.5
	270	0.830	52.5
	270	1.66	35.8
	270	3.32	23.7

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 min. initial warmup and equilibration.
20-30 min. equilibration after temperature change.
10 min. equilibration after shear rate change.

b) Viscosity readings at 210°F were beyond the range of the viscometer with the spindle in use. Readings tended to drift with this material and gradually decreased with time.

TABLE VIII

Solvent Extraction of Distillation Residues
Runs DOE 343R and 344R

Run No.	343RA		343RB		343RC		344RB			344RC			344RD		
Product No.	51	59	88	94	106	109	62	69	74	106	111	120	149	155	156
Conditions															
Dissolver	Downflow						Upflow								
Preheater Outlet, °C	425	425	401	401	401	401	425			400			401		
Pressure, psig	2000	2000	2000	2000	1800	1800	2000						1800		
Solubility of Distillation Residue, wt % in															
Hexane	24.3	20.6	20.7	22.2	19.2	18.5	22.7	21.1 20.7	22.5 20.2	23.1 23.9	20.7 26.6	27.6 29.1	10.8 16.9	15.4 19.1	21.8 21.7
Benzene	51.6	52.3	53.0	54.5*	54.9*	51.4	53.4 53.8	52.4 54.1	52.6 53.6	49.4 53.9	55.6 56.7	57.3 51.9	52.0 48.9	54.6 52.4	53.9 54.3
Toluene	53.6	55.4	56.7	54.6	54.1	54.4	52.4 55.6	53.5 53.8	51.5 54.9	55.8 57.6	56.4 58.3	56.7	52.2 52.8	54.0 55.4	53.6 55.4
Pyridine	63.1	63.7	65.1	64.3	65.5	65.0	64.3 62.6	62.1 62.2	61.9 62.2	63.9 64.0	66.3 64.6	64.8	62.6 62.7	64.4 64.4	63.0 65.0
Ratio of Solubilities (average)															
Hexane/Pyridine	0.385	0.324	0.319	0.345	0.293	0.285	0.358	0.336	0.344	0.368	0.362	0.438	0.222	0.268	0.340
Benzene/Pyridine	0.818	0.821	0.815	0.847	0.838	0.791	0.844	0.857	0.856	0.808	0.858	0.842	0.805	0.831	0.846
Toluene/Pyridine	0.850	0.869	0.870	0.848	0.826	0.838	0.851	0.863	0.857	0.887	0.861	0.875	0.838	0.850	0.851
Distillation Residue Properties															
% Carbon	67.7	68.1	68.6	69.9	69.0	67.9	66.6	66.4	66.5	67.2	67.1	67.4	66.8	67.8	68.1
% Hydrogen	3.92	4.06	4.08	4.06	4.07	4.04	3.77	3.88	3.92	4.14	4.03	4.18	3.87	4.02	4.17
Ratio H/C	0.691	0.710	0.710	0.692	0.703	0.709	0.674	0.695	0.701	0.735	0.716	0.738	0.691	0.706	0.729
Fusion Point, °C	128	128	123	121	120	120	109	120	115	135	131	133	128	122	110

* Extracted for 48 hours, results are average of two trials.

TABLE IX

Unfiltered Coal Solution Viscosities
Runs DOE 345B and 347

Run No. DOE	Temperature, °F	Shear Rate sec^{-1}	Viscosity cP
345B P-203	210	3.96	138
	210	7.93	131
	210	8.30[b]	136
	210	15.86	129
	210	16.61[b]	126
	230	7.93	72.5
	230	8.30[b]	76.1
	230	15.86	69.3
	230	16.61[b]	74.5
	230	39.64	67.5
	270	15.86	31.3
	270	16.61[b]	34.1
	270	39.64	28.8
	270	79.28	27.3
347 P-91	210	7.93	45.5
	210	15.86	37.5
	210	39.64	29.9
	210	79.28	28.8
	230	15.86	30.3
	230	39.64	21.7
	230	79.28	19.5
	270	39.64	11.4
	270	79.28	10.6

a) Brookfield Model LV viscometer, Spindle No. 18.
Procedure: 45 minute initial warmup and equilibration.
20-30 minute equilibration after temperature change.
10 minute equilibration after shear rate change.

b) Spindle No. 28.

TABLE X

Unfiltered Coal Solution Viscosities
Runs DOE 346 and 348R

Run No. DOE-	Temperature °F	Shear Rate Sec^{-1}	Viscosity cP
346R P-49	210	8.30	220
	210	16.61	210
	230	8.30	152
	230	16.61	128
	270	8.30	85.6
	270	16.61	68.2
348R P-47	210	3.32	202
	210	8.30	170
	210	16.61	155
	230	8.30	113
	230	16.61	102
	270	8.30	69.8
	270	16.61	56.3

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

TABLE XI

Feed Slurry Viscosities[a]
Runs DOE 346R and 348R

Run No. DOE	Temperature °F	Shear Rate Sec^{-1}	Viscosity 10^2 cP
346R P-49	210	0.083	200
	210	0.166	121
	210	0.415	84.1
	210	0.830	47.1
	210	1.66	37.4
	210	3.32	30.8
	230	0.415	51.7
	230	0.830	38.4
	230	1.66	28.7
	230	3.32	20.8
	270	0.830	37.6
	270	1.66	25.6
	270	3.32	16.0
	270	8.30	9.82
348R P-47	210	0.166	86.4
	210	0.415	47.9
	210	0.830	32.8
	210	1.66	24.7
	210	3.32	16.4
	210	8.30	10.6
	230	0.415	40.6
	230	0.830	25.5
	230	1.66	17.7
	230	3.32	13.5
	230	8.30	7.50
	230	16.61	5.91
	270	1.66	15.1
	270	3.32	9.63
	270	8.30	5.87
	270	16.61	4.24

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

FIGURE 1

UNFILTERED COAL SOLUTION VISCOSITIES

RUNS DOE 340 AND 341

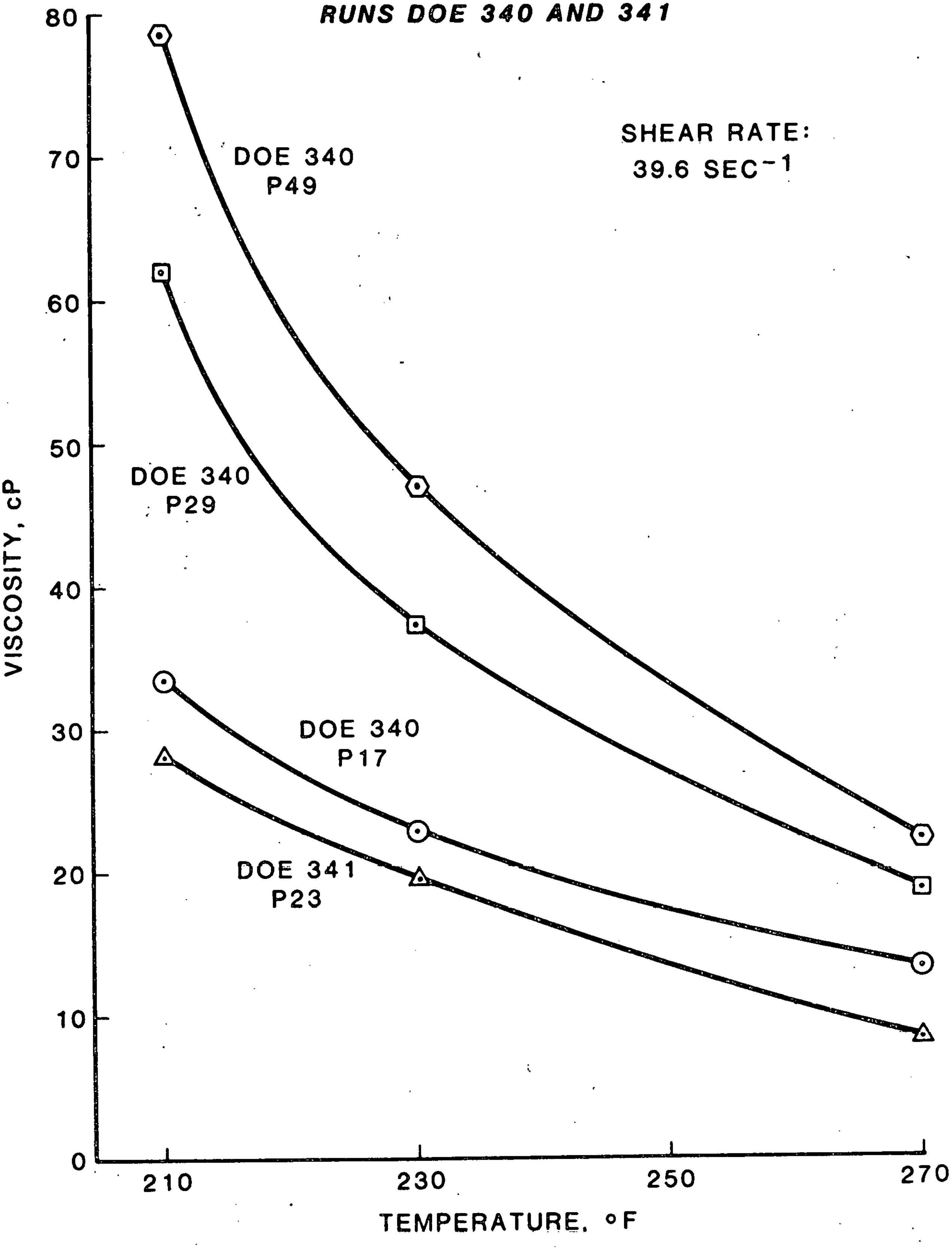
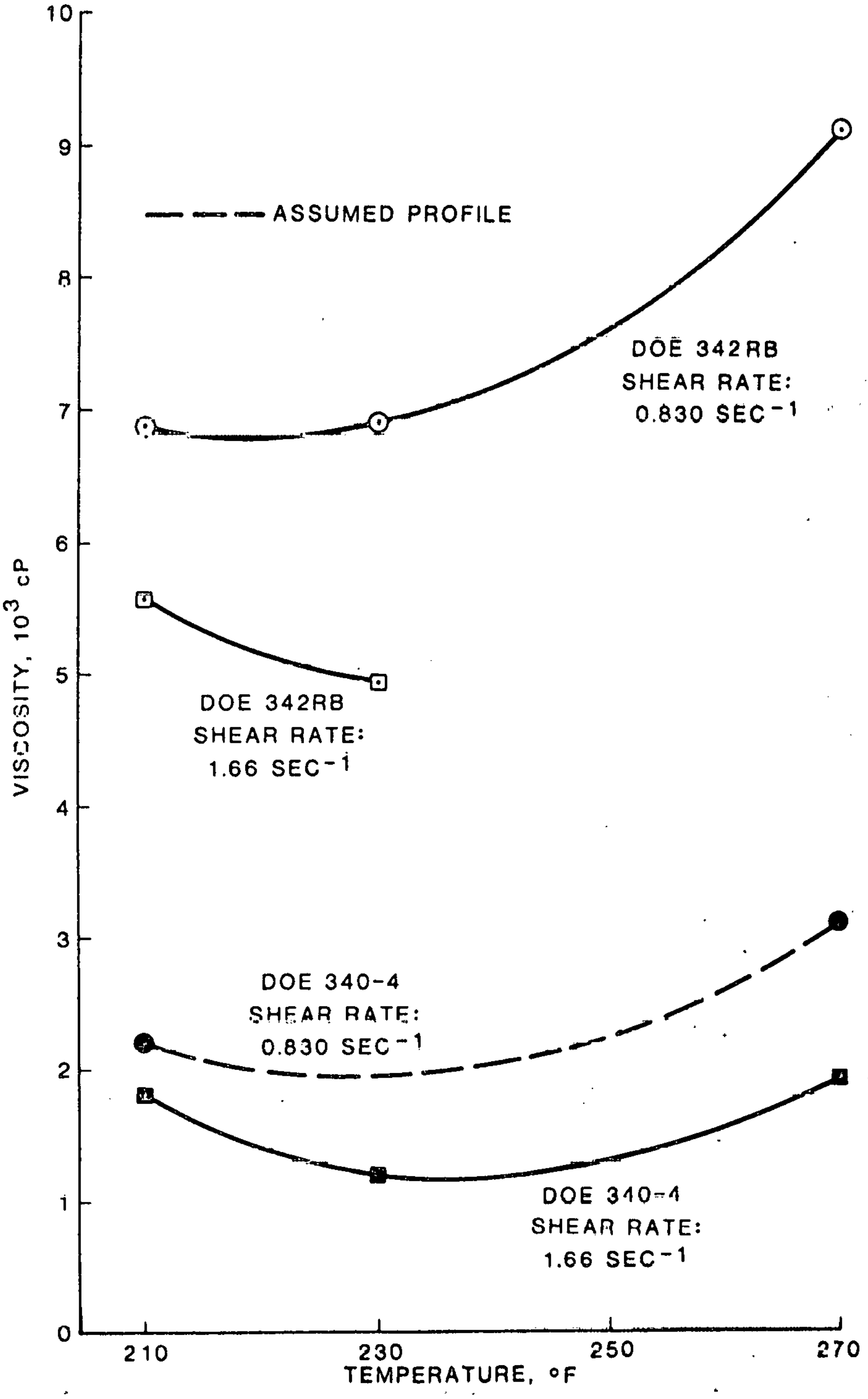


FIGURE 2

FEED SLURRY VISCOSITIES

RUNS DOE 340 AND 342R



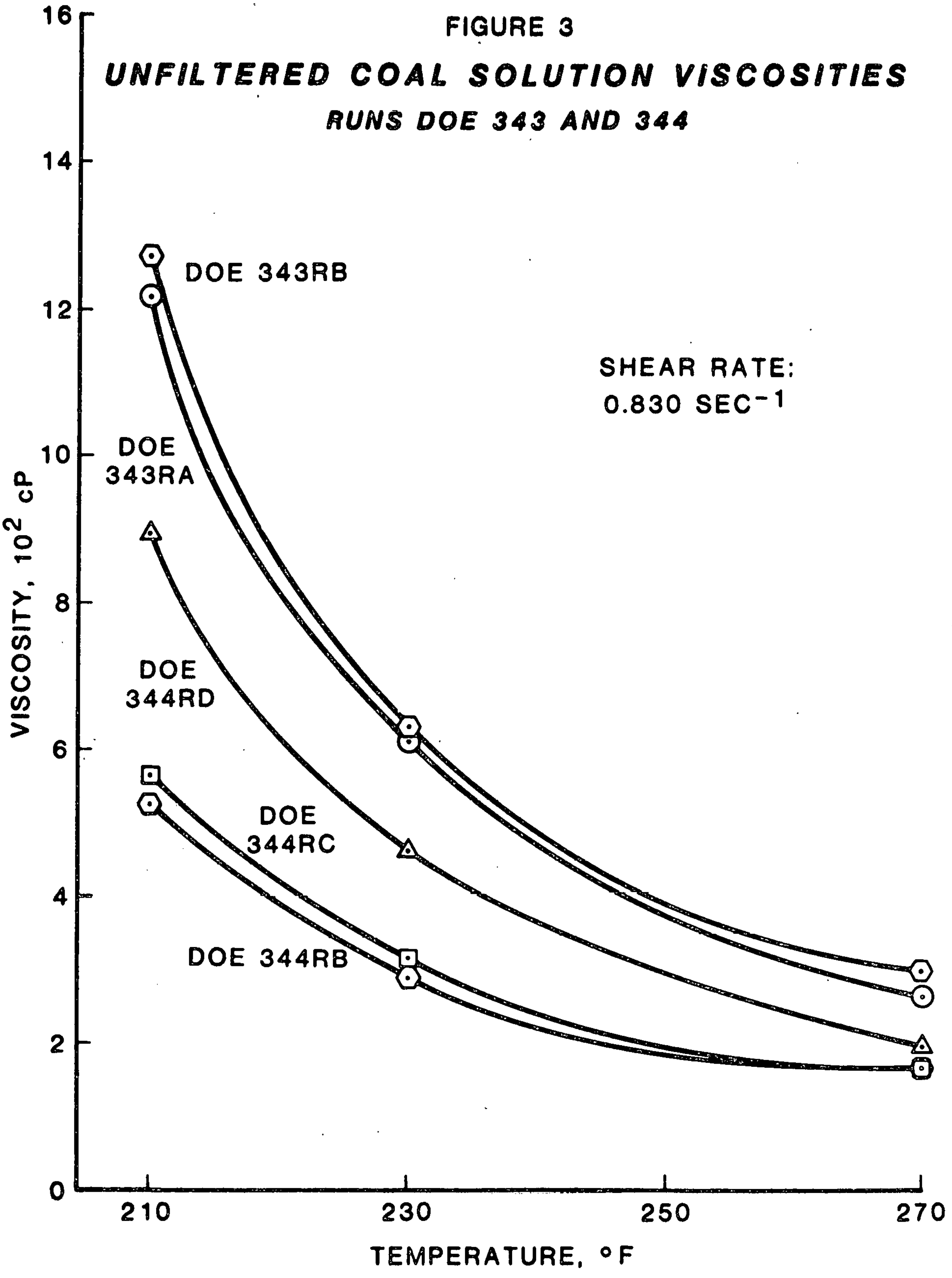


FIGURE 3

UNFILTERED COAL SOLUTION VISCOSITIES

RUNS DOE 343 AND 344

FIGURE 4

FEED SLURRY VISCOSITIES

RUNS DOE 343RA AND 344RB

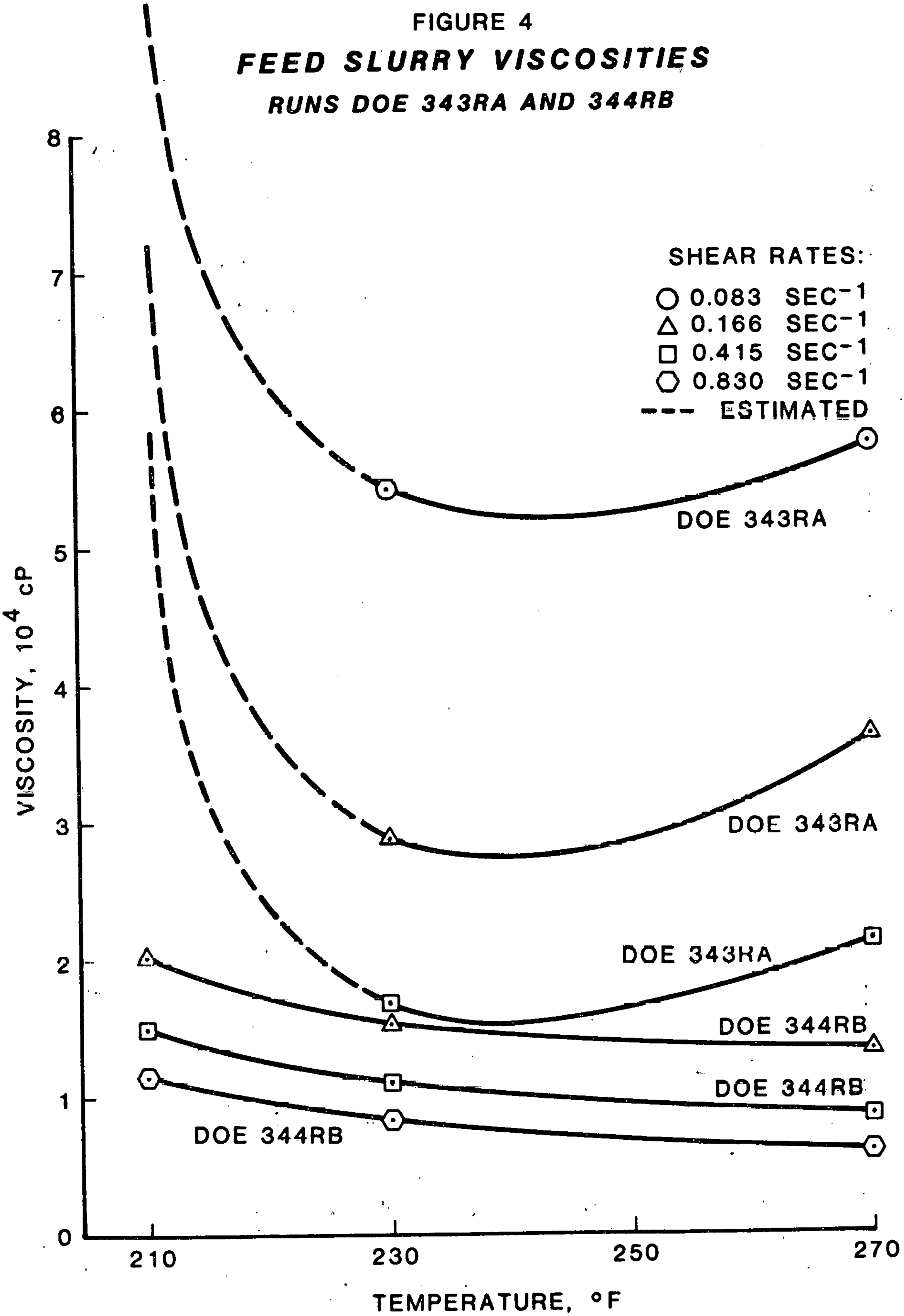


FIGURE 5

FEED SLURRY VISCOSITIES

RUNS DOE 343RC AND 344RD

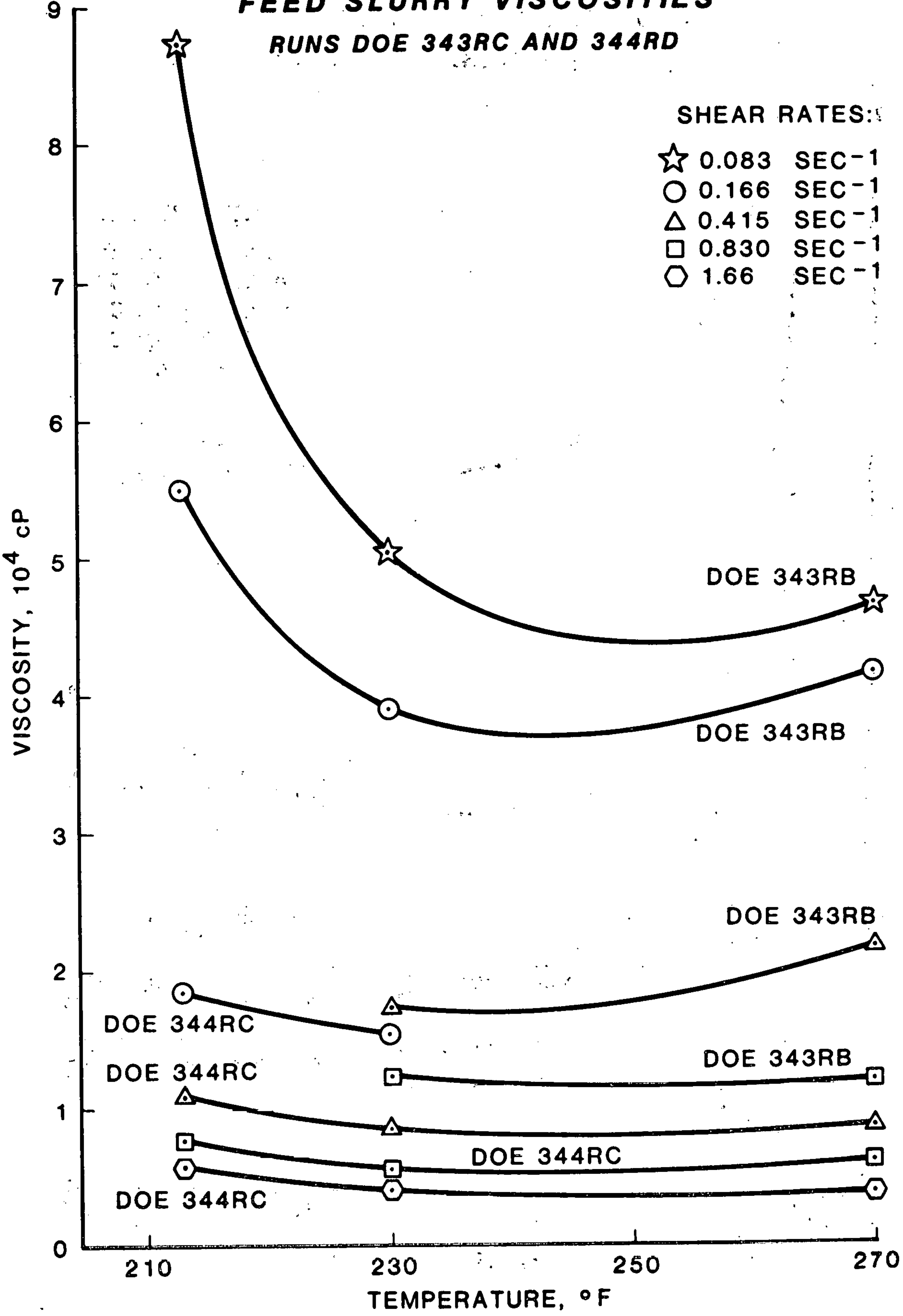


FIGURE 6

FEED SLURRY VISCOSITIES

RUNS DOE 343RC AND 344RD

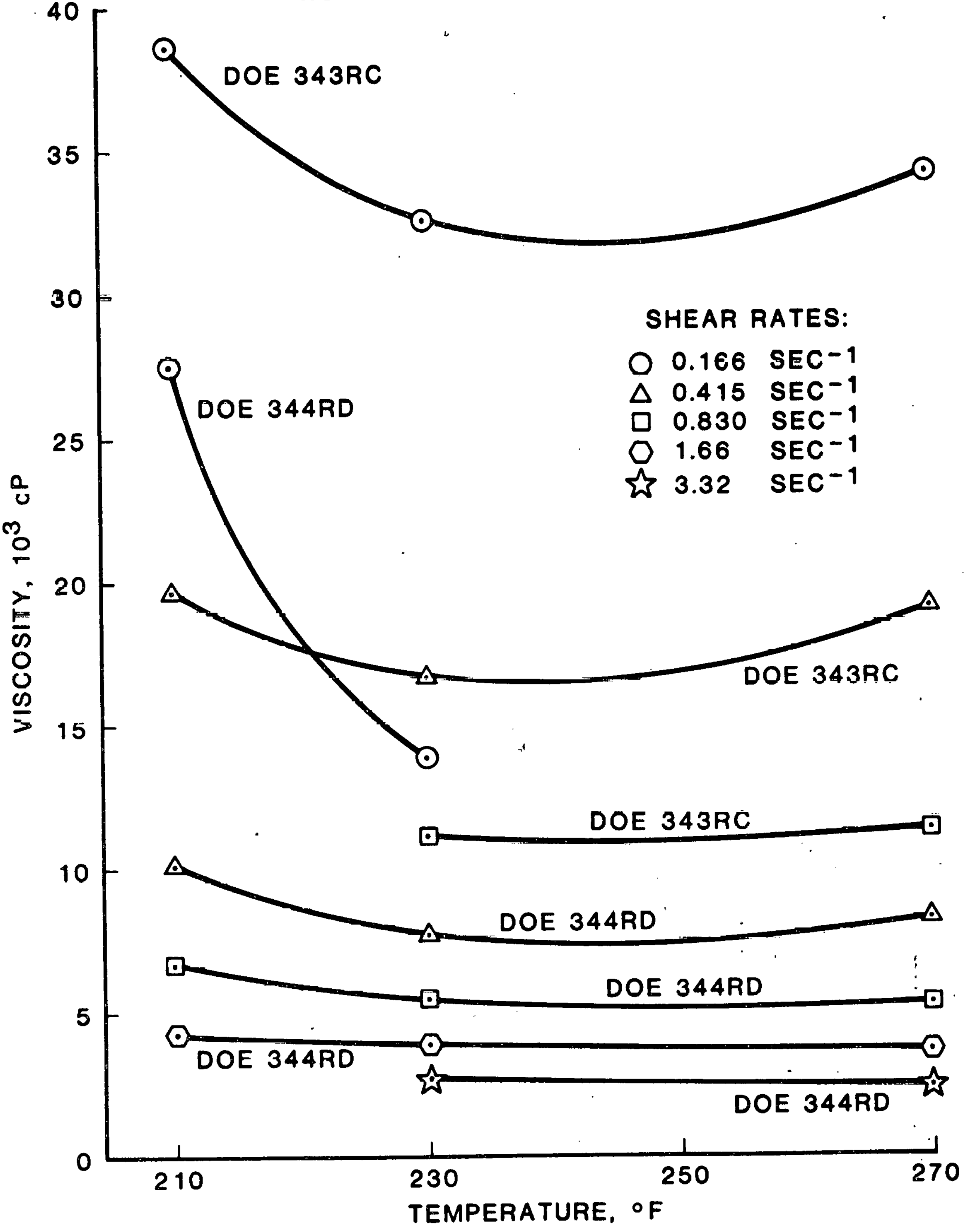
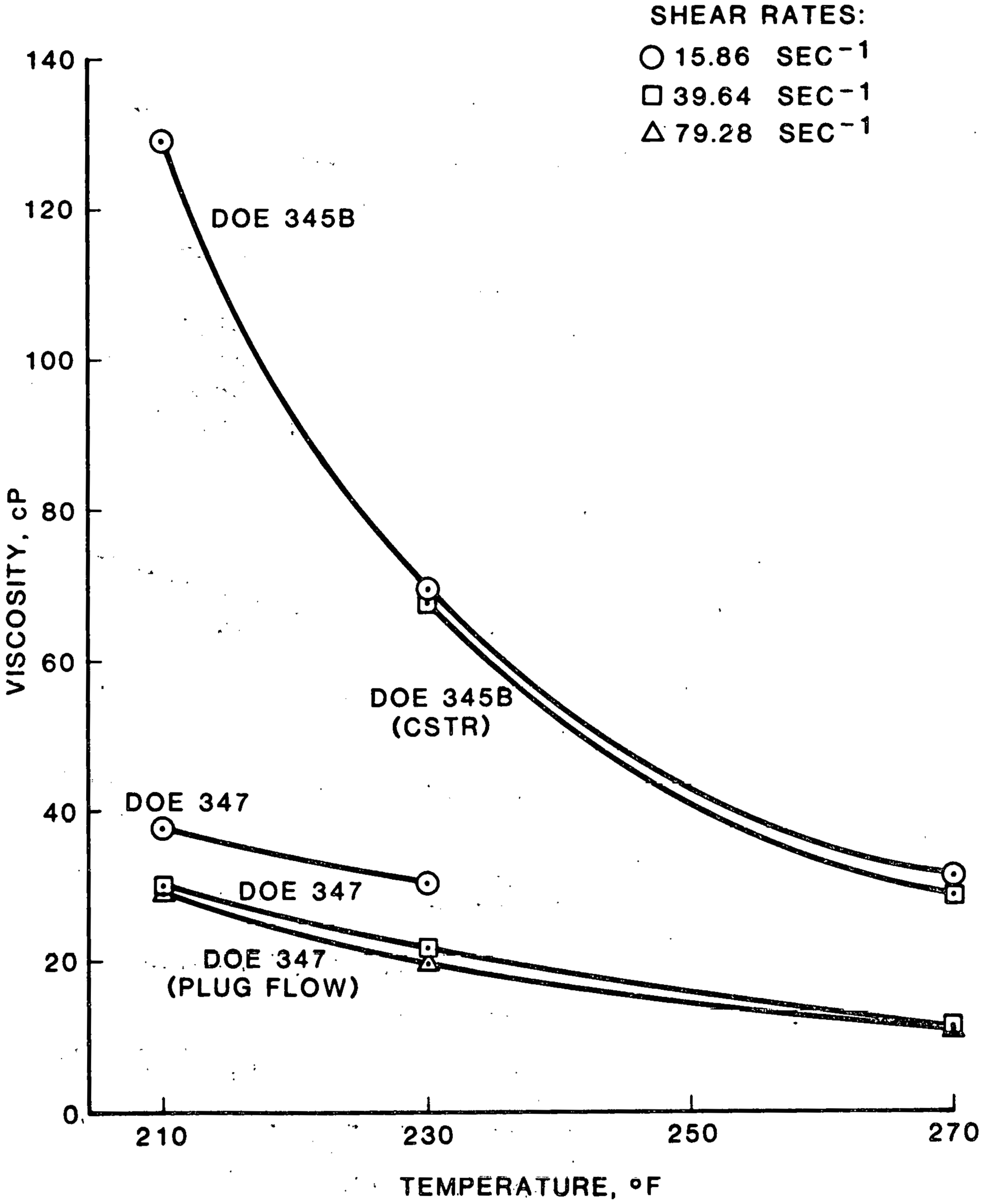


FIGURE 7

UNFILTERED COAL SOLUTION VISCOSITIES

RUNS DOE 345 AND 347



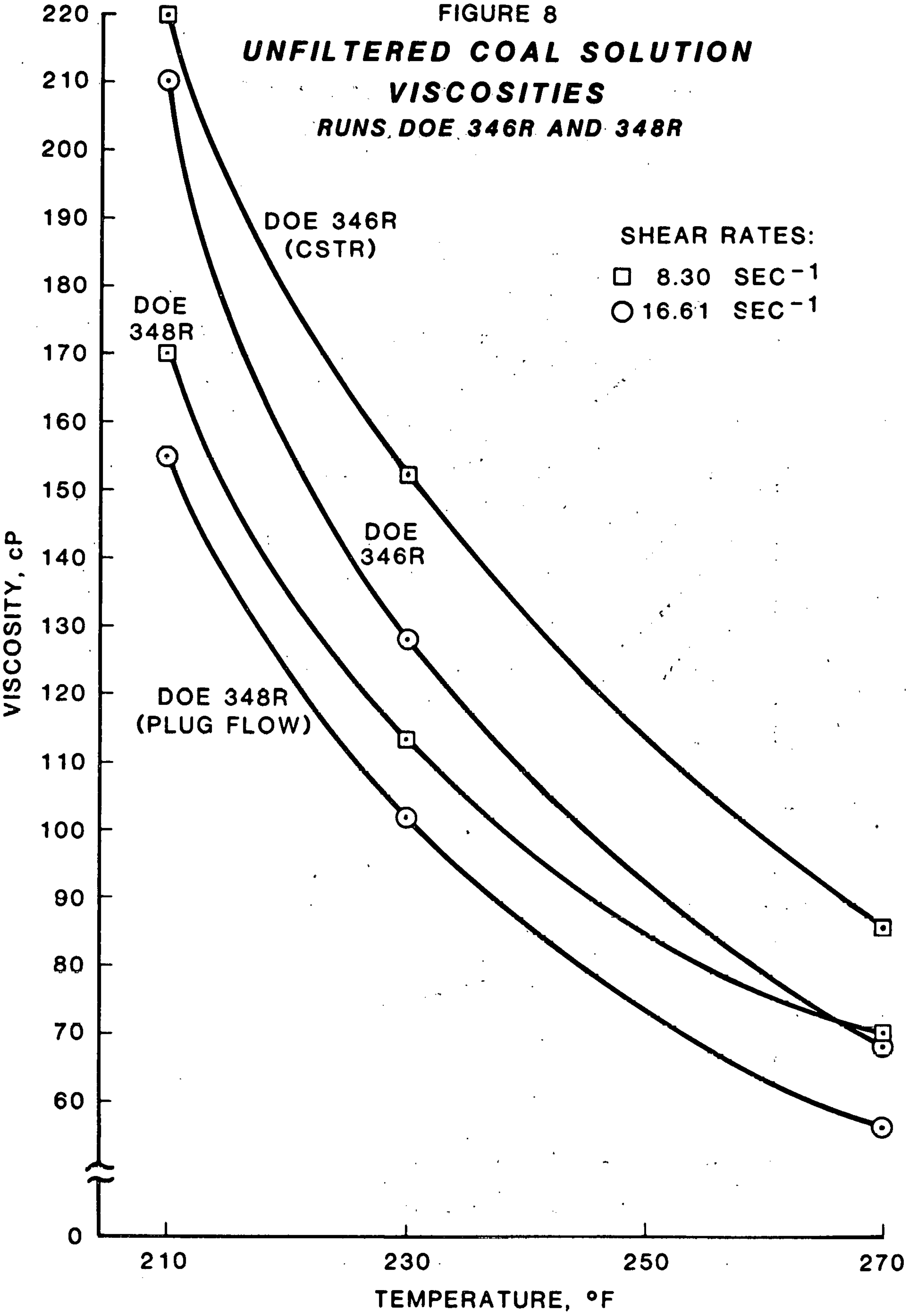


FIGURE 8

UNFILTERED COAL SOLUTION VISCOSITIES

RUNS DOE 346R AND 348R

FIGURE 9

FEED SLURRY VISCOSITIES

RUNS DOE 346R AND 348R

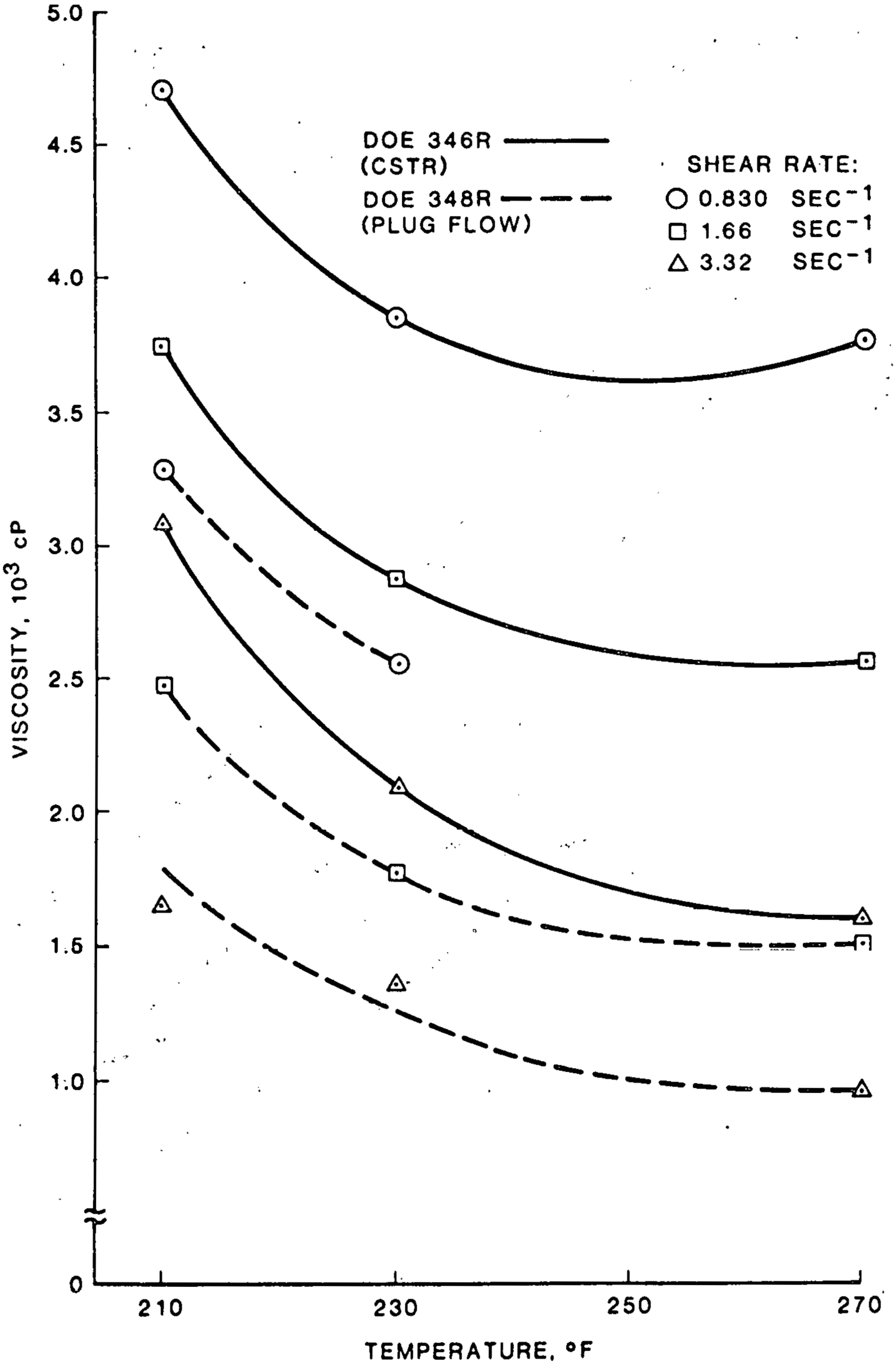


FIGURE 10

COMPARISON OF SIMULATED DISTILLATION AND TRUE BOILING POINT CURVES

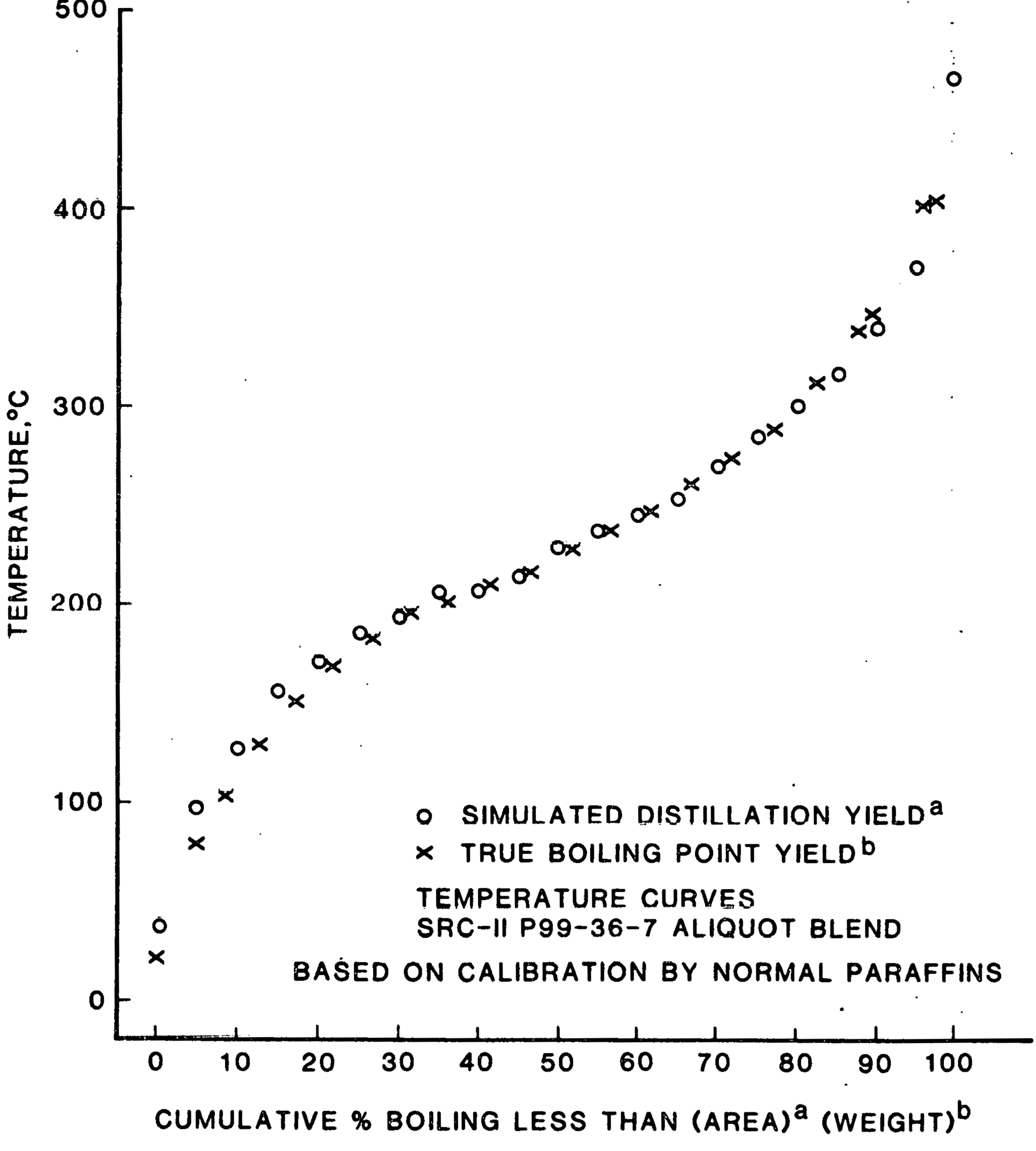


FIGURE 11

COMPARISON OF TRUE BOILING POINT AND SIMULATED DISTILLATION TEMPERATURE CURVES FOR P99-36-7 ALIQUOT BLEND USING AROMATIC HYDROCARBON STANDARD

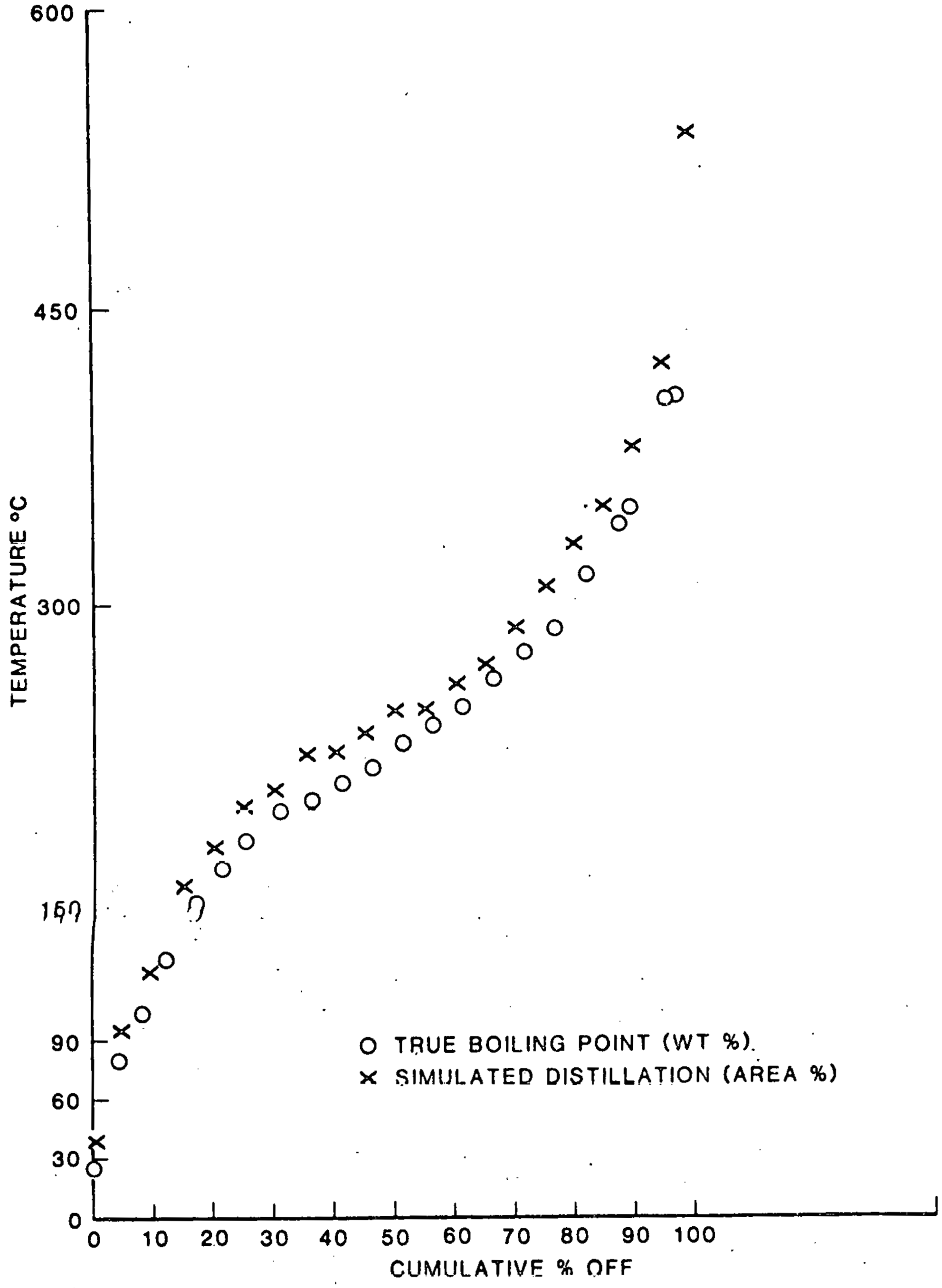


FIGURE 12

COMPARISON OF SIMULATED DISTILLATION AND TRUE BOILING POINT CURVES

P99-36-7

DEBUTANIZER BOTTOMS

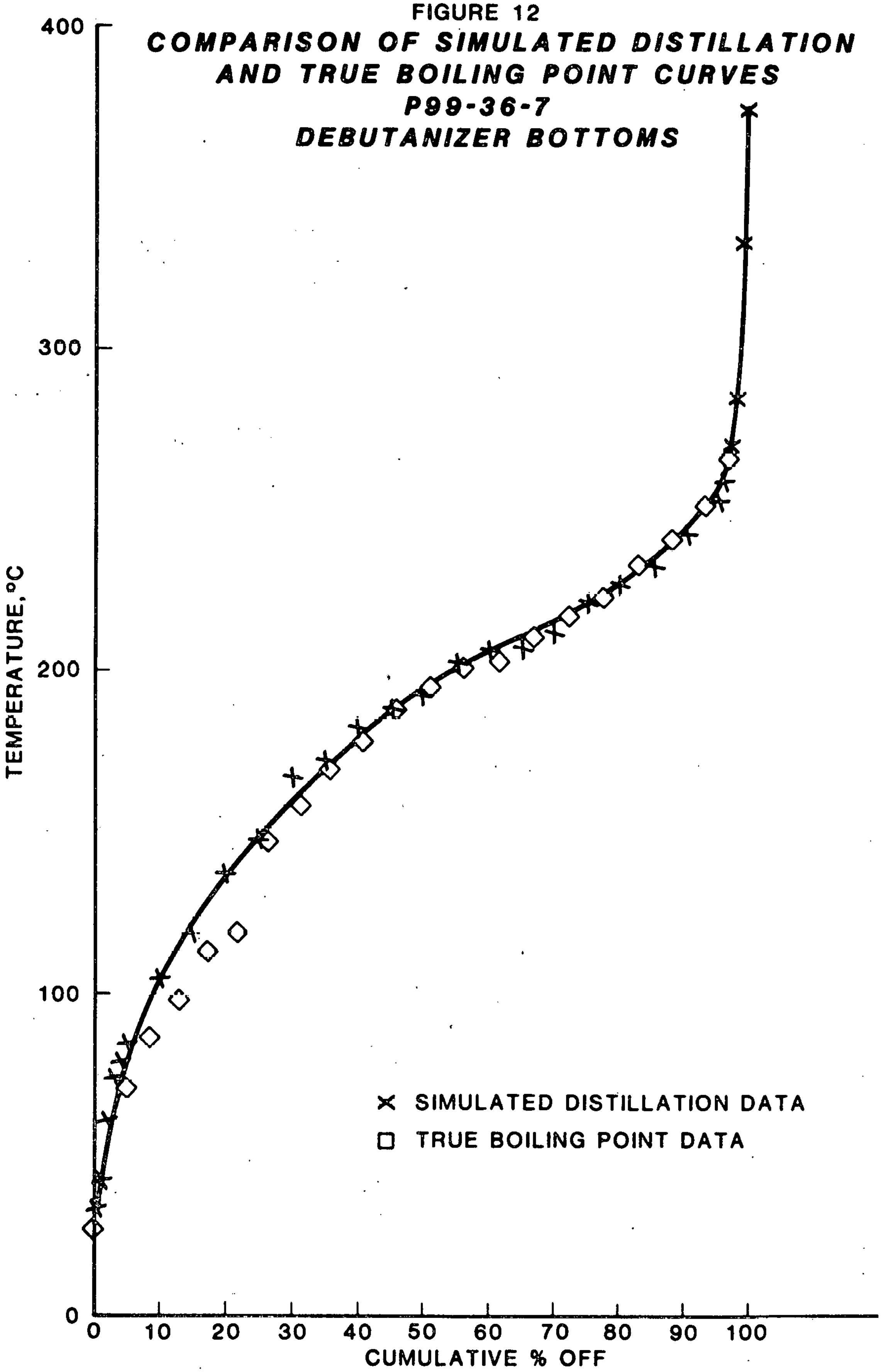
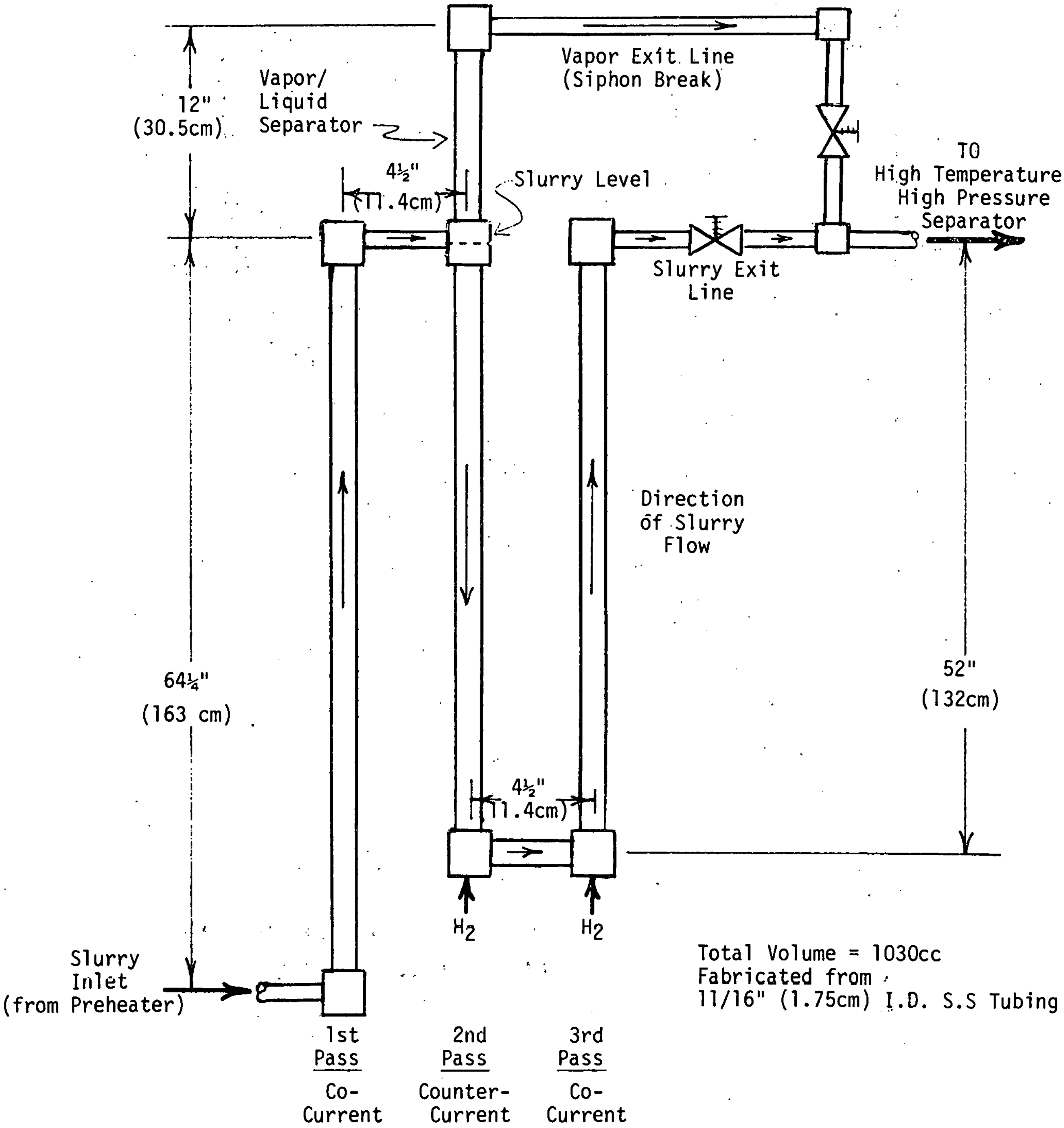


Figure 13

THREE-PASS DISSOLVER
(Used in Run DOE 340)



Total Volume = 1030cc
Fabricated from
11/16" (1.75cm) I.D. S.S Tubing

Figure 14

Downflow Dissolver
(Used in Runs DOE 341, 342R and 343R)

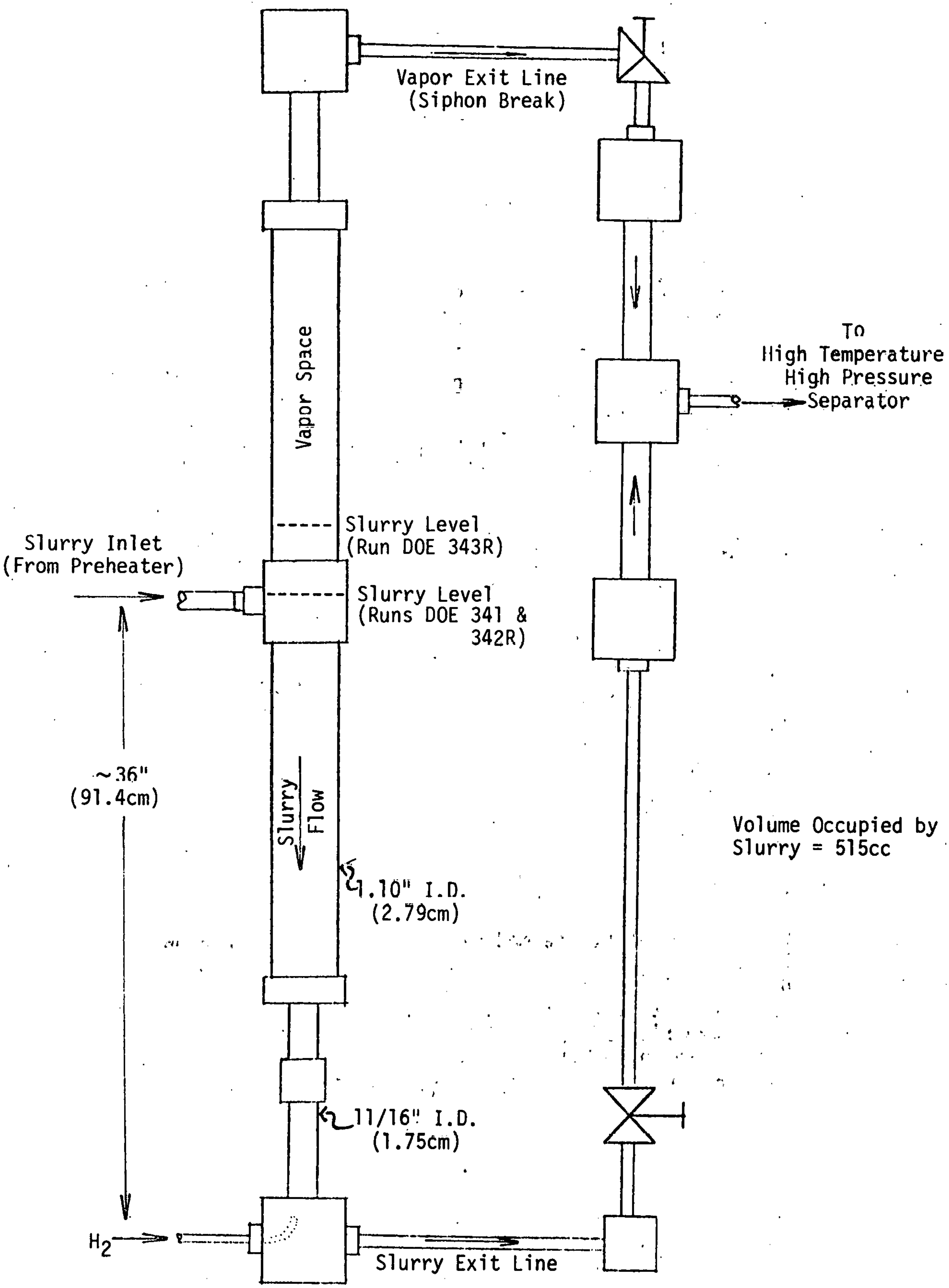


Figure 15

Upflow Dissolver
(Used in Run DOE 344R)

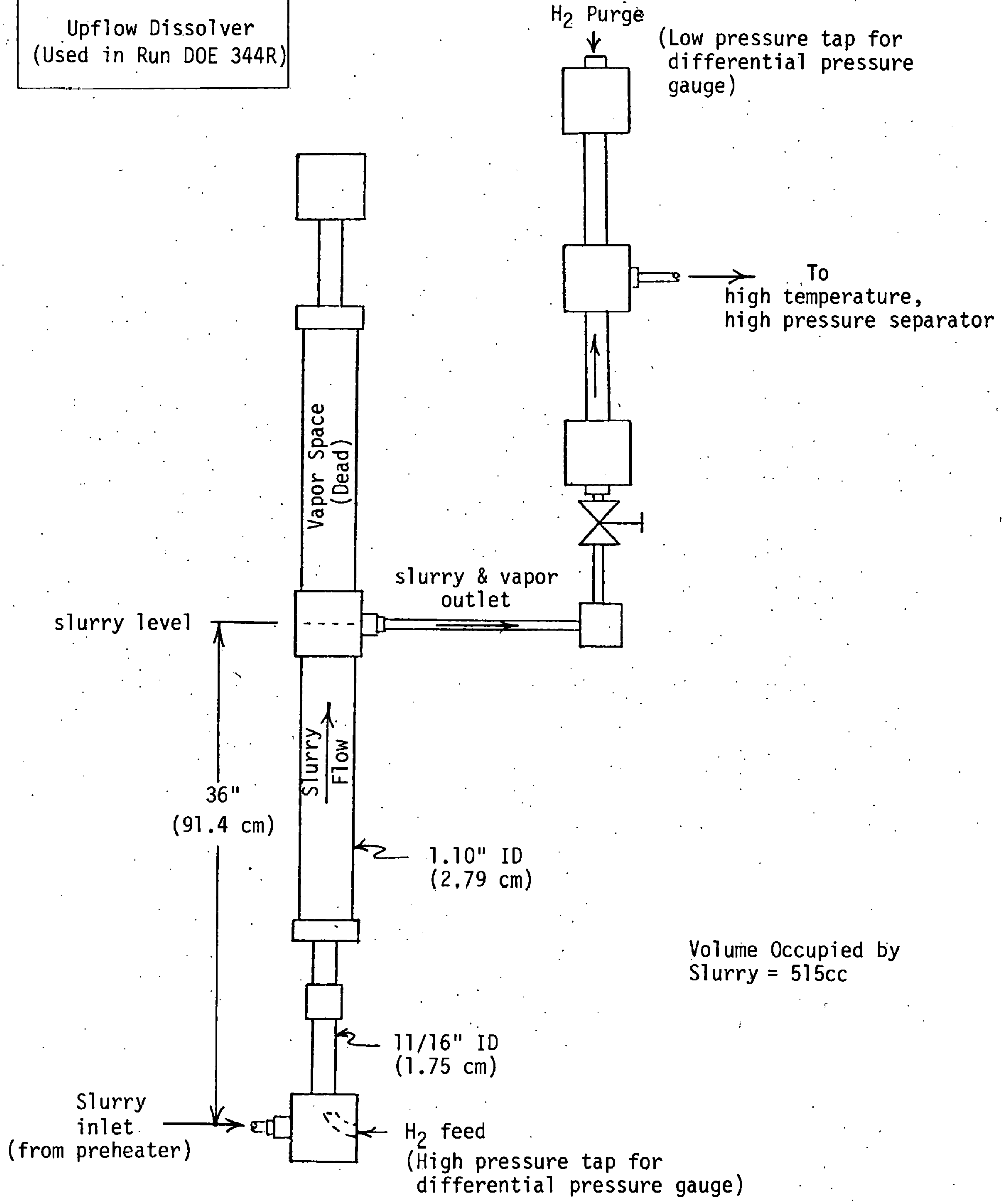
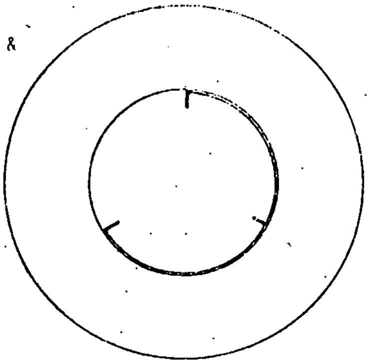


Figure 16

Continuous Stirred Tank Reactor Used in Runs DOE 345R and 346R

TOP VIEW

Showing location of baffles in DOE 345R & DOE 346R



Volume Occupied By Slurry = 1018 cm^3

SIDE VIEW

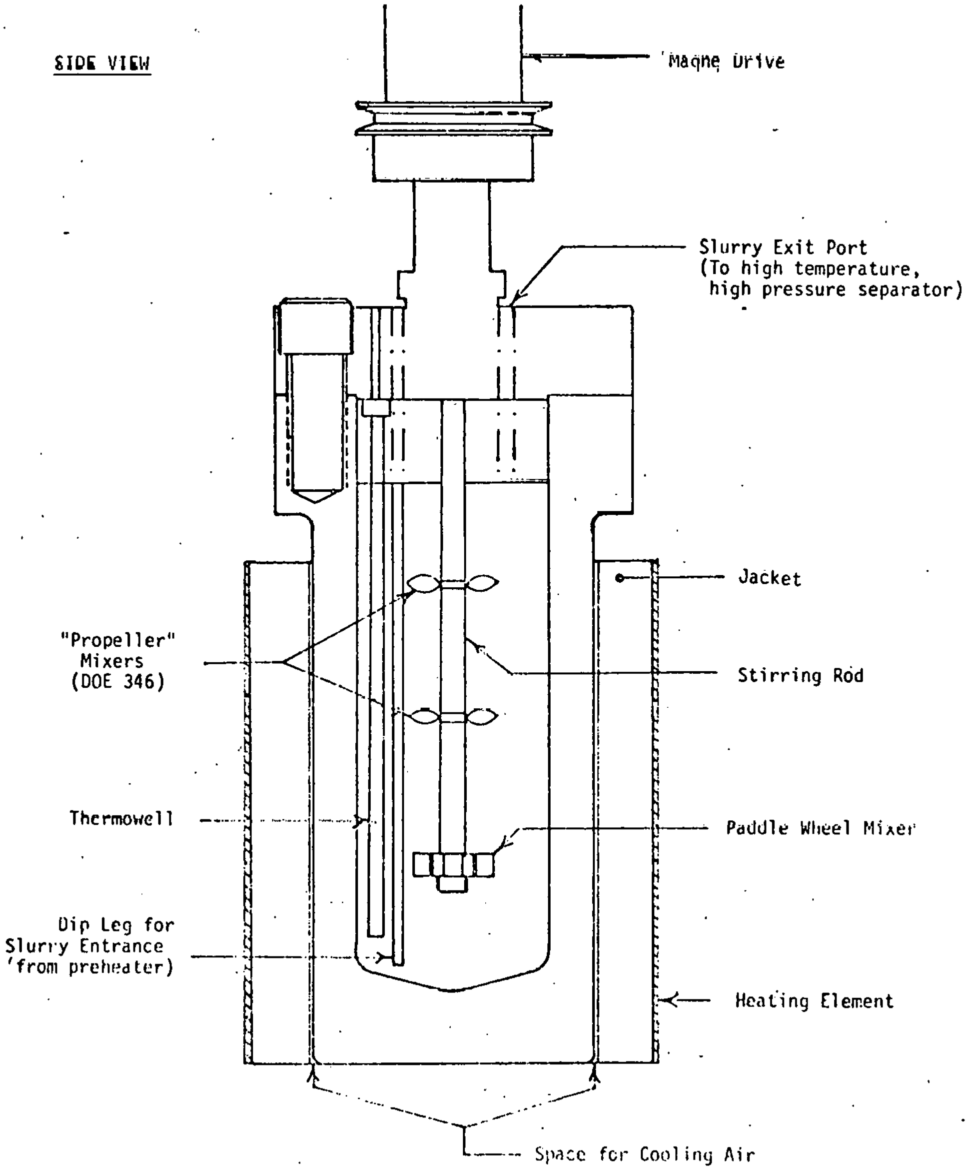


Figure 17

Tubular Reactor
(Run DOE 347)

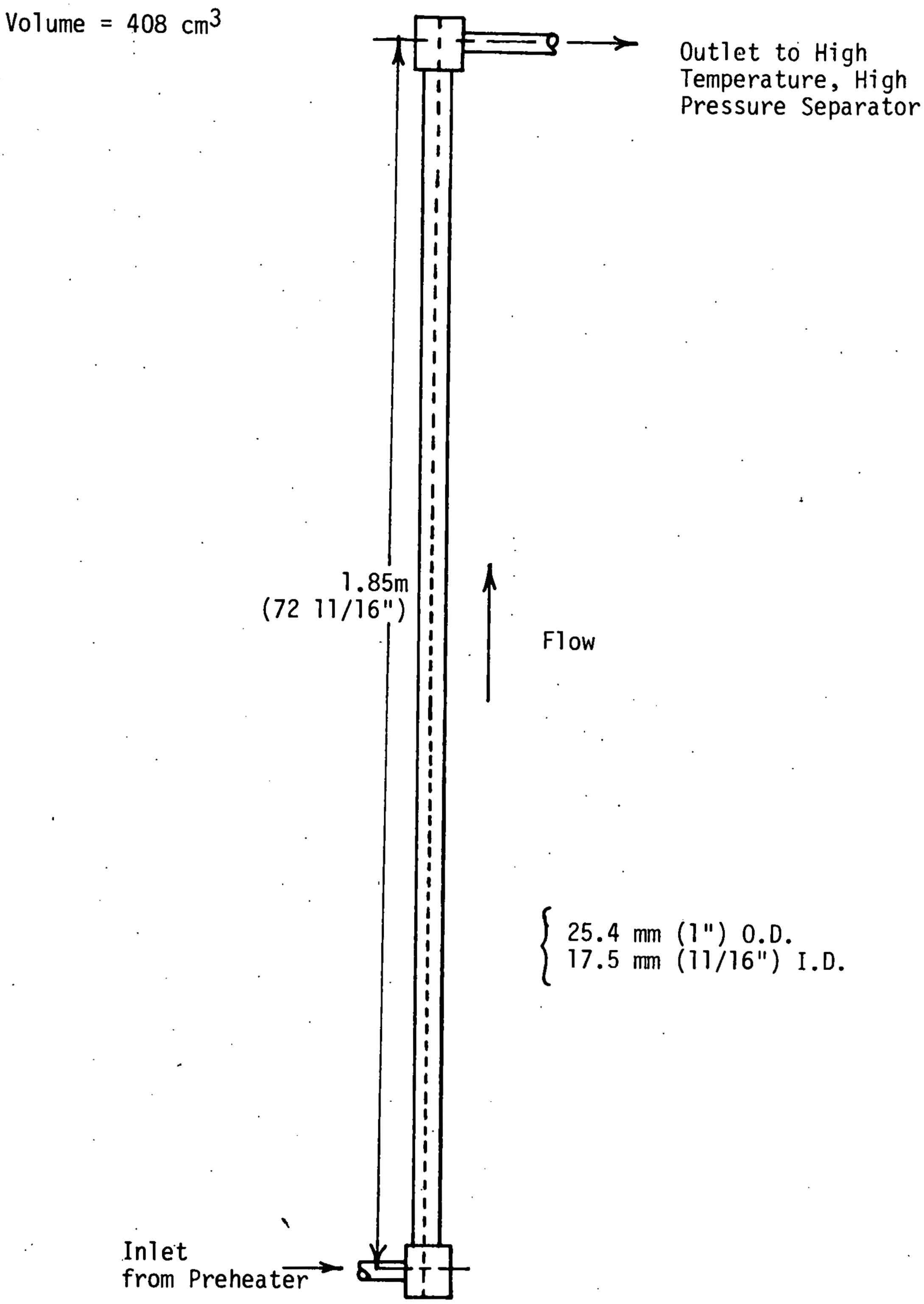
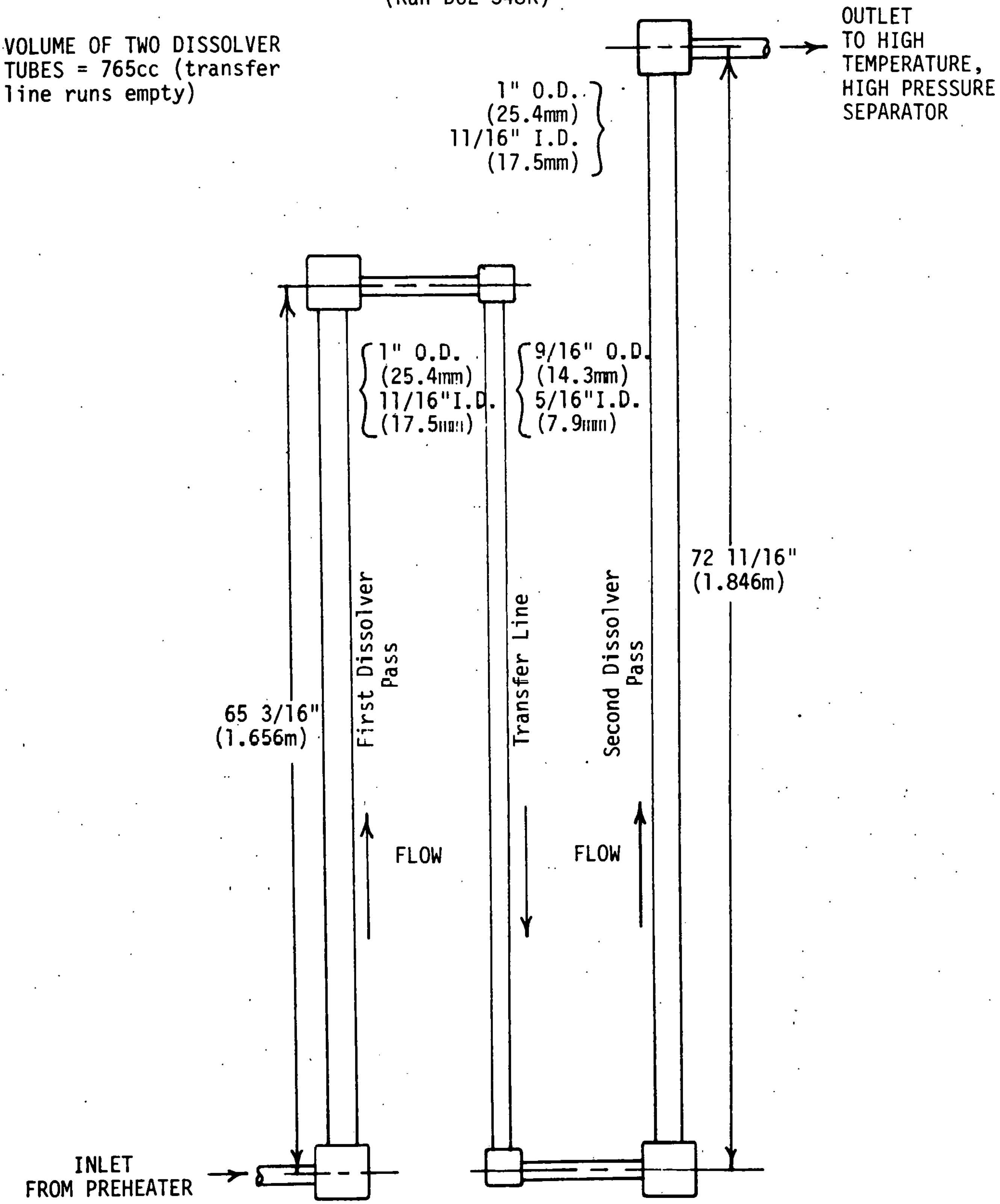


Figure 18

Modified GU5 Dissolver
(Run DOE 348R)



APPENDIX A

EXTRACTION ANALYSIS OF DISTILLATION RESIDUES FROM SRC PROCESSES

I. INTRODUCTION

A complete description of the solvent extraction procedure was given in the third quarter 1979 progress report*.

Work has continued to study the repeatability of the method by including a large number of replicate determinations on three separate samples from each major reaction condition in run DOE 344R.

In addition, the inspection of extracts has been continued. This includes elemental analyses of materials recovered from the extraction solvents and inspection for incomplete removal of process solvent using the simulated distillation gas chromatographic method.

II. REPEATABILITY OF RESULTS

In the replication work, one analyst ran duplicate extractions using hexane and one extraction each with pyridine and toluene. Another analyst ran duplicate trials with benzene and one trial each with toluene and pyridine. This resulted in at least eight separate extractions on nine separate samples from run DOE 344R, a total of 77 trials in all. This allowed determination of the variation between distillations for a particular "lined-out" period and the changes in solubility brought about by relatively small changes in run conditions. Results were generally reproducible except for some trouble with hexane extractions which have been repeated in an attempt to discover the cause. All values obtained are presented on Table A-1.

Poor repeatability with benzene on 24-hour extractions was eliminated by allowing extractions to run for 48 hours. The pyridine and toluene extractions were allowed to run 48 hours also for the set paired with benzene. Hexane extractions and pyridine and toluene extractions paired with the hexane extraction were run for 24-hour periods. In the case of poor precision using hexane, the repeat extractions were run longer. In general, the longer extractions using benzene, toluene or hexane tended to increase the amount of soluble material recovered a little, but had no effect on the solubility in pyridine.

Pyridine extraction is the most precise procedure used throughout the whole study. Duplicates on a particular sample were closer together than duplicates between samples, which is a consequence of sample variability (either reaction conditions or distillation procedure variation). The average solubility in pyridine for samples 62, 69 and 74 (run DOE 344RB) was 62.55% with a standard deviation of 0.90. The average ash in this set of distillation residues was 25.15%. Duplicates on individual samples frequently fell within 0.1 to 0.2% (absolute) even allowing for a 24-hour difference in extraction time. Samples 106, 111 and 120 (run DOE 344RC) averaged 64.71% pyridine soluble material with a standard deviation of 1.00. Samples in this set contained an average of 23.92% ash. Samples 149, 155 and 156 (run DOE 344 RD) averaged 63.67% pyridine soluble with a standard deviation of 1.01. These samples

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period July 1, 1979 through September 30, 1979; July 1980, FE/14800-11.

contained an average of 24.04% ash. The variation in ash implies slightly different conversions of coal to the nondistillable molecular weight range under study and different average solubility should be expected as a consequence. Significant variation in pyridine solubility was indeed observed.

The solubility in the various solvents is also reported as the fraction soluble in the solvent in question compared to the fraction soluble in pyridine (Table A-1). For the first condition in run DOE 344R (samples 62, 69 and 74), the average hexane solubility was 0.3461 of the amount soluble in pyridine. The mean deviations were 0.0079 for hexane, 0.0056 for benzene, and 0.0042 for toluene results. The suggestion, therefore, arises that results are more precise for the best solvent (pyridine) and become more scattered as the solvent becomes less active in its attack on the distillation residue.

This is certainly the case for the second and third sets of data. Some difficulty in reproducing both the hexane and benzene results developed, and it was considered necessary first to use longer extraction times with benzene, and later to repeat some work with hexane. No point of technique or operating error is now evident which would justify the rejection of points which appear to be outliers. In some cases, the thimble may have plugged with mineral or organic material and error would be most reasonably assigned to the low value in a troublesome pair. It is not clear how or why such problems may have developed.

One component in this problem may be the normal operating temperature of the extractor. The apparatus which normally runs at the lower temperatures (that using benzene and hexane for example) may be more prone to nonreproducible plugging or precipitation of material on the external surface or in the pores of the thimble. All extractions give some precipitate in the extractor and on the thimble and, therefore, the problem is a general one. It must be agreed that the method has limitations in accuracy and in repeatability which are not likely to be overcome.

When major changes in reaction conditions or operating mode are imposed, the solubility and the relative solubility in various solvents does respond. Low hexane solubility is obtained in SRC I distillation residues (normally a few percent will dissolve). In SRC II distillation residues the hexane solubility increases substantially and runs about one-third of the total material soluble in pyridine. Some response to catalysis or hydrogen partial pressure was indicated in data reported previously. In general, these results have probably not suffered major deflections as a consequence of minor variations in conditions during a run or in distillation technique. This conclusion is based on the similarity of results from sample to sample in the DOE 344R data set and other less careful replication studies inherent in results reported earlier.

Since the benzene and toluene results are close together, and since the benzene results tend to be more troublesome to obtain, it appears reasonable to drop benzene solubility out as an extraction result. The work will be continued through the next few experiments to get results with some standard SRC I products. After that, it is planned to use only hexane, toluene and pyridine as standard solvents.

III. RETENTION OF PROCESS SOLVENT AND EXTRACTION SOLVENT BY RESIDUES

Since the hexane soluble fraction could be readily redissolved in carbon disulfide, the presence of volatile solvent range material could be determined by injecting these rather concentrated solutions into the simulated distillation gas chromatograph.

A. Percent Volatile in Hexane Extract

Data for the hexane extract from run DOE 344R-62 are given below for example:

Weight of hexane extract	104.74 mg
Weight of naphthalene internal standard	10.80 mg
Weight of carbon disulfide	1.1029 grams

The simulated distillation chromatograph chart obtained is shown on Figure A-1. Carbon disulfide does not give much response with the flame ionization detector; therefore, little peak area is associated with the solvent used to inject the sample. The second response is probably due to a residue of hexane or some impurity associated with the hexane. The third peak area is associated with the naphthalene internal standard and is recorded as 85,096 counts by the integrator. The area associated with the volatile material is recorded as 278,964 counts. Since the identity of the materials is not well known, it is necessary to assume that the flame ionization detector response per unit of volatile material will be about the same as the response for naphthalene. Thus, the peak area can be converted to an estimated weight by simple ratio:

$$\text{Estimated weight of volatile material} = \frac{(10.80\ \text{mg})\ (278964)}{85096} = 35.40\ \text{mg}$$

$$\text{Estimated percentage volatile} = \frac{(35.40)\ (100)}{104.74} = 33.8\%$$

B. Boiling Range of the Volatile Material

Using the simulated distillation equipment in the mode which reports percentage distillate versus temperature corrected to atmospheric pressure gives an idea of the boiling range of the volatile material in the extract. The computer printout for the areas and the printout for the percentage distilled versus temperature is shown as Figure A-2. Following the naphthalene area, the temperature breaks upward abruptly and the volatile matter in the extract can be seen to distill from about 410°C to an endpoint of 582°C.

C. Comparison to Process Solvent

These results can be compared to the simulated distillation results for a typical process solvent reclaimed by distillation using a vacuum system regulated to 2.0 mm. In our recent work the distillation has usually been started with about 1.5 to 2.0 kg of product. A preliminary cut is taken from the initial point to 108°C at 2.0 mm and a main solvent recovery cut is taken from this temperature to a vapor temperature of 270°C.

Figure A-3 shows the simulated distillation chromatogram of the recovered process solvent from DOE 342RB-24. The results relating percentage distilled to the temperature are shown as Figure A-4. A comparison of the simulated distillation results shows that only about 54%* of the volatile material from the hexane extract boils in the same range as a typical recycled solvent (<900°F, <482°C).

D. Percent Volatile in Distillation Residue

For the particular distillation in question (DOE 344R-62), the distillate was 38.33% and the residue was 61.67% of the sample. Upon extraction with hexane, the residue gave a yield of 22.73% soluble material. Of this, 33.8% was volatile in the chromatograph. The maximum volatile component of the distillation residue is, therefore, estimated as follows:

$$\text{Percentage Volatile in Distillation Residue} = (100)(0.2273)(0.338) = 7.68\%$$

Workers at Sandia National Laboratories have done similar examinations of distillation residues and have reported higher percentages of volatile material. The cause for the difference in the amount of volatile material observed here may relate to the use of larger samples in the distillation procedure at Merriam or to the difference between SRC II samples examined here and the SRC I samples examined at Sandia.

Since 54% of this volatile material is in the recycle solvent range, the distillation residue was found to retain 4.1% process solvent. This includes a considerable amount of material which appears in quite small concentrations in the usual recycle solvent and which is of unknown utility as a solvent or as a hydrogen transfer agent. Recent experiments at Wilsonville in which light SRC I material is returned as solvent suggest that these materials would be useful if available (and, of course, they are returned as a component of the UFCS recycle in the SRC II process feed slurry).

E. Extension to Benzene, Toluene and Pyridine Extracts

The above analysis was repeated for benzene, toluene and pyridine extracts from run DOE 343R-51:

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* This 54% distills at the extreme high end of the recycle solvent distillation range; compare Figures A-1 and A-3 or Figures A-2 and A-4.

Extraction Solvent	% Volatile* in Extract	% Extract in Distillation Residue	% Volatile in Dist. Residue
Benzene	21.05	51.61	10.86
Toluene	16.28	53.58	8.72
Pyridine	12.48	63.07	7.87

* Corrected for imbibed extraction solvent.

It is not clear whether or not the carbon disulfide used as a chromatograph solvent will dissolve all of the volatile material in benzene, toluene and pyridine extracts when a solid phase is present. An extraction resulting in a distribution between solid and liquid phases may be operating here instead.

The chromatograms used for the above analyses are presented in Figures A-5, 6 and 7. Tables from the integrator are included in order to show the nature of the data available. When the spectra and the tables are studied, it will be seen that some of the areas in question tail rather badly and that the cutoff points had to be taken in an arbitrary manner. This is the result of holding the column at a high temperature at the end to bring the volatile components out in a convincing display. This damages the column and results in frequent column replacement. For that reason, this kind of work will not be done routinely.

IV. COMPARISON OF HEXANE EXTRACT AND PROCESS SOLVENT TO KNOWN COMPOUNDS

In order to gain some intuition regarding the kinds of aromatic material in the boiling ranges covered, a standard solution of known materials has been run through the chromatograph at about the same conditions. Figure A-8 shows the simulated distillation chromatogram with identification of known substances written on the chart. The numbers refer to retention time in hundredths of minutes. It should be borne in mind that matching the retention time of a known peak with a peak in a sample is not conclusive proof that the substance is present in the sample. It is necessary to isolate the material corresponding to the peak and analyze it or to match retention times on several columns for a more positive identification. Since the column used for the simulated distillation is short, the probability of a close match for retention times of a number of compounds is larger than the case for an analytical column. With these reservations in mind, it is still evident that the maximum boiling point of the process solvent is in the range of chrysene to perylene (molecular weights of 228.3 and 252.3, respectively), while the hexane extract tends to contain materials higher boiling than chrysene and gives the greatest response past the retention time for perylene.

It is not likely that the coal derived materials are simple fused ring type aromatic materials of the type discussed above. It is more likely that should these type materials be present, hydrogenation and substitution would have somewhat modified the basic aromatic structure and dispersion into a variety of peaks associated with a particular aromatic skeleton would be expected.

It appears that the recycle solvent is dominated by three fused ring aromatic structures (phenanthrene-like) and two fused ring structures (naphthalene-like) and that compact four ring structures (pyrene-like) are near the upper limit in molecular weight for those structures which are observed in significant amounts. The higher molecular weight and more complex volatile materials in the hexane extract and the soluble but less well understood materials (probably with higher molecular weights) must be regarded as precursors for solvent range materials.

V. COMPOSITION OF SOLUBLE MATERIAL

Extracts from run DOE 343-51 were subjected to elemental analysis. A sample of each extract was also run with an internal standard to determine the amount of imbibed extraction solvent using the gas liquid chromatograph method discussed above. From these results a corrected elemental analysis for each of the extracts in question was calculated:

Solvent Used for Extraction	Analyses of Extracted Material					
	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Oxygen	% Ash
Benzene	90.40	5.73	0.36	1.85	1.44	0.22
Toluene	90.24	5.78	0.42	1.87	1.60	0.09
Pyridine	89.49	5.10	0.43	2.32	2.52	1.14

These results show quite clearly the progressive elimination of oxygen, nitrogen and sulfur as the material becomes more soluble (and presumably becomes lower in its average molecular weight). Because of the chance for minor errors in the hydrogen analysis, it may not be reasonable to conclude from the data here whether or not hydrogen is also gained systematically as the molecular weight is decreased. It appears that this should be the case and that the examples at hand have some residual experimental error in them.

TABLE A-1

SOLVENT EXTRACTION RESULTS FOR DOE 344R DISTILLATION RESIDUE

SAMPLE NO.	62	69	74	106	111	120	149	155	156
Solubility In									
Hexane	22.73	21.11 20.66	22.52 20.19	23.12 23.87	23.86 20.70 26.62	27.64 29.12	13.35 19.16 10.82 16.94	22.73 18.32 15.44 19.11	21.78 21.69
Benzene	53.35 53.76	52.37 54.14	52.57 53.63	49.39 53.87	55.56 56.74	57.34 51.88	51.98 48.91	54.58 52.43	53.89 54.34
Toluene	52.36 55.62	53.48 53.80	51.48 54.86	55.77 57.60	56.39 58.28	56.72 57.60	52.20 52.80	54.01 55.44 49.39	53.57 55.39
Pyridine	64.32 62.62	62.08 62.19	61.91 62.19	63.87 63.96	66.34 64.57	64.83 64.64	62.63 62.68	64.35 64.39 64.27	63.04 64.95
Fraction: Average Solubility/Average Pyridine Solubility									
Hexane	0.3581	0.3361	0.3442	0.3676	0.3625	0.4384	0.2405	0.2937	0.3397
Benzene	0.8438	0.8570	0.8558	0.8077	0.8578	0.8436	0.8051	0.8316	0.8456
Toluene	0.8506	0.8633	0.8569	0.8868	0.8607	0.8830	0.8379	0.8229	0.8514
Properties of Vacuum Bottoms									
% Carbon	66.58	66.40	66.53	67.15	67.13	67.44	66.80	67.76	68.10
% Hydrogen	3.77	3.88	3.92	4.14	4.03	4.18	3.87	4.02	4.17
% Sulfur	2.96	2.89	2.62	2.83	2.72	2.77	2.89	2.58	2.33
% Ash	25.15	25.25	25.05	24.18	23.82	23.77	24.88	23.86	23.38
Fusion Point	109	120	115	136	131	133	128	122	110
Ratio H/C	0.674	0.695	0.701	0.735	0.716	0.738	0.691	0.706	0.729

Experimental Conditions

Coal: All samples are run with Powhatan Mine 5 sample LS 8275.
Nominal retention time for all samples is approximately one hour.
All samples are run in the upflow reactor SRC II mode of operation.

	62	69	74	106	111	120	149	155	156
Pressure, psig	2000	2000	2000	2000	2000	2000	1800	1800	1800
Preheater Temp.	425	425	425	400	400	400	401	401	401
Reactor Temp.	454	454	454	454	454	454	454	454	454

Slurry Formulation: For all samples the slurry consisted of 30% coal, 6% of solvent range oil boiling above 108°C at 2 mm pressure, 2.5% solvent range oil boiling above 250°C atmospheric pressure, and 61.5% of unfiltered coal solution from the process.

Figure A-1
Volatile Material in Hexane Extract

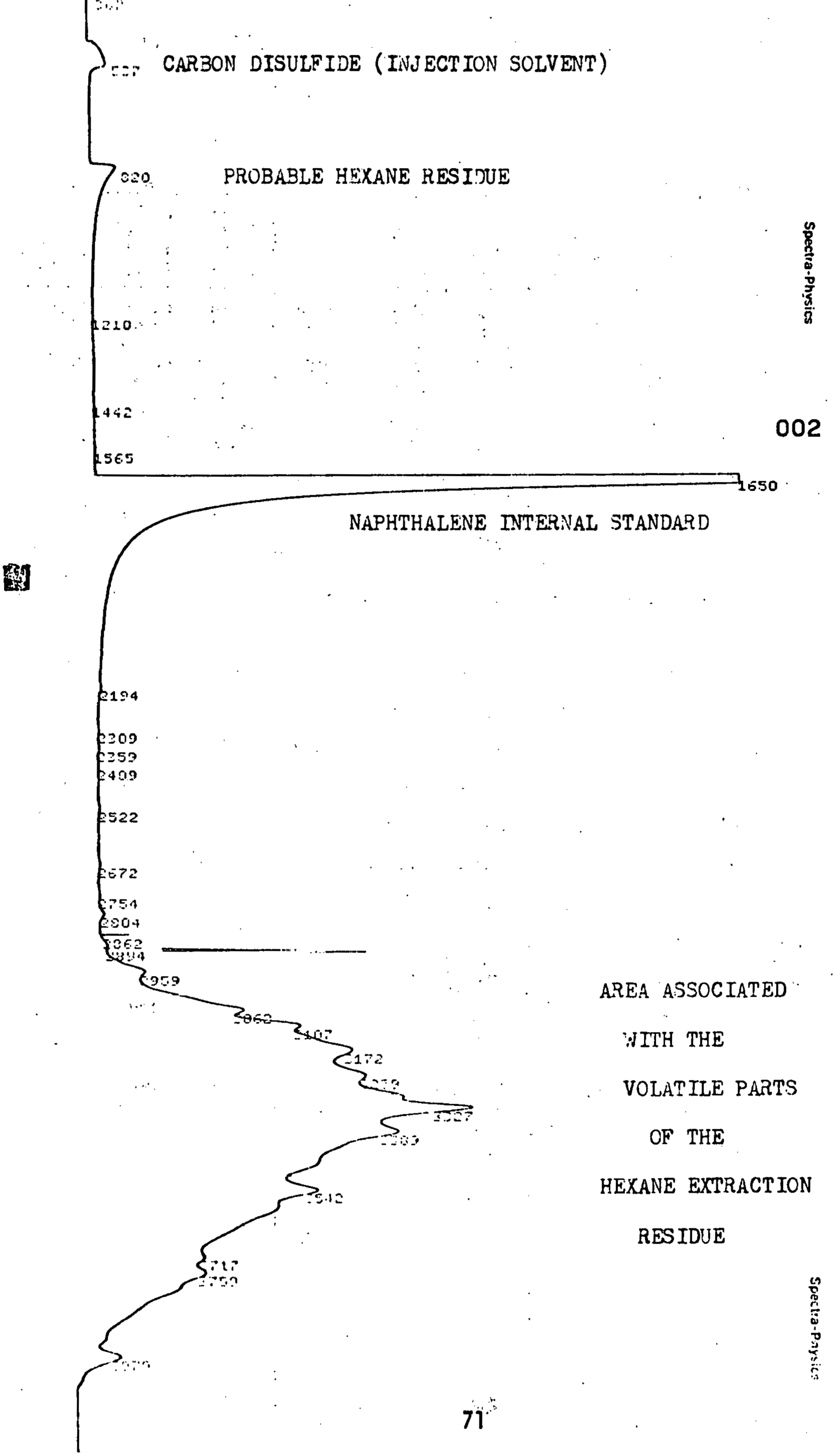


Figure A-2

Boiling Range of the Volatile Material in Hexane Extract

003

DOE 344R   62   HEX. SOLN. IN CS ~ (1)

```
*** CALIBRATION RT CC ***  1979 NOV 08 12:09:55
CHANNEL   1    RUN  43    FILE   2    METHOD  0
VIAL   9
INDEX  41    SAMPLE  40
PEAK #          AREA %    RT      AREA

   1              .416    537     1535
   2              .805    820     2970
   3            23.07    1650    85096    -
   4              .01    2194       38
   5              .009   2359       35  L
   6              .012   2522       43
   7              .015   2672       56
   8              .006   2754       23  1
   9              .053   2804      195  L
  10              .015   2862       56  1
  11              .081   2894      299  1
  12              .924   2959     3407  1
  13             3.786   3062    13964  1
  14             3.483   3107    12849  1
  15             7.711   3172    28443  1
  16             6.208   3239    22900  1
  17            14.19    3327    52326  1
  18            15.65    3389    57739
  19            21.95    3542    80952  S
  20              .177   3717      655
  21             1.057   3759     3898
  22              .4     3979     1476
TOTALS          99.99            368955
```

INTERNAL STANDARD
85096

VOLATILE MATERIAL
278,964

SIMULATED DISTILLATION RESULTS -- HEXANE EXTRACTION RESIDUE IN CARBON DISULFIDE

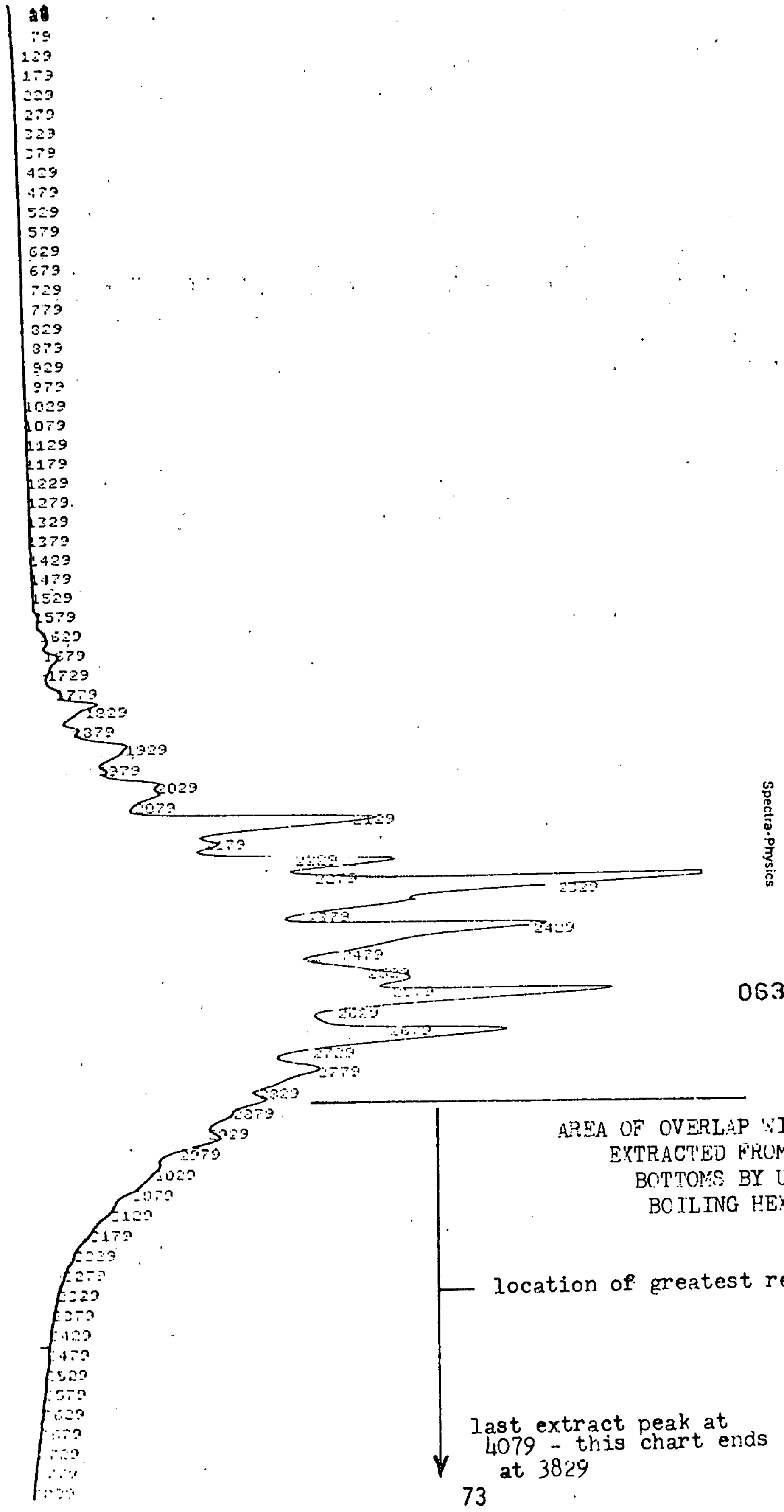
```
% OFF               TEMP (DEGREES CENTIGRADE)
```

007

```
  .5       64.63
 5         205.5
10         212.8
15         213
20         220.3
25         243.9
30         410.0
35         442.8
40         451
45         459.1
50         467.2
55         474.8
60         482.3
65         482.7
70         490.3
75         497.9
80         513
85         520.8
90         536.1
95         551.6
99.5       582.5
```

Figure A-3

Simulated Distillation Chromatogram for Run DOE 342RB-24 Process Solvent



063

AREA OF OVERLAP WITH MATERIAL EXTRACTED FROM VACUUM BOTTOMS BY USE OF BOILING HEXANE

location of greatest response in extract

last extract peak at 4079 - this chart ends at 3829

Figure A-4

Boiling Range of Process Solvent from
Run DOE 342RB-24

```
 SIMULATED DISTILLATION      1979 OCT 01 14:06:34
CHANNEL    1    RUN  99     FILE   1     METHOD  8
VIAL  13
INDEX  91    SAMPLE   1
    % OFF                    TEMP

       .5                     43.13
      5                     233.3
     10                     273.5
     15                     288.5
     20                     296.7
     25                     312.7
     30                     313
     35                     321
     40                     328.9
     45                     336.8
     50                     344.8
     55                     352.6
     60                     360.4
     65                     368.1
     70                     376
     75                     383.8
     80                     391.8
     85                     399.8
     90                     415.5
     95                     439.3
     99.5                   509.5
```

DISTILLATION RANGE FOR
RECYCLE SOLVENT FROM AN
SRC II PROCESS

APPROXIMATE IBP OF THE HEXANE
EXTRACT

Figure A-5

Simulated Distillation of
DOE 343-51 Benzene Extract

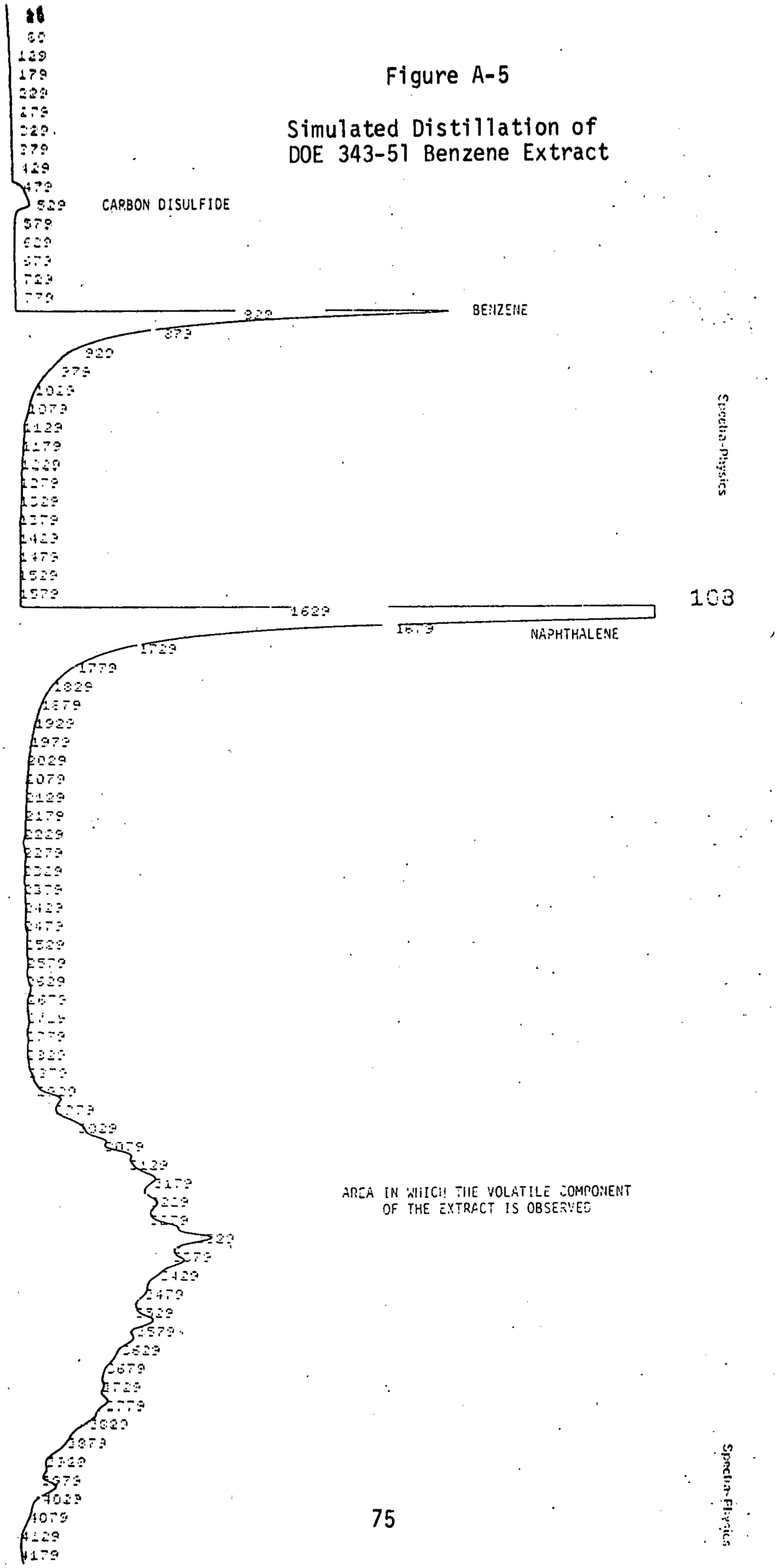


Figure A-5 Data

```
DOE 343  P-51  BENZENE SOLUBLES FROM VACUUM BOTTOMS
 SIMULATED DISTILLATION      1979 NOV 16 16:09:19
CHANNEL    1     RUN   24      FILE    1     METHOD   8
VIAL   11
INDEX   17     SAMPLE    1
PEAK #            AREA %      RT      AREA         RF

   1               <.001      14          2
   2               <.001      18          1
   3               <.001      21          2
   4                .001      24          3
   5               <.001      28          2
   6                .039     129        157
   7                .057     179        230
   8                .071     229        283
   9                .081     279        326
  10                .092     329        368
  11                .099     379        397
  12                .106     429        424
  13                .113     479        454
  14                .354     529       1416
  15                .29      579       1163
  16                .159     629        638
  17                .155     679        622
  18                .154     729        618
  19                .159     779        635
  20                .324     829       1299
  21               5.715     879      22877
  22               1.99      929       7967
  23               1.1       979       4404
  24                .733    1029       2936
  25                .504    1079       2016
  26                .39     1129       1561
  27                .322    1179       1291
  28                .295    1229       1183
  29                .271    1279       1087
  30                .265    1329       1062
  31                .253    1379       1012
  32                .233    1429        931
  33                .238    1479        952
  34                .235    1529        941
  35                .234    1579        939
  36                .427    1629       1710
  37              23.8      1679      95284
  38               4.424    1729      17709
  39               1.911    1779       7650
  40               1.126    1829       4510
  41                .771    1879       3088
  42                .59     1929       2362
  43                .482    1979       1931
  44                .408    2029       1632
  45                .359    2079       1437
  46                .33     2129       1320
  47                .307    2179       1231
  48                .289    2229       1159
  49                .259    2279       1037
  50                .273    2329       1093
  51                .255    2379       1023
  52                .267    2429       1070
  53                .275    2479       1100
  54                .289    2529       1157
  55                .293    2579       1175
  56                .303    2629       1214
  57                .342    2679       1368
  58                .304    2729       1219
  59                .313    2779       1253
  60                .295    2829       1183
  61                .3      2879       1203
  62                .406    2929       1627
  63                .797    2979       3190
  64               1.014    3029       4058
  65               1.577    3079       6312
  66               2.15     3129       8609
  67               2.608    3179      10441
  68               2.734    3229      10946
  69               2.842    3279      11378
  70               3.203    3329      12821
  71               3.614    3379      14466
  72               3.289    3429      13167
  73               2.791    3479      11171
  74               2.545    3529      10188
  75               2.653    3579      10620
  76               2.355    3629       9428
  77               2.027    3679       8114
  78               1.788    3729       7156
  79               1.782    3779       7133
  80               1.671    3829       6690
  81               1.24     3879       4964
  82                .872    3929       3489
  83                .585    3979       2343
  84                .668    4029       2675
  85                .349    4079       1396
  86                .187    4129        750
  87                .08     4179        319
  88                .112    4229        449
  89                .159    4279        636
  90               <.001    4329          2

 % OFF                    TEMP

    .5                    31.66
   5                      96.34
  10                     110.1
  15                     199.7
  20                     213.4
  25                     213.5
  30                     213.7
  35                     213.8
  40                     221
  45                     229.2
  50                     300.2
  55                     419.9
  60                     451.5
  65                     460.2
  70                     475.7
  75                     490.8
  80                     498.8
  85                     514
  90                     529.4
  95                     552.1
  99.5                   597.8
```

Figure A-6

Simulated Distillation of DOE 343-51 Toluene Extract

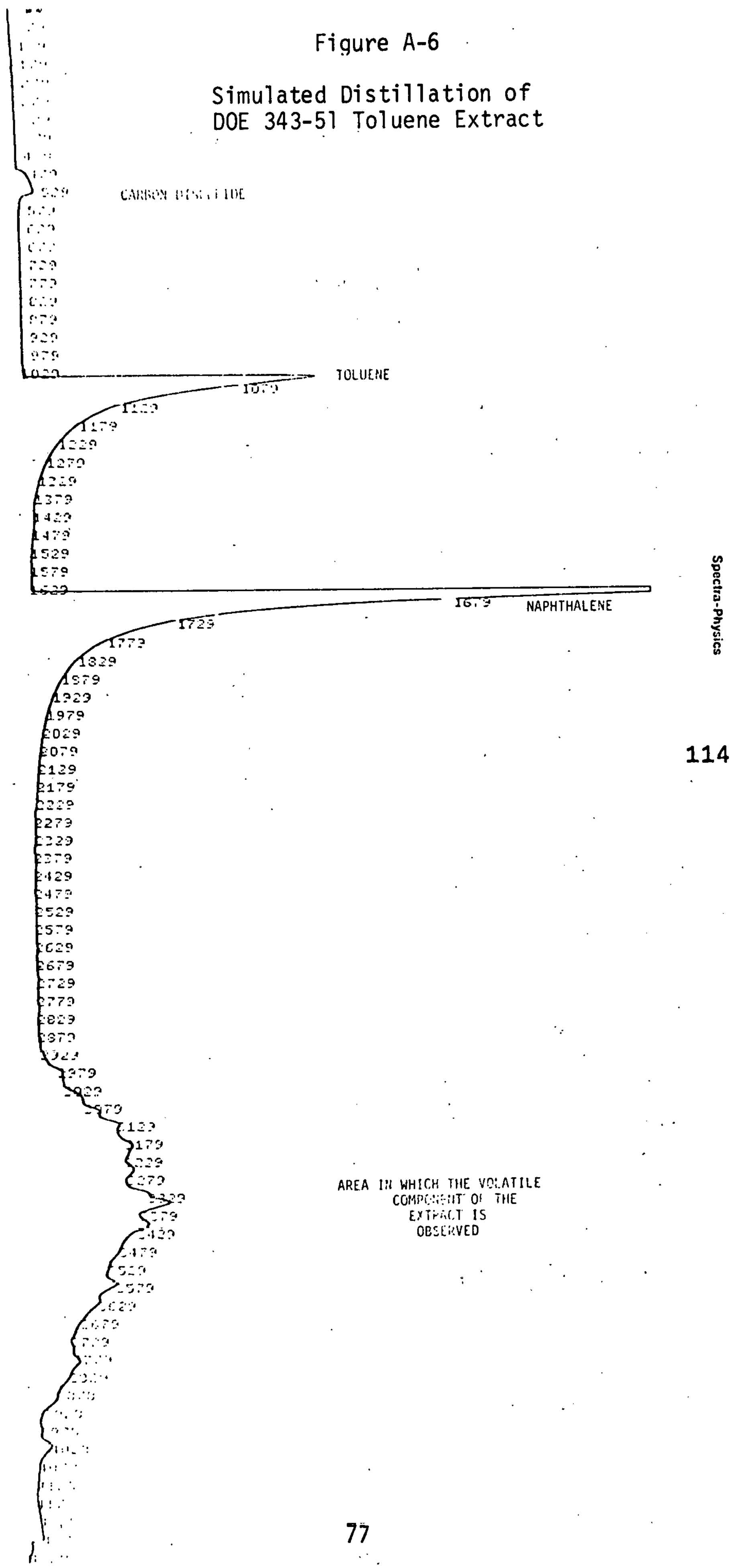


Figure A-6 Data

```
DOE 343 P-51 TOLUENE SOLUBLES
 SIMULATED DISTILLATION      1979 NOV 19 09:11:45
CHANNEL    1     RUN  25     FILE   1     METHOD  8
VIAL  12
INDEX   18     SAMPLE   1


PEAK #             AREA %     RT      AREA          KF

   1                <.001     11         1               77            2.093    3629      6210
   2                <.001     14         1               78            1.685    3679      5000
   3                 .001     18         2               79            1.295    3729      3842
   4                 .001     21         3               80            1.181    3779      3503
   5                 .001     24         4               81            1.256    3829      3728
   6                 .001     28         3               82             .929    3878      2757
   7                 .067    129       200               83             .609    3928      1806
   8                 .097    179       288               84             .257    3978       763
   9                 .12     229       356               85             .334    4028       991
  10                 .137    279       406               86             .354    4078      1049
  11                 .15     329       446               87             .160    4128       499
  12                 .163    379       483               88             .124    4178       368
  13                 .173    429       514               89             .147    4228       436
  14                 .192    479       570               90             .212    4278       629
  15                 .538    529      1597               91             .002    4328         6
  16                 .413    579      1227
  17                 .253    629       752
  18                 .249    679       739
  19                 .253    729       752
  20                 .256    779       761                 % OFF                TEMP
  21                 .265    829       786
  22                 .269    879       799                    .5                 18.9
  23                 .275    929       815                   5                  124.5
  24                 .28     979       831                  10                  132
  25                 .286   1029       849                  15                  139.7
  26                4.637   1079     13759                  20                  169.8
  27                4.506   1129     13370                  25                  214.1
  28                2.379   1179      7058                  30                  214.3
  29                1.567   1229      4649                  35                  221.7
  30                1.107   1279      3286                  40                  222
  31                 .823   1329      2442                  45                  230
  32                 .65    1379      1929                  50                  262.1
  33                 .542   1429      1610                  55                  334
  34                 .523   1479      1548                  60                  428.9
  35                 .47    1529      1395                  65                  452.8
  36                 .431   1579      1279                  70                  468.7
  37                 .422   1629      1253                  75                  476.7
  38               11.86    1679     35185                  80                  491.8
  39                7.296   1729     21648                  85                  507.1
  40                3.381   1779     10032                  90                  522.6
  41                2.097   1829      6193                  95                  545.0
  42                1.472   1879      4367                  99.5                599.8
  43                1.122   1929      3330
  44                 .894   1979      2652
  45                 .742   2029      2202
  46                 .636   2079      1886
  47                 .563   2129      1671
  48                 .506   2179      1503
  49                 .466   2229      1383
  50                 .418   2279      1240
  51                 .409   2329      1215
  52                 .386   2379      1145
  53                 .39    2429      1156
  54                 .376   2479      1115
  55                 .374   2529      1109
  56                 .373   2579      1103
  57                 .364   2629      1081
  58                 .373   2679      1106
  59                 .375   2729      1112
  60                 .376   2779      1117
  61                 .379   2829      1125
  62                 .363   2879      1076
  63                 .396   2929      1174
  64                 .601   2979      1784
  65                1.022   3029      3032
  66                1.462   3079      4337
  67                2.068   3129      6138
  68                2.585   3179      7670
  69                2.873   3229      8525
  70                2.87    3279      8518
  71                2.955   3329      8767
  72                3.626   3379     10760
  73                3.232   3429      9589
  74                2.737   3479      8122
  75                2.383   3529      7071
  76                2.249   3579      6674
```

Spectra-Physics

Figure A-7
Simulated Distillation of
DOE 343-51 Pyridine Extract

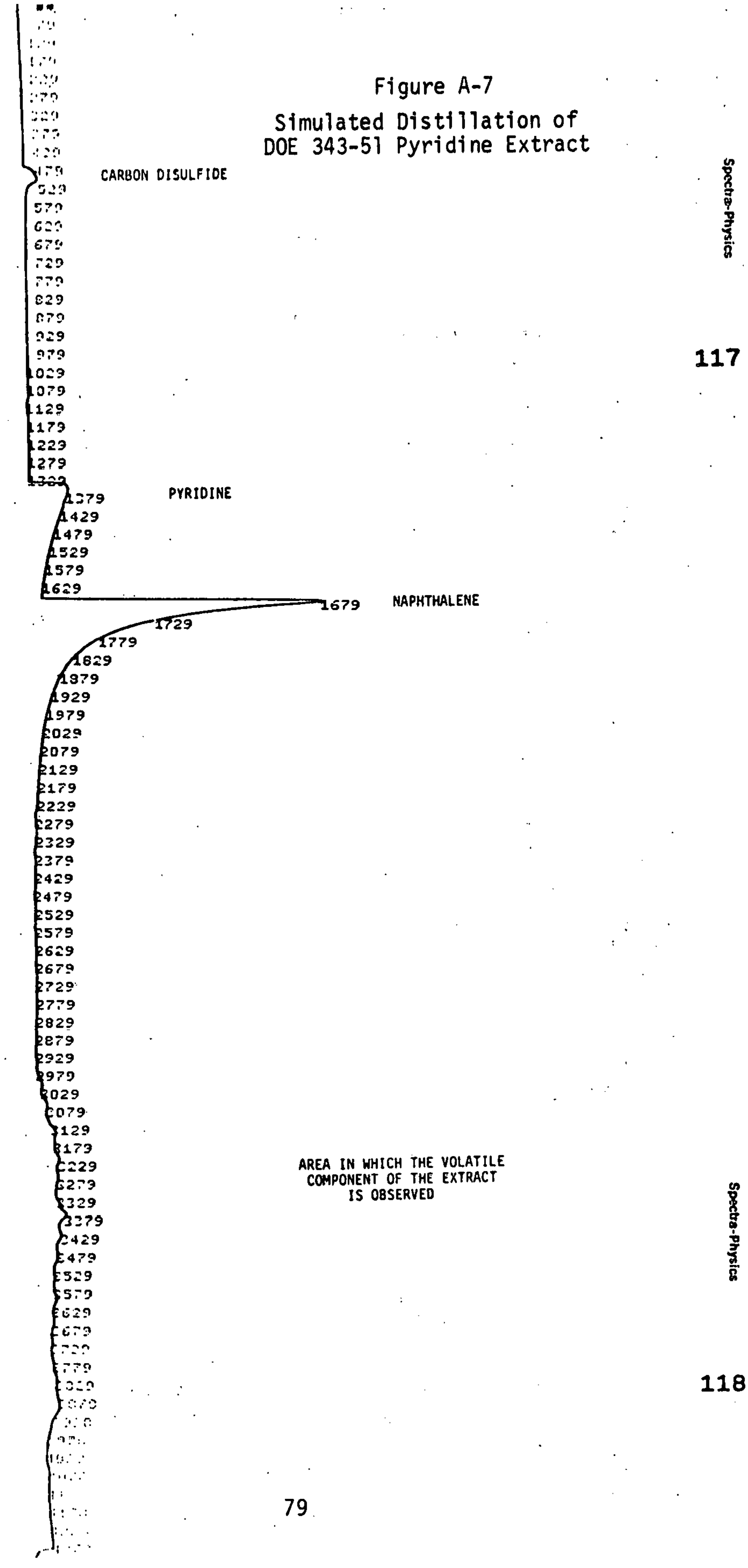


Figure A-7 Data

DOE 343 P-51   PYRIDINE SOLUBLES

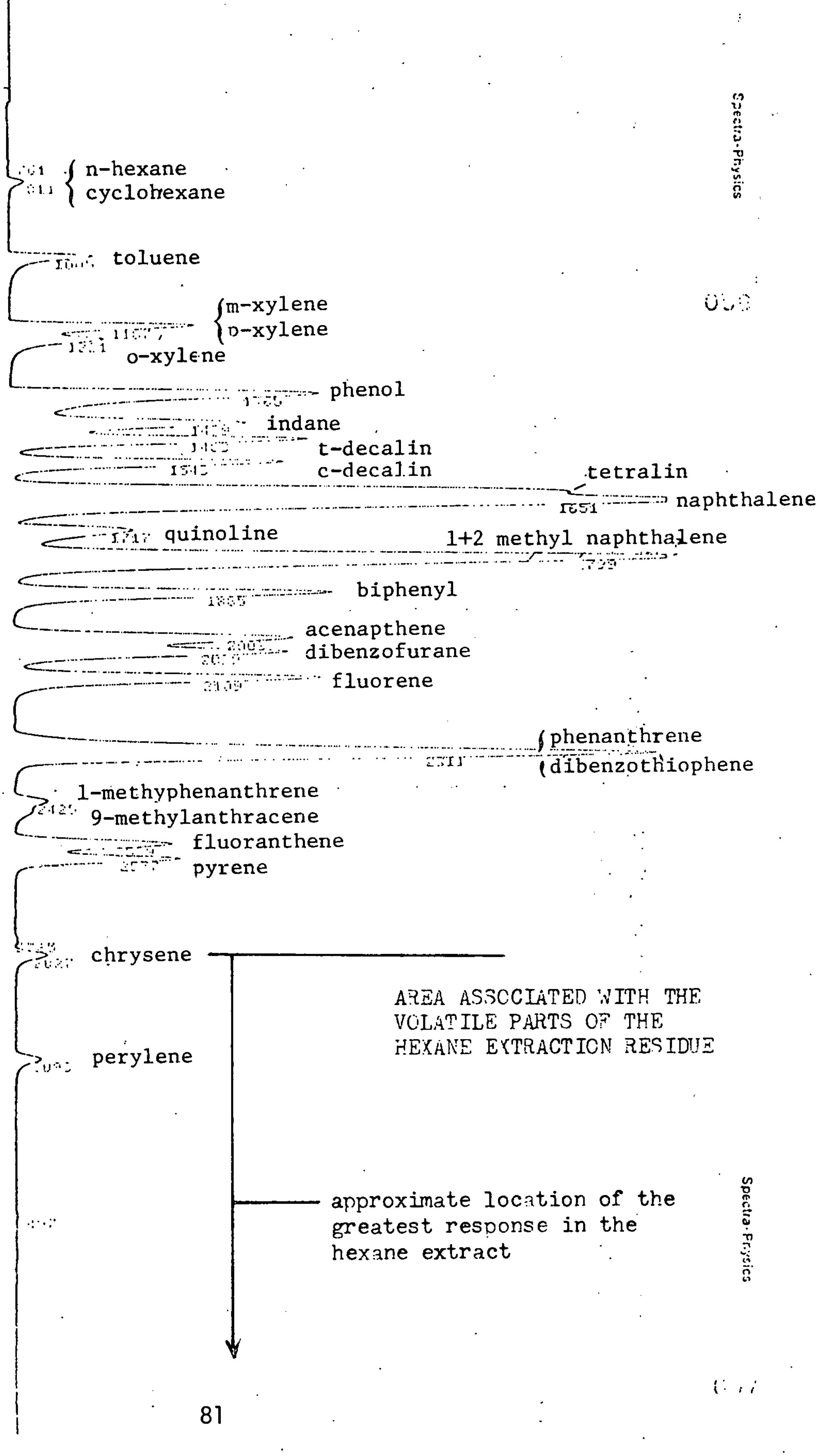
```
 SIMULATED DISTILLATION      1979 NOV 19 10:11:55
CHANNEL    1     RUN  26     FILE    1     METHOD  8
VIAL   13
INDEX   19     SAMPLE    1
PEAK  #           AREA %     RT      AREA        KF

   1               .001      11         1               49            .714    2229      868
   2               .001      14         1               50            .591    2279      719
   3               .002      18         2               51            .594    2329      723
   4               .002      21         2               52            .513    2379      624
   5               .002      24         3               53            .513    2429      624
   6               .002      28         2               54            .467    2479      568
   7               .094     129       115               55            .456    2529      554
   8               .14      179       170               56            .445    2579      541
   9               .183     229       223               57            .442    2629      538
  10               .216     279       263               58            .47     2679      572
  11               .238     329       289               59            .479    2729      583
  12               .268     379       326               60            .458    2779      557
  13               .285     429       347               61            .451    2829      549
  14               .307     479       373               62            .381    2879      464
  15               .993     529      1208               63            .351    2929      427
  16               .505     579       614               64            .363    2979      441
  17               .432     629       525               65            .613    3029      745
  18               .419     679       510               66            .858    3079     1043
  19               .42      729       511               67           1.074    3129     1306
  20               .426     779       518               68           1.511    3179     1838
  21               .426     829       518               69           1.626    3229     1978
  22               .435     879       529               70           1.648    3279     2004
  23               .434     929       528               71           1.541    3329     1874
  24               .44      979       535               72           1.904    3379     2316
  25               .445    1029       541               73           1.78     3429     2165
  26               .451    1079       549               74           1.61     3479     1958
  27               .438    1129       533               75           1.433    3529     1743
  28               .427    1179       519               76           1.303    3579     1584
  29               .466    1229       567               77           1.359    3629     1652
  30               .472    1279       574               78           1.215    3679     1478
  31               .479    1329       583               79           1.1      3729     1338
  32              2.205    1379      2681               80           1.089    3779     1324
  33              2.775    1429      3375               81           1.272    3829     1547
  34              2.358    1479      2868               82           1.384    3878     1683
  35              1.966    1529      2391               83           1.41     3928     1715
  36              1.65     1579      2006               84            .918    3978     1116
  37              1.396    1629      1697               85            .658    4028      800
  38              4.275    1679      5199               86            .656    4078      798
  39             13.68     1729     16631               87            .727    4128      884
  40              6.595    1779      8020               88            .719    4178      875
  41              4.036    1829      4903               89            .768    4228      934
  42              2.787    1879      3389               90            .872    4278     1061
  43              2.068    1929      2515               91            .006    4328        8
  44              1.628    1979      1380
  45              1.304    2029      1586
  46              1.082    2079      1316
  47               .928    2129      1128
  48               .804    2179       978
                                                           % OFF                  TEMP

                                                              .5                  12.24
                                                             5                    88.45
                                                            10                   169.4
                                                            15                   184.6
                                                            20                   199.9
                                                            25                   214.3
                                                            30                   221.8
                                                            35                   222
                                                            40                   222.1
                                                            45                   229.9
                                                            50                   237.9
                                                            55                   253.7
                                                            60                   285.5
                                                            65                   349.5
                                                            70                   436.8
                                                            75                   468.7
                                                            80                   491.7
                                                            85                   515.
                                                            90                   545.0
                                                            95                   576.5
                                                            99.5                 622.8
```

Figure A-8

Simulated Distillation Chromatogram Showing the Location of Known Compounds



APPENDIX B

REACTOR CHARACTERIZATION BY RESIDENCE TIME DISTRIBUTION ANALYSIS

INTRODUCTION

Residence time distribution (RTD) measurements were used to characterize the macromixing in five reactor configurations. Two of these reactors, the single tube reactor and modified GU 5 reactor, are shown in Figures 17 and 18, respectively, in the body of the report. The two configurations of the continuous stirred tank reactor are shown in Figure 16. One of these configurations had one impeller and no baffles and the other had three impellers and baffles. The final reactor investigated was the standard DOE 1 configuration.

Two mathematical models were used to correlate the RTD measurements and the results are presented in terms of Holdback Numbers for all reactors and Peclet Numbers for the tubular reactors (GU 5, single tube and DOE 1).

THEORY

The term Holdback, defined by Danckwerts[1], describes the fraction of the fluid flowing through a reactor that spends more or less than the mean residence time in the reactor. This parameter is useful for describing reactors which are highly backmixed. Mathematically, Holdback is defined by the equation:

$$H = \frac{\nu}{V}\int_{\theta=0}^{\frac{V}{\nu}} F(\theta)d\theta \qquad (1)$$

where H = Holdback
ν = volumetric flow rate
V = volume of the reactor
θ = time
$F(\theta)$ = fraction of material that has been in the system for less than θ (resulting from a step change in input)

Holdback Numbers range from $H=0$ for ideal plug flow to $H=1/e$ for a continuous stirred tank reactor (CSTR) with intermediate values representing varying degrees of backmixing. The numbers may also extend to a maximum value of $H=1$ which represents a dead reactor in which no flow occurs in the bulk of the fluid (total bypassing). Intermediate values between $H=1/e$ and $H=1$ represent an increasing fraction of dead space (and bypassing) in the reactor.

The Peclet Number is useful for describing deviations from ideal plug flow in tubular reactors and is defined as follows:

$$N_{Pe} = \frac{uL}{D_E} \qquad (2)$$

where N_{Pe} = Peclet Number
u = linear flow velocity
L = characteristic length
D_E = axial dispersion coefficient

For tubular reactors, the dispersion (dispersed plug flow) model is often applied to determine the Peclet number. Based on the E curve*, the following equation is applied to closed vessels with large extents of dispersion, and open vessels with large extents of dispersion in which measurements are made by the "mixing cup" method (see Levenspiel[2]):

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = 2\frac{D_E}{uL} - 2\left(\frac{D_E}{uL}\right)^2 (1 - e^{\frac{-uL}{D_E}}) \tag{3}$$

where σ_θ^2 = E curve variance
σ^2 = variance
$\bar{t}$ = mean residence time

E curves are related to F curves by the relation

$$F(\theta) = \int E(\theta)d\theta \tag{4}$$

Therefore, in theory, determination of one curve allows calculation of the other. In practice, however, it must be realized that since the E or F curves are determined experimentally, graphical integration or differentiation may increase the error.

The general relationship for the effect of gas flow rate and diameter on the axial dispersion coefficient in a two-phase system is:

$$D_E \propto Vg^{0.3} D^{1.4} \tag{5}$$

where D_E = axial dispersion coefficient
Vg = superficial gas velocity
D = column diameter

Peclet Numbers may then be estimated for all of the tubular reactors at the same gas flow rate.

EXPERIMENTAL

E and F curves were determined experimentally using the two apparatuses shown in Figures B-1 and B-2. Two-phase flow was used to approximate the real conditions of slurry and hydrogen flow. Acetone was used for the liquid phase and air for the gas phase.**

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* The E curve represents the fraction of material that has been in the reactor for less than time θ, based on an impulse injection of tracer material.

** It has been shown that axial dispersion is only a weak function of fluid properties.

The procedure for an E curve experiment was to first establish acetone and air flow at the desired rates and then inject a pulse of dyed acetone (crystal violet indicator was used as the dye) at time = 0. Fifteen to 20 ml samples were collected from the outlet stream at regular time intervals, every 3 or 5 minutes depending on the experiment, for a specific time duration, either 30 or 60 seconds.

The outlet flow between samples was collected and measured volumetrically to verify the flow rate of liquid through the reactor. The optical densities of the samples were measured on a Bausch and Lomb Spectronic 20 colorimeter at a wavelength of 575 nm (the strongest peak for crystal violet). E curve experiments were run with the modified GU 5, single tube and DOE 1 reactors.

F curve experiments differed from E curve experiments only in that a second vessel containing dyed acetone was connected to the feed line with a three-way valve. At time=0, the valve was switched from clear acetone to dyed acetone for delivery to the reactor (a step change). F curve experiments were performed for the two configurations of the 1 liter stirred autoclave reactor.

The optical densities were normalized for the tubular reactor and stirred autoclave runs by dividing each measured result by the optical density associated with the characteristic concentration of dye. These dimensionless values provided the ordinate for the E and F curves. The abscissas for the curves were determined using the summation of the measured flows through the reactor, $\nu\theta$, (corrected to provide a continuous summation over time), and dividing this quantity by V, the reactor volume.

Holdback Numbers were determined from the F curves by computing the areas under the curves from $\nu\theta/V=0$ to $\nu\theta/V=1$. For the two stirred autoclave runs this was accomplished by first fitting the data to an exponential function and integrating the mathematical expression from 0 to 1. The equation for the stirred autoclave without baffles was:

$$H = \int_0^1 (1-0.98e^{1.17x})dx$$

and for the configuration with baffles

$$H = \int_0^1 (1-1.08e^{1.31x})dx.$$

The areas under the curves for the tubular reactors were determined by physically cutting out the areas under the curves on graph paper, weighing them, and dividing by the weight of a unit area.

Peclet Numbers were determined using a discrete approximation (2):

$$\sigma^2 = \frac{\Sigma\, t_i\, C_i}{\Sigma\, C_i} - \left[\frac{\Sigma\, t_i\, C_i}{\Sigma\, C_i}\right]^2 \qquad (6)$$

where t_i = time at i

C_i = concentration (or optical density) at i

and the equation for mean residence time

$$\bar{t} = \frac{V}{v}$$

The values from these two equations were then used in equation 3 to determine the Peclet Numbers.

RESULTS

F curves for all reactor configurations considered are compared to ideal curves in Figure B-3. The curves for the two stirred autoclave configurations are virtually the same, while the GU 5 more closely approximates plug flow than the single tube reactor. It is also noted that the DOE 1 reactor exhibits a large amount of backmixing.

Figure B-4 shows the E curves for the GU 5 configuration, single tube reactor and the DOE 1 reactor. Again, the GU 5 shows the greatest degree of plug flow (the least tailing of the Gaussian distribution). The DOE 1 reactor displays so much tailing that it approaches the exponential decay of a CSTR.

Holdback and Peclet Numbers are shown in Table B-1 for the various reactors. The Holdback Numbers for the stirred autoclaves are larger than 1/e (0.368) which indicates some dead space in the reactors. The CSTR configuration with baffles and three impellers shows less dead volume than the CSTR without baffles, as expected. It should be noted that the improvement in holdback from adding two impellers and baffles to the reactor is rather small (from H = 0.422 to 0.398).

The Holdback Numbers show that the single tube reactor gives conditions which are more plug flow than the GU 5 reactor. This contradicts the results shown by Peclet Numbers and may be due to the fact that the F curves for the modified GU 5, single tube, and DOE 1 reactors were determined by numerical methods from the E curves rather than by experiment which may be less accurate.

There was also a significant difference in flow rates and nominal residence times as evidenced by the liquid linear viscosities and residence times shown in the table. The disparity persists even when the Peclet numbers are adjusted for mixing caused by different gas flow rates through the liquid.

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TABLE B-1

Results of the Residence Time Distribution Studies

Reactor	Peclet Number[1] N_{Pe}	Holdback[2] Number H	Superficial Liquid Velocity	Superficial Gas Velocity	Adjusted[3] Peclet Number	Nominal Residence Time	Derived Mean Residence Time	Ratio Nominal/Mean Residence Time
Modified GU5 L/D - 211	4.35	0.290	0.09 cm/sec	0.99 cm/sec	4.35	0.987 hr	0.967 hr	1.02
Single Tube L/D = 106	1.94	0.275	0.14 cm/sec	0.88 cm/sec	1.87	0.344 hr	0.358 hr	0.961
DOE 1 L/D = 56	1.61	0.343	0.05 cm/sec	0.44 cm/sec	1.26	0.587 hr	0.853 hr	1.16
1 liter Autoclave no baffles 1 impeller	--	0.422						
1 liter Autoclave baffles 3 impellers	--	0.398						

1. Plug Flow, $N_{Pe} = \infty$; Completely Backmixed, $N_{Pe} = 0$
2. Plug Flow, H = 0; Completely Backmixed, H = 0.368; Completely Bypassed, H = 1
3. Estimated Peclet Number for a superficial gas velocity of 0.99 cm/sec

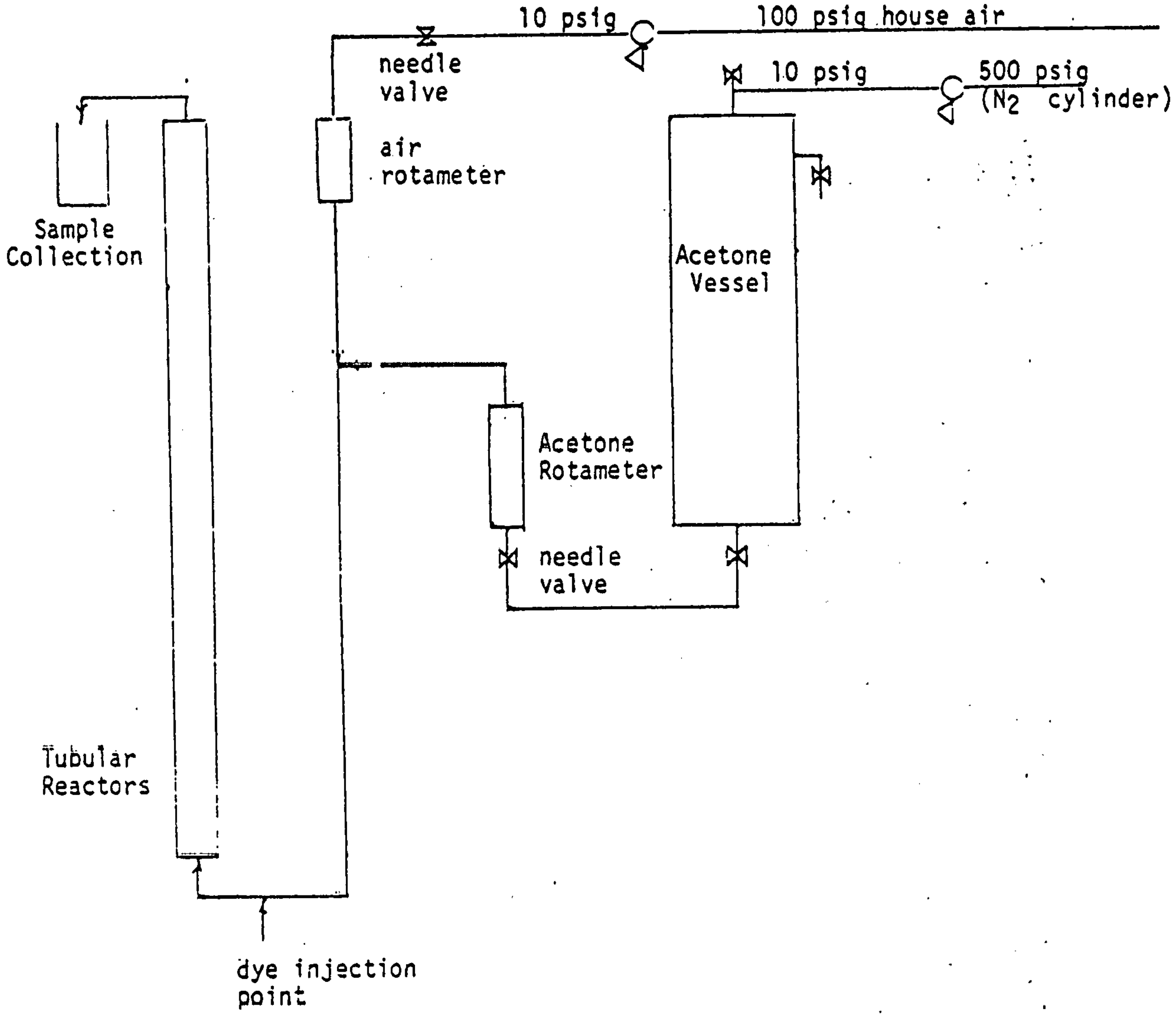


Figure B-1 Experimental Apparatus - E Curve determination

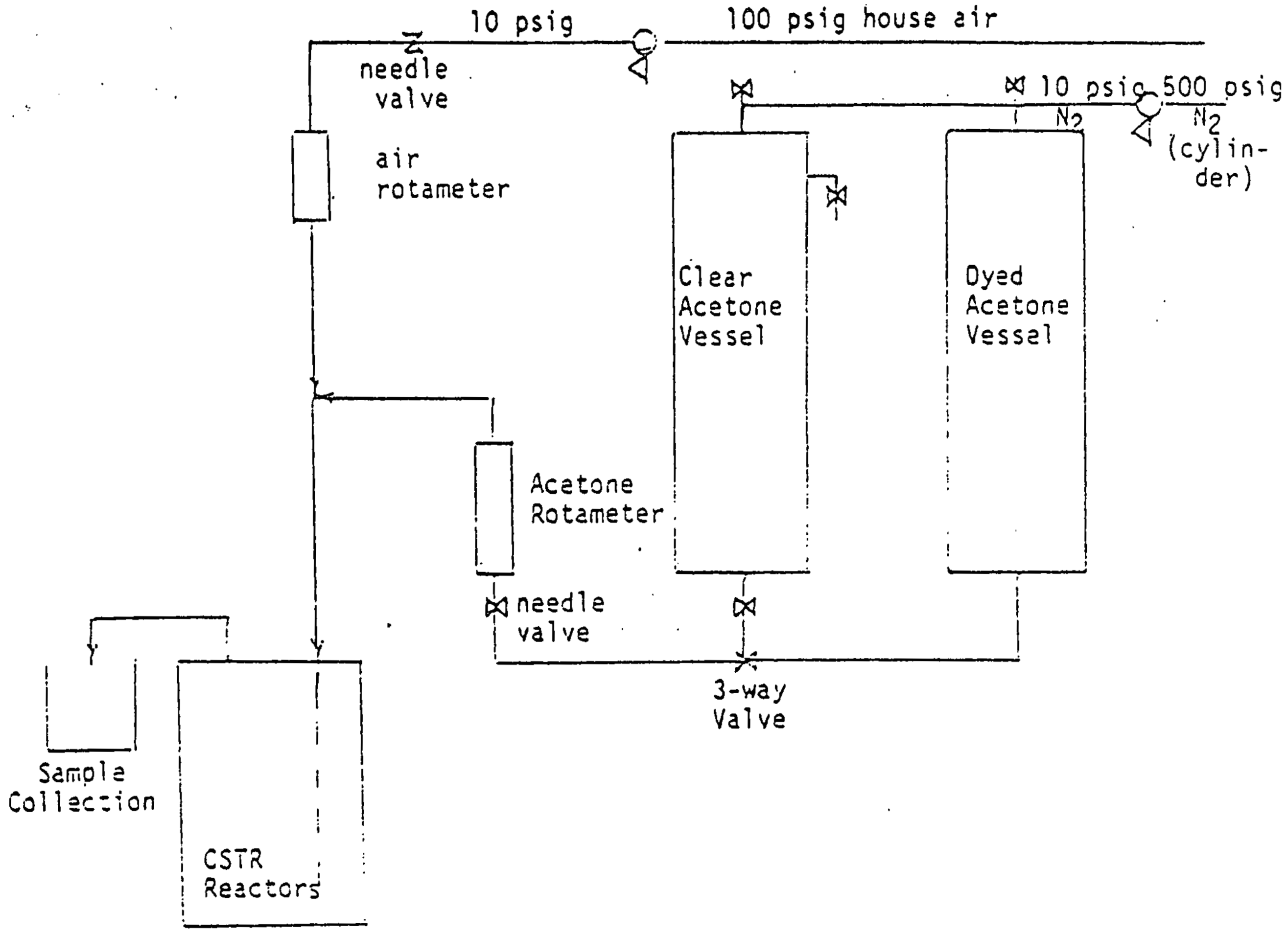


Figure B-2 Experimental Apparatus - F curve determination

FIGURE B-3

F CURVES. COMPARISON OF CURVES FOR 1 LITER STIRRED AUTOCLAVE, DOE 1, SINGLE TUBE AND MODIFIED GU 5; ALSO IDEAL CURVES

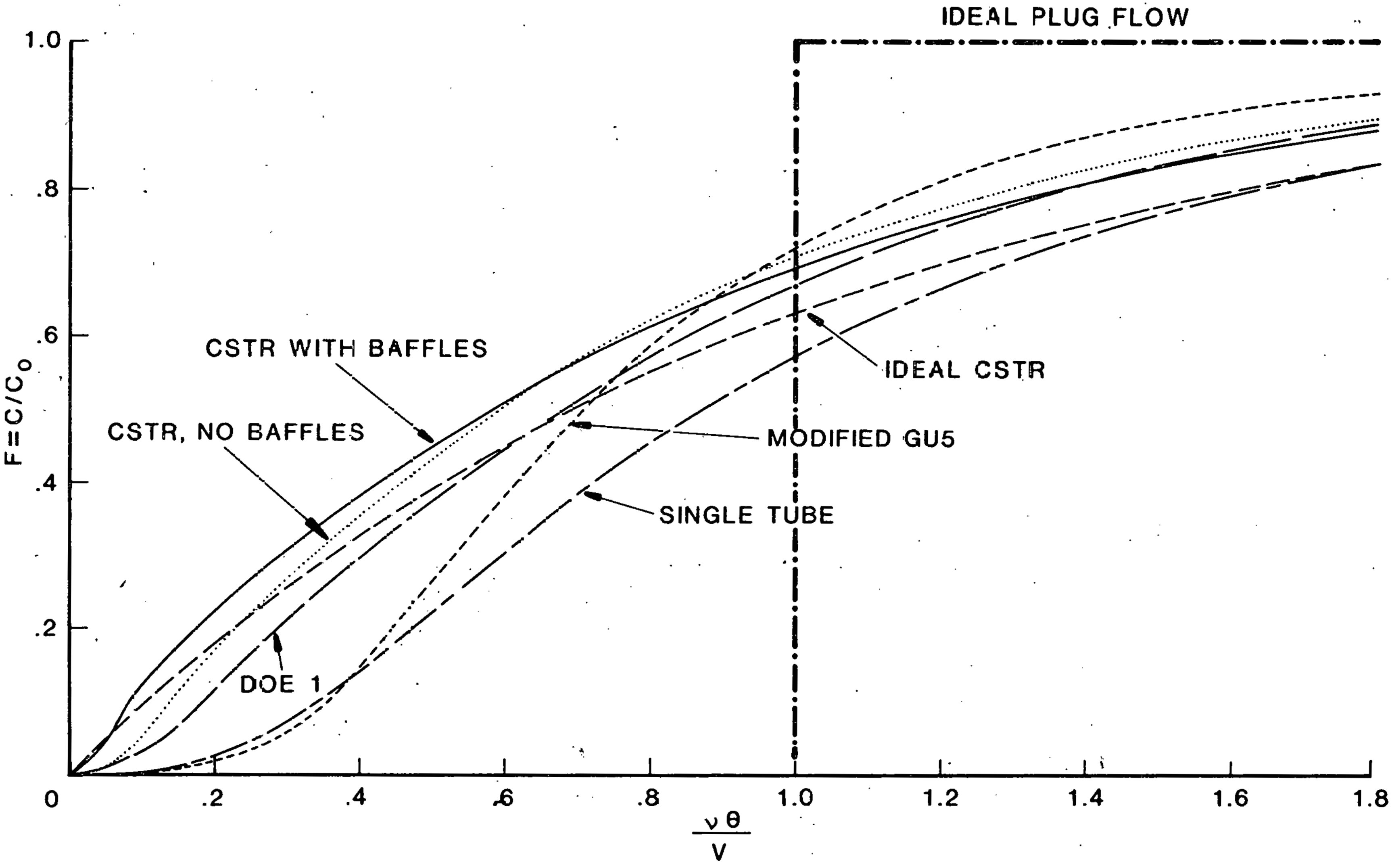
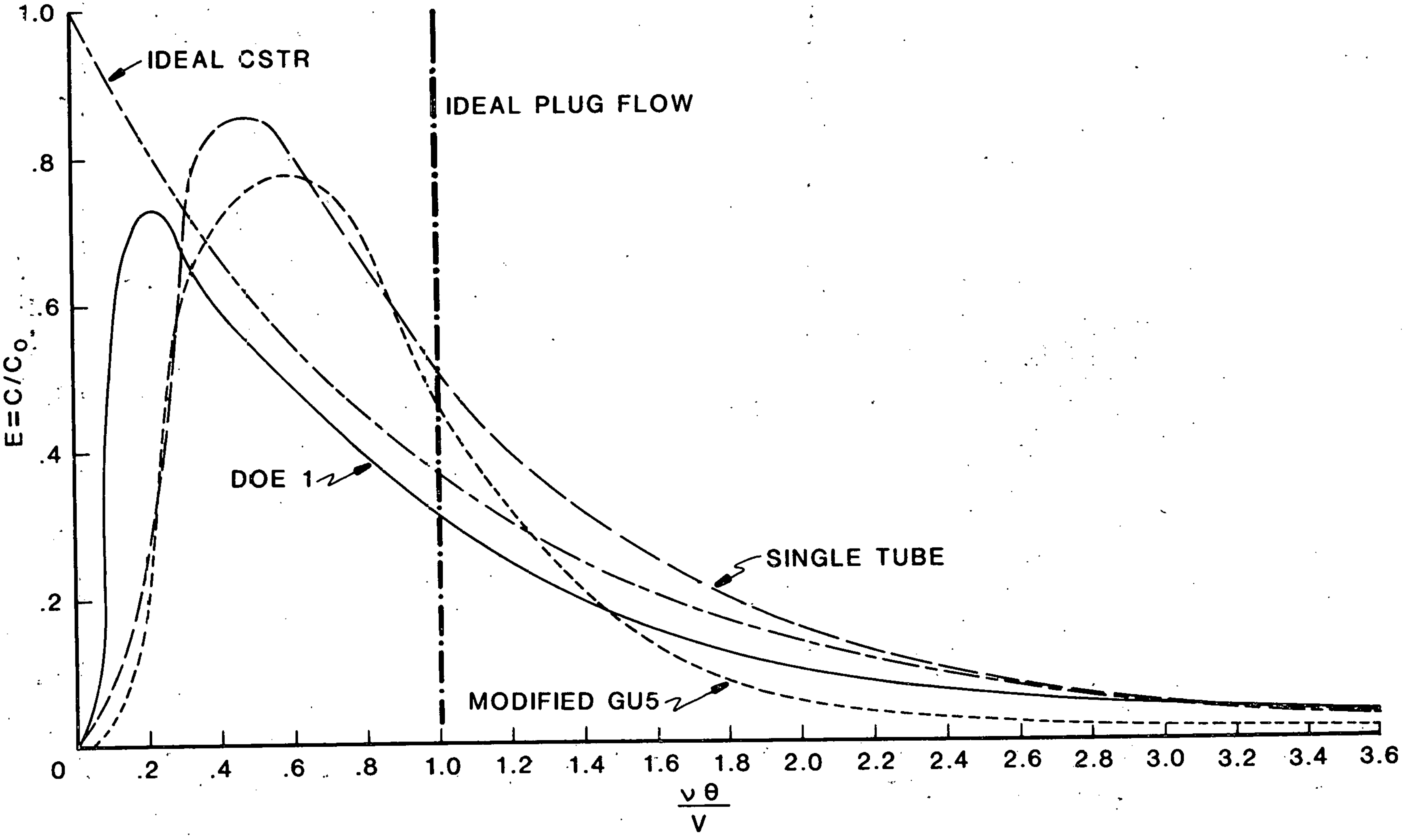


FIGURE B-4

E CURVES. COMPARISON OF MODIFIED GU 5, SINGLE TUBE, AND DOE 1; ALSO IDEAL CURVES



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