

DIRECT LIQUEFACTION

WILSONVILLE CC-ITSL PROCESS DEVELOPMENT

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LIQUEFACTION CONTRACTORS' REVIEW MEETING
U. S. DEPARTMENT OF ENERGY
PITTSBURGH, PENNSYLVANIA

SEPTEMBER 3-5, 1991

ABSTRACT

The results of the two most recent runs completed at Wilsonville are presented. In Run 260, the effects of thermal/catalytic and catalytic/thermal staging on solids buildup were studied in the liquefaction of Black Thunder mine subbituminous coal. Also, some design changes were made to reduce solids buildup in the interstage separator and other process lines. Although no solids buildup was observed in the interstage separator, operational problems due to inadequate vapor-slurry separation and solids buildup in process lines resulted in termination of thermal/catalytic operation. An "all-distillate" product was obtained in catalytic/thermal mode with a distillate yield of about 60 wt% maf coal. The catalytic first stage appeared to have mitigated the solids buildup between the reactors, but some solids were observed in the thermal second stage. This run indicated the need for pretreatment of low-rank coals to remove some mineral components that contribute to solids buildup. Also, the presence of a transition metal catalyst in both reactors may help reduce the solid deposits, and tests are being performed in Run 262 using a dispersed molybdenum catalyst.

In Run 261, a Ni-Mo bimodal catalyst (EXP-AO-60, 1/16" cyl. extrudate) was tested for its activity and physical integrity. These tests were made in low/high temperature staging (790/810°F) with Illinois #6 coal from Burning Star #2 mine. At a total catalyst replacement rate (CRR) of 6 lb/ton of coal an "all-distillate" product was obtained at a space velocity of 67 lb coal/hr/ft³ cat. Moreover, the resid concentration in process solvent was only 38 wt% which indicated the potential for further improvements. The significance of higher CRR in improving reactor efficiency was demonstrated with EXP-AO-60 catalyst. The physical strength of EXP-AO-60 catalyst appeared to be satisfactory at the end of this test. In additional tests with Criterion 324 unimodal catalyst, although reasonable yields were obtained at a space velocity of 61 lb coal/hr/ft³ cat and 6 lb/ton of CRR, the process performance was not satisfactory with respect to slurry viscosity and space velocity at lower CRR. The new resid circulation system that could reduce the time required to obtain steady-state operation and possibly reduce resid degradation was briefly tested.

INTRODUCTION

The results of the two most recent runs conducted at Wilsonville are presented. In Run 260, tests with the Black Thunder mine subbituminous coal were useful in identifying and interpreting the operational problems associated with the liquefaction of low-rank coals. The near-term studies with subbituminous coals would be made based on Run 260 with the primary objective of improving the operating efficiency. In Run 261, a new bimodal catalyst, EXP-AO-60 was tested for its activity and physical strength. Using Illinois No. 6 coal, high space velocity operation was achieved with resid extinction in this run with the EXP-AO-60 catalyst.

THE WILSONVILLE PROGRAM

The current program at the Advanced Coal Liquefaction Research and Development Facility is sponsored by:

- U. S. Department of Energy
- Electric Power Research Institute
- Southern Company Services
- Amoco Corporation

This facility is being operated by Southern Clean Fuels, a division of Southern Electric International, Inc. Kerr-McGee Corporation and Hydrocarbon Research, Inc. are participating in the program. Coal liquefaction has evolved from a simple, single-stage process into the present, advanced, close-coupled integrated two-stage liquefaction (CC-ITSL) configuration that is being developed for producing high-quality liquid fuels. The present configuration primarily consists of two ebullated bed reactors (designed by Hydrocarbon Research Inc.) in series followed by Kerr McGee's Residuum Oil Supercritical Extraction - Solids Rejection (ROSE-SRSM) unit. (For a simplified process flow diagram of catalytic/catalytic operation, see Figure 1.) A more detailed process description was reported in the literature [1]. Considerable progress has been made during the past five years in the development of the CC-ITSL configuration at Wilsonville. In addition to expanding the database by testing new coals of different ranks and seams with unimodal and bimodal catalysts, various new concepts and processing methods have been effectively demonstrated.

RUN 260

The major objectives of Run 260 were:

- to evaluate thermal/catalytic vs. catalytic/thermal operation with respect to solids buildup in the process lines;
- to determine the effect of a smaller interstage separator on solids buildup in the separator; and,
- to determine the distillate product end point with vacuum flash recycle.

The Black Thunder mine subbituminous coal from Powder River Basin was used in Run 260 because it was found to be a good liquefaction feedstock in Run 258. A typical analysis of this coal is given in Table 1. The initial tests were made with thermal-first stage ('thermal' refers to operation without a supported catalyst) and catalytic-second stage. Criterion 324, an alumina supported Ni-Mo unimodal catalyst, was used in the second stage (300 lb) at a replacement rate of 3 lb/ton coal. The catalyst properties are given in Table 2. In order to maintain a reasonable catalyst activity, some aged, that is deactivated, catalyst in the reactor is usually replaced periodically at Wilsonville with fresh, sulfided catalyst at a specified rate. This operation is referred to as catalyst replacement. Iron oxide along with a sulfiding agent was introduced as a slurry catalyst before the preheater. Typical operating conditions used in this run are given in Table 3.

INTERSTAGE SEPARATOR

In Run 258, significant solid deposits were observed in the interstage separator [2]. It was thought that the low slurry velocity in the separator was probably contributing to solids buildup in the separator. Thus, in Run 260, tests were made in periods 260A and 260B with a new interstage separator that had a smaller diameter. Indeed, possibly due to higher slurry velocity, no significant solid deposits were observed in the interstage separator; however, because of reduced slurry residence time in the separator, adequate vapor-slurry separation could not be achieved. Individual stage yields could not be determined accurately and interstage separation was discontinued after period 260B in this run. The pressure drop between the reactors started increasing during this time; later it was evident that solids were building up in the transfer line between the first stage and the interstage separator.

THERMAL/CATALYTIC

In the material balance period 260C, the coal feed rate was 251 lb mf coal/hr and the first and second stage temperatures were 825°F and 790°F, respectively. (Each period represents an average of daily material balance yields for about five days.) The overall coal conversion and C₄+ distillate yield were about 94-95 wt% and 54 wt% (maf coal), respectively. A significant amount of excess resid was produced (7.5 wt%, see Table 4). The pressure drop between the reactors continued to increase more or less throughout the thermal/catalytic operation. Thus, this operation was terminated at the end of period 260C.

CATALYTIC/THERMAL

The purpose of this test was to study the benefits of placing a supported catalyst in the first stage. The presence of a supported catalyst would improve the hydrogenation conditions, and thus could produce a material that is less prone to regressive reactions and coking in further stages of liquefaction. The Criterion 324 catalyst was placed in the first stage and the second stage was

operated thermally starting from period 260D. In this period, the coal feed rate, slurry composition, and catalyst replacement were similar to period 260C. The catalytic first stage temperature was 790°F and thermal second stage temperature was 774°F. In period 260D, compared to period 260C:

- distillate yield was significantly higher.
(59.8 wt% in 260D vs. 54.1 wt% in 260C)
- C₁-C₃ gas yield was significantly lower.
(5.6 wt% in 260D vs. 11.2 in 260C)
- TSL coal conversion was lower
(88.5 wt% in 260D vs. 94.2 wt% in 260C)

Although the second stage temperature was lower than the target of 825°F, good distillate yield was obtained; however, the coal conversion was lower. Thus, the ash-free solid product was higher and resid yield was lower. In general, there seems to be a significant improvement in performance when the catalyst was present in the first stage possibly due to the following reasons:

- The hydrogen partial pressures are usually higher in the first stage than second stage. As the stream flows continuously from one stage to another, there would be pressure drop, and thus, the second stage pressure would be less than the first stage. When the catalyst was present in the first stage hydrogenation would be more effective because of higher hydrogen partial pressures.
- The first stage resid concentration would be higher than that in the second stage. When the catalyst was present in the first stage, it would improve resid catalytic conversion kinetics.

COAL CONVERSION

The coal conversion in Run 260 was in the range of 94-95 wt% maf coal in the thermal/catalytic mode and 86-89 wt% maf coal in catalytic/thermal mode. Although the thermal reactor volume was the same in both modes, the operating temperatures were different which contributed to differences in coal conversions. It may be noted that in Run 258, at high space velocities, the coal conversion was in the range of 89-93 wt%. As shown in Figure 2, over a wide range of catalytic space velocities, the coal conversions remained in the same range, i.e., 86-95 wt% despite the presence of externally added iron catalyst. A mathematical correlation is used at Wilsonville to calculate "thermal reaction severity" which is a function of space velocity, reactor temperature, and hydrogen partial pressure. A description of the thermal reaction severity was reported elsewhere [3]. As shown in Figure 3, this severity correlated reasonably with coal conversion. A plot of (resid+coal) conversion is also given as a function of thermal reaction severity in Figure 4. As shown in this figure, despite lower thermal severity in the catalytic/thermal mode, somewhat similar (resid+coal) conversions could be observed. Thus,

it appeared that the presence of catalyst in the first stage significantly improved the (resid+coal) conversion as discussed previously.

DISTILLATION SYSTEM AND PRODUCT QUALITY

A schematic diagram of the distillation scheme used in Run 260 is shown in Figure 5. The first-stage products were sent to an interstage separator to remove hydrogen, light gases and distillate. This distillate was then separated as V164 stream. The second-stage products were also sent to another high-pressure separator (to remove light gases and hydrogen) and then to an atmospheric flash unit (to remove distillate as overhead stream, V1078). The interstage separator overhead distillate stream and the atmospheric flash overhead stream, both containing mostly a distillate that was below 850°F, were combined as feed to T105 atmospheric distillation column. The overhead stream of the T105 column, containing mostly light distillate (below 500°F), was one of the two major liquid product streams. The bottoms of T105 was sent to a vacuum distillation column.

In runs prior to 259 and in periods 261A and 261B, a major portion of the atmospheric flash bottoms, which usually contained a considerable amount of distillate that was below 650°F, was recycled for process solvent make-up. The remaining fraction used to go to a vacuum flash unit that separated the distillate from the resid, unconverted coal, and ash. In Run 260, all the atmospheric flash bottoms was sent to the vacuum flash unit and the vacuum flash overhead stream (V1072) was sent to the T102 vacuum distillation column. As shown in Figure 5, the T105 bottoms and V1072 stream were combined as feed to T102 column. The T102 column overhead stream was the second major liquid product stream (mostly below 800°F). The T102 column bottoms constitutes the heavy gas oil portion of the recycle solvent.

The overall distillate properties are given in Table 5 for periods 261C and 261D (a representative sample for analysis was obtained by blending T105 and T102 distillate products). As shown in this table, the product qualities with respect to elemental analysis look similar in thermal/catalytic and catalytic/thermal modes. The carbon and hydrogen contents are high and heteroatom contents were low in these periods. The distillate product end points, as determined by gas chromatographic simulated distillation, in periods 260C and 260D were 778 and 723°F, respectively.

SOLIDS BUILDUP

To reduce solids buildup, in addition to testing thermal/catalytic and catalytic/thermal modes of operation, and the new interstage separator, some minor modifications were also made. For example, the transfer line length between the first stage outlet and interstage separator was reduced and heat losses in this line were minimized by heat tracing the line. The heat tracing would help maintain the slurry at higher temperatures, thus preventing solids deposition. However, during the thermal/catalytic tests, after

about four weeks of operation, both the pressure drops, i.e., between the first stage and the interstage separator and between the reactors gradually increased to unacceptable levels due to buildup of solids in the transfer line. The pressure drop increased more rapidly after increasing the first stage temperature from 825°F to 840°F (see Figure 6). Upon inspection, severe deposit formation was observed in this transfer line as well as the transfer line between the interstage separator and the second stage. As mentioned earlier no deposits were observed in the interstage separator. The transfer lines and reactors were also inspected after completing the catalytic/thermal tests in this run (interstage separator was bypassed in these tests). In this mode of operation, solid deposits were observed between the second stage and ebullating pump. Moreover the thermal second stage also had a significant amount of solids on the walls and at the bottom of the reactor. Some solid deposits were also observed in the vapor-slurry separator after the second stage.

The presence of a supported catalyst in the first stage has to some extent prevented the formation of deposits before the second reactor. However, since there was no catalyst in the second stage, solids buildup appeared to have shifted to process areas present in and after the second stage. Thus, it may be speculated that the presence of a transition metal catalyst in the reactor could produce materials that are less prone to coking or buildup. It may be pointed out that although the iron catalyst was present in the slurry, it was used only to increase coal conversion and relatively, transitional metal catalysts have much higher hydrogenation activity than iron catalysts. Thus, in Run 262, a dispersed (slurry) molybdenum catalyst is being tested to study its effect on solids buildup.

In addition, Run 258 results with Black Thunder coal indicated that solids buildup could be caused by basic components such as calcium present in coal. For example, ash analysis of Black Thunder coal indicated significant amounts of calcium, which under liquefaction conditions could be converted to compounds such as calcium carbonate which was found in solid deposits. Coal pretreatment will be explored to remove these basic components from low-rank coals prior to liquefaction. One such method is coal pretreatment with aqueous sulfur dioxide. The SO_2 would react to form sulfides of above components. Some of these are water soluble and can easily be removed; others may be oxidized to give compounds such as calcium sulfate that may not contribute to solids buildup.

Because of the high oxygen content in the feed coal (18-19 wt% mf coal), the Black Thunder coal produced a significant amount of water (16-19 wt% maf coal). The hydrogen consumption in Run 260 was in the range of 5.5 to 6.5 wt% maf coal. In other words, about 33% of this hydrogen was consumed in water production. Coal pretreatment methods need to be explored (e.g., hydrothermal treatment) for low-rank coals to remove/reduce oxygen content prior to liquefaction.

RUN 261

The main objectives of Run 261 were:

- to test a new Ni-Mo bimodal catalyst (EXP-AO-60) for its catalytic activity and physical strength using Illinois No. 6 coal from Burning Star #2 mine;
- to obtain high space velocity operation with full-volume reactors; and,
- to test a unimodal Ni-Mo catalyst (Criterion 324) at comparable conditions.

EXP-AO-60 CATALYST

The EXP-AO-60 catalyst was made by Akzo per Amoco's specifications. This was a 1/16 inch, Ni-Mo on alumina, cylindrical extrudate catalyst. The catalyst charge in each reactor was 270 lb. The catalyst was initially batch deactivated in low/high mode at 790/810°F starting with fresh, sulfided catalyst to an age equivalent to 3 lb/ton replacement rate in each stage. Typical operating conditions in Run 261 are given in Table 6.

In period 261B, reasonably smooth operation was obtained even at a high coal feed rate of 548 lb/hr. The coal conversion and the distillate yield were 91.7 and 64.4 wt% (maf coal), respectively (see Table 7).

After period 261B, further catalyst batch deactivation was started. Then the coal feed rate was reduced to about 423 lb/hr and resid concentration in process solvent was increased to about 48 wt%. In addition, vacuum flash recycle was also started after period 261B. In period 261D, the following yields were obtained compared to period 261B (wt% maf coal):

- higher C₄+ distillate
(65.6 wt% in 261D vs. 64.4 wt% in 261B)
- lower resid
(3.7 wt% in 261D vs. 4.7 wt% in 261B)
- higher C₁-C₃ gas make
(6.5 wt% in 261D vs. 5.1 wt% in 261B)
- higher coal conversion
(93.0 wt% in 261D vs. 91.7 wt% in 261B)
- lower solid product (ash-free)
(15.3 wt% in 261D vs. 17.9 wt% in 261B)

Although these yields were somewhat better in period 261D, there was a significant reduction in space velocity compared to period 261B. Since period 261B was obtained only at a resid concentration of about 38 wt%, it was estimated that at 50 wt% resid

concentration and 3 lb/ton replacement rate (each stage), the allowable coal feed rate that gives similar yields could be about 650 lb coal/hr (80 lb/hr/ft³ cat). That is, at similar process solvent composition, by increasing the total catalyst replacement rate from 3 to 6 lb/ton, it was projected that the coal feed rate would be increased by about 50%. It could be more economical to operate at higher catalyst replacement rates and higher coal feed rates, thereby utilizing the reactor volume more effectively.

CRITERION 324

In the following part of Run 261, Criterion 324 catalyst was used in both reactors. The catalyst charge was about 440 lb per stage. In period 261E, the coal feed rate, catalyst replacement rate, first and second stage temperatures were, 494 lb/hr, 3 lb/ton (per stage), 809°F and 824°F, respectively. The maf wt% yields in periods 261E may be compared with period 261B as given below, keeping in mind that the resid concentration in process solvent was higher in period 261E (see Tables 6, 7, and 8):

- C₄+ Distillate yield was lower
(60.6 wt% in 261E vs. 64.4 wt% in 261B)
- C₁-C₃ gas make was higher
(7.7 wt% in 261E vs. 5.1 wt% in 261B)
- Coal conversion was higher
(92.7 wt% in 261E vs. 91.7 wt% in 261B)

Although resid concentration was higher and coal feed rate was lower in period 261E, resid conversion to distillate was lower compared to period 261B, indicating that EXP-AO-60 could be a better catalyst for resid conversion/hydrogenation. In addition, higher temperatures with Criterion 324 catalyst were necessary for operability.

After completing period 261E, the catalyst was further batch deactivated to an age equivalent to 2.25 lb/ton replacement rate (further batch deactivation to an age equivalent to 1.5 lb/ton replacement rate could not be achieved due to increasing slurry viscosity) and catalyst replacement was started. Moreover, coal feed rate was further reduced to about 360 lb/hr and coal concentration was reduced from 33 to 30 wt% in order to maintain operability at the lower catalyst replacement rate. Under these conditions, the new resid circulation system was also tested. The new resid circulation system, though found to reduce the resid inventory in the system thereby reducing the time required for obtaining steady-state operation, caused some pumping difficulties probably due to inadequate mixing of coal and heavy gas oil in the slurry tanks. The means to improve the mixing conditions in the slurry tank are being addressed. Periods 261G and 261D may be compared for assessing the performance of the two catalysts. Both periods appear to give similar yields; however, the coal feed rate was lower and Criterion 324 catalyst replacement rate was higher in period 261G compared to period 261D with the EXP-AO-60 catalyst. Thus, these results again indicate better resid conversion kinetics

with the bimodal catalyst.

SOLVENT HYDROGENATION

The process solvent quality was measured as the conversion of the standard Indiana V coal (wt% maf coal) in the process solvent at 750°F. The reaction was carried out for 30 min. in a 30-cc microautoclave reactor. The process solvent quality was better in periods 261A - 261D (82.1±1.9, with EXP-AO-60 catalyst) compared to periods 261E -261G (76.3±0.5, with Criterion 324 catalyst). As shown in Figure 7, the wt% hydrogen in process solvent gradually decreased in this run.

CATALYST ACTIVITY AND DEACTIVATION

The catalyst activity and deactivation can be measured by following the reaction kinetics. In general, the (resid+coal) conversion to distillate was found to be approximately represented by first-order kinetics [4, 5]. The rate constant was calculated according to the following equation:

$$k = \text{WHSV} \{x/(1-x)\}$$

where:

$$\begin{aligned} \text{WHSV} &= \text{weight hourly space velocity} \\ &\quad (\text{lb feed/hr/ft}^3 \text{ cat}), \\ x &= (\text{resid+coal}) \text{ conversion to distillate} \end{aligned}$$

A plot of the first stage catalyst activity is given as a function of catalyst age for the EXP-AO-60 catalyst in Figure 8. Although the first stage was at a lower temperature (first stage: 790°F vs. second stage: 810°F), it seemed to have slightly higher deactivation rate, probably due to differences in the nature of the reactor feed. For example, first stage had higher resid concentration and fresh coal in its feed. However, under steady-state conditions at similar catalyst ages, both stages seem to have similar rate constants. The catalytic rate constants for the Criterion 324 catalyst are plotted in Figure 9. A single line can be noted for the first stage as it was maintained at 810°F; whereas, two lines can be noted for the second stage, as it was operated initially at 825°F and then at 800°F. In the catalyst age region shown in this figure, the first stage average rate constants seem to be only slightly lower than the second stage rate constants. Considering the variability in the experimental data, both stages seem to perform similarly and the effects of temperature seem to be marginal.

In Run 261, in low/high mode of operation (periods 261A - 261E), the average (resid+coal) conversions (based on feed) in the first and second stages were about 22 and 19 wt%, respectively. Whereas in the past, in the high/low mode, the first stage conversions were sometimes twice that in the second stage. Thus, the low/high mode seemed to improve the second stage utilization. A plot of hydrogen consumption in each stage is shown in Figure 10 for different

periods. It was interesting to note that whenever there was an increase in the consumption in the first stage there was a corresponding decrease in the second stage consumption and vice versa. Thus, it appears that different mechanisms may be taking place for hydrogen transfer, e.g., from coal liquids, from hydrogen gas, etc.; it may be speculated that if one is predominant in one stage, the other may be predominant in the other.

DISTILLATION SYSTEM AND PRODUCT QUALITY

The distillation scheme used in Run 261 was similar to that used in Run 260 (see Figure 5). As mentioned earlier, all the heavy products could not be sent to the vacuum flash unit due to some operational difficulties and part of the atmospheric flash bottoms was recycled in periods 261A and 261B to makeup the process solvent. From period 260C onwards, vacuum flash bottoms was recycled. In general, the distillate product end points were in the range of 750 to 780°F.

The product quality with EXP-AO-60 and Criterion 324 catalysts are given in Table 9. As shown in this table, the hydrogen content was higher in periods 261B and 261D compared to 261E; the heteroatoms (nitrogen, sulfur, and oxygen) were lower in periods 261B and 261D compared to 261E.

ACCOMPLISHMENTS/CONCLUSIONS (1990-91)

RUN 260

- Tested the performance of thermal/catalytic and catalytic/thermal operating modes with respect to yields and solids buildup with Black Thunder subbituminous coal.
- Severe solids buildup was experienced in the transfer line between the first stage and the interstage separator in the thermal/catalytic operation; however, no solids were observed in the interstage separator probably due to higher slurry velocities.
- Catalytic/thermal operation seemed to be very effective with low C₁-C₃ gas make and high distillate yield; this improvement was partly because of higher hydrogen partial pressure and resid concentration in the catalytic first stage.
- Because of catalytic first stage and lower reactor/preheater temperatures, the transfer line after the second stage did not have significant solids deposition; however, solids were observed after the thermal second stage, indicating that high thermal temperatures (either in the reactor or in the interstage preheater) produced materials prone to coking/buildup.
- The catalytic/thermal tests seem to indicate that continuous presence of a transition metal dispersed catalyst could help reduce solids deposition.

RUN 261

- The EXP-AO-60 bimodal catalyst was found to have good activity and physical strength in low/high mode tests with Illinois No. 6 coal from Burning Star #2 mine.
- A distillate yield of about 65 wt% was obtained in period 261B with EXP-AO-60 catalyst at a high space velocity of 67 lb coal/hr/ft³ cat with full-volume reactors at only 38 wt% resid concentration in solvent using low/high temperature mode (790/810°F).
- Based on the two test periods obtained at a total catalyst replacement rates of 6 and 3 lb/ton coal, it appeared that the coal feed rate could be increased by about 50% by doubling the catalyst replacement rate (EXP-AO-60). This would significantly improve the economics because the above advantage in coal feed rate was achieved at constant reactor volume.
- The low/high temperature operation seemed to give somewhat similar (resid+coal) conversions in each stage indicating that the second stage utilization improved compared to previous high/low runs.
- Tests were also made with Criterion 324 catalyst and Illinois No. 6 coal at two catalyst replacement rates.
- The process solvent quality was higher with the EXP-AO-60 catalyst compared to Criterion 324 catalyst.
- The EXP-AO-60 catalyst had satisfactory physical strength to withstand ebullated bed reactor operation.
- At a total catalyst replacement rate of 6 lb/ton, EXP-AO-60 catalyst could be operated at a higher space velocity compared to Criterion 324 catalyst to give similar distillate yield.
- The product quality seemed to be better with the EXP-AO-60 catalyst compared to Criterion 324 catalyst under the conditions tested.
- At lower replacement rates of Criterion 324 catalyst, coal feed rates and coal concentration in slurry were reduced due to an increase in slurry viscosity.

FUTURE PLANS

Run 262 is in progress with Black Thunder subbituminous coal. In this run, a dispersed molybdenum catalyst (Molyvan L) is being tested to study its effects on solids buildup and process performance. Future runs with bituminous and subbituminous coals would focus on improving the space velocities and product yields/quality.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy under Contract No. DE-AC22-90PC90033 (Project Manager: Dr. E. B. Klunder) and Electric Power Research Institute under Contract No. RP1234-1-2 (Project Manager: Mr. W. H. Weber).

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TABLE 1

TYPICAL ANALYSES OF BLACK THUNDER AND ILLINOIS No. 6 COALS

	<u>BLACK THUNDER</u>	<u>ILLINOIS NO.6</u>
	RUN 260	RUN 261
Moisture (wt%)	22.1	4.1
<u>PROXIMATE (mf wt%)</u>		
Ash	6.3	12.1
Volatile Matter	44.4	50.8
Fixed Carbon	49.3	37.1
<u>ULTIMATE (mf wt%)</u>		
Carbon	69.0	70.3
Hydrogen	5.2	4.9
Nitrogen	1.0	1.4
Sulfur	0.5	3.7
Ash	6.3	12.1
Oxygen (by diff.)	18.0	7.6
<u>SULFUR FORMS (mf wt%)</u>		
Pyritic	0.0	1.0
Sulfatic	0.0	0.0
Organic	0.4	2.6
<u>MINERAL ANALYSIS OF ASH (wt%)</u>		
Silica	35.3	46.9
Ferric Oxide	5.3	19.1
Alumina	16.3	17.7
Titania	1.2	-
Lime	24.0	5.6
Magnesia	4.9	1.1
Potassium Oxide	0.4	0.9
Sodium Oxide	1.2	0.6

TABLE 2

TYPICAL PROPERTIES OF FRESH CRITERION 324 (RUNS 260, 261)
AND EXP-AQ-60 (RUN 261) CATALYSTS

	<u>CRITERION 324</u>	<u>EXP-AQ-60</u>
Size (in)	1/16	1/16
Shape	Cylindrical Extrudate	Cylindrical Extrudate
Bulk Density (lb/ft ³)	54	33
Pore Volume (cc/g)	0.48	0.78
Alumina Support	Unimodal	Bimodal
Active Metals (wt%)	Ni (2.7) Mo (13.2)	Ni (2.5) Mo (10.7)

TABLE 3

TYPICAL OPERATING CONDITIONS IN RUN 260

Solvent-to-Coal Ratio	2.3
Recycle Solvent (wt%):	
Resid	40
Solids (CI)	20
Distillate	40
Catalyst Replacement Rate (lb cat/ton coal)	3
Catalyst Age (lb coal/lb cat)	650
Space Velocity	45 (260C) (ther/cat)
(lb coal/hr/ft ³ cat)	45 (260D); 62 (260E) (cat/ther)
Iron Oxide Addition Rate (wt% mf coal)	2
Typical Reactor Inlet H ₂ Partial Pressures (psia)	
First stage	2700
Second stage	2200

TABLE 4

EFFECTS OF OPERATING MODE ON PERFORMANCE IN RUN 260

RUN PERIOD -->	<u>260C</u>	<u>260D</u>	<u>260E</u>
Operating Mode	Ther/Cat	Cat/Ther	Cat/Ther
Coal Feed Rate (lb/hr)	251	253	348
Av. Temperatures (°F)			
1st Stage	825	790	789
2nd Stage	790	774	797
<u>YIELD DATA (wt% maf Coal)</u>			
Hydrogen Consumption	-6.3	-6.2	-5.6
Water	18.8	18.6	17.2
H ₂ S+CO _x +NH ₃	4.1	3.4	4.3
C ₁ -C ₃ Gas	11.2	5.6	6.2
C ₄ + Distillate	54.1	59.8	52.2
Resid ^a	7.5	0.3	5.6
Solid Product ^a (ash-free)	10.7	18.5	20.1
Coal Conversion ^a	94.2	88.5	87.0

^a A sample of (liquid+solid) product is distilled in the laboratory at 600 °F and 0.1 mm Hg (about 1100 °F at 1 atm). The non-distillable portion contains resid, unconverted coal, and ash. The resid is soluble and unconverted coal and ash are insoluble in cresol. Thus, unconverted coal and ash are referred to as cresol insolubles (CI). The ash-free organics (mostly unconverted coal and resid) are present in the ROSE-SRSM unit solid product.

TABLE 5

PRODUCT QUALITY OF BLACK THUNDER COAL

	<u>THERMAL/CATALYTIC</u>	<u>CATALYTIC/THERMAL</u>
RUN PERIOD -->	260C	260D
API Gravity	26.2	22.1
<u>ANALYSIS (wt%)</u>		
Carbon	87.20	87.10
Hydrogen	11.80	11.10
Nitrogen	0.40	0.45
Sulfur	0.04	0.04
Oxygen (diff.)	0.50	1.30
Product End Point (°F)	778	723 (by D1160)

TABLE 6

TYPICAL OPERATING CONDITIONS IN RUN 261

	<u>EXP-AQ-60</u>		<u>Criterion 324</u>	
Period	261B	261D	261E	261G
Solvent-to-Coal Ratio	2.3	2.3	2.3	2.0
Recycle Solvent (wt%):				
Resid	38	48	49	47
Solids (CI)	12	12	12	12
Distillate	50	40	39	41
Reactor Temp. (°F):				
1st stage	790	790	810	810
2nd stage	810	810	825	800
Catalyst Replacement Rate (lb cat/ton coal)	3	1.5	3	2.25
Catalyst Age (lb coal/lb cat)	670	1370	660	880
Space Velocity (lb coal/hr/ft ³ cat)	67	52	61	44
Reactor Inlet H ₂ Partial Pressures (psia)				
1st stage	2610	2660	2540	2640
2nd stage	2510	2470	2350	2310

TABLE 7

HIGH SPACE VELOCITY OPERATION WITH EXP-AD-60 CATALYST:
EFFECT OF CATALYST REPLACEMENT RATE
(ILLINOIS No. 6 COAL)

Run Period ->	<u>261B</u>	<u>261D</u>
Coal Feed Rate (lb/hr)	548	423
Catalyst Replacement Rate (lb/ton)	3	1.5
<u>YIELD DATA (wt% maf coal)</u>		
Hydrogen Consumption	-5.7	-6.0
Water	8.3	9.7
H ₂ S+CO ₂ +NH ₃	5.3	5.2
C ₁ -C ₃ Gas	5.1	6.5
C ₄ + Distillate	64.4	65.6
Resid	4.7	3.7
Solid Product (ash-free)	17.9	15.3
Coal Conversion	91.7	93.0

TABLE 8

OPERATION WITH CRITERION 324 CATALYST:
EFFECT OF CATALYST REPLACEMENT RATE
(ILLINOIS No. 6 COAL)

Run Period ->	<u>261E</u>	<u>261G</u>
Coal Feed Rate (lb/hr)	494	357
Catalyst Replacement Rate (lb/ton)	3	2.25
<u>YIELD DATA (wt% maf coal)</u>		
Hydrogen Consumption	-5.4	-6.2
Water	9.7	9.0
H ₂ S+CO ₂ +NH ₃	5.3	4.6
C ₁ -C ₃ Gas	7.7	7.6
C ₄ + Distillate	60.6	64.3
Resid	5.4	5.1
Solid Product (ash-free)	16.7	15.6
Coal Conversion	92.7	92.2

TABLE 9

**PRODUCT QUALITIES OF ILLINOIS NO. 6 COAL WITH
EXP-AO-60 AND CRITERION 324 CATALYSTS**

RUN PERIOD -->	<u>EXP-AO-60</u>		<u>CRITERION 324</u>
	261B	261D	261E
<u>DISTILLATE (wt%)</u>			
IBP-350 °F	21.2	30.0	24.3
350-450 °F	11.9	14.5	15.4
450-EP °F	66.8	55.5	60.3
API Gravity	23.3	22.1	23.2
<u>ANALYSIS (wt%)</u>			
Carbon	87.25	87.49	86.28
Hydrogen	11.42	11.27	10.86
Nitrogen	0.22	0.32	0.43
Sulfur	0.03	0.02	0.06
Oxygen (diff.)	1.07	0.90	2.38
Product End Point (°F) (by D1160)	772	780	786

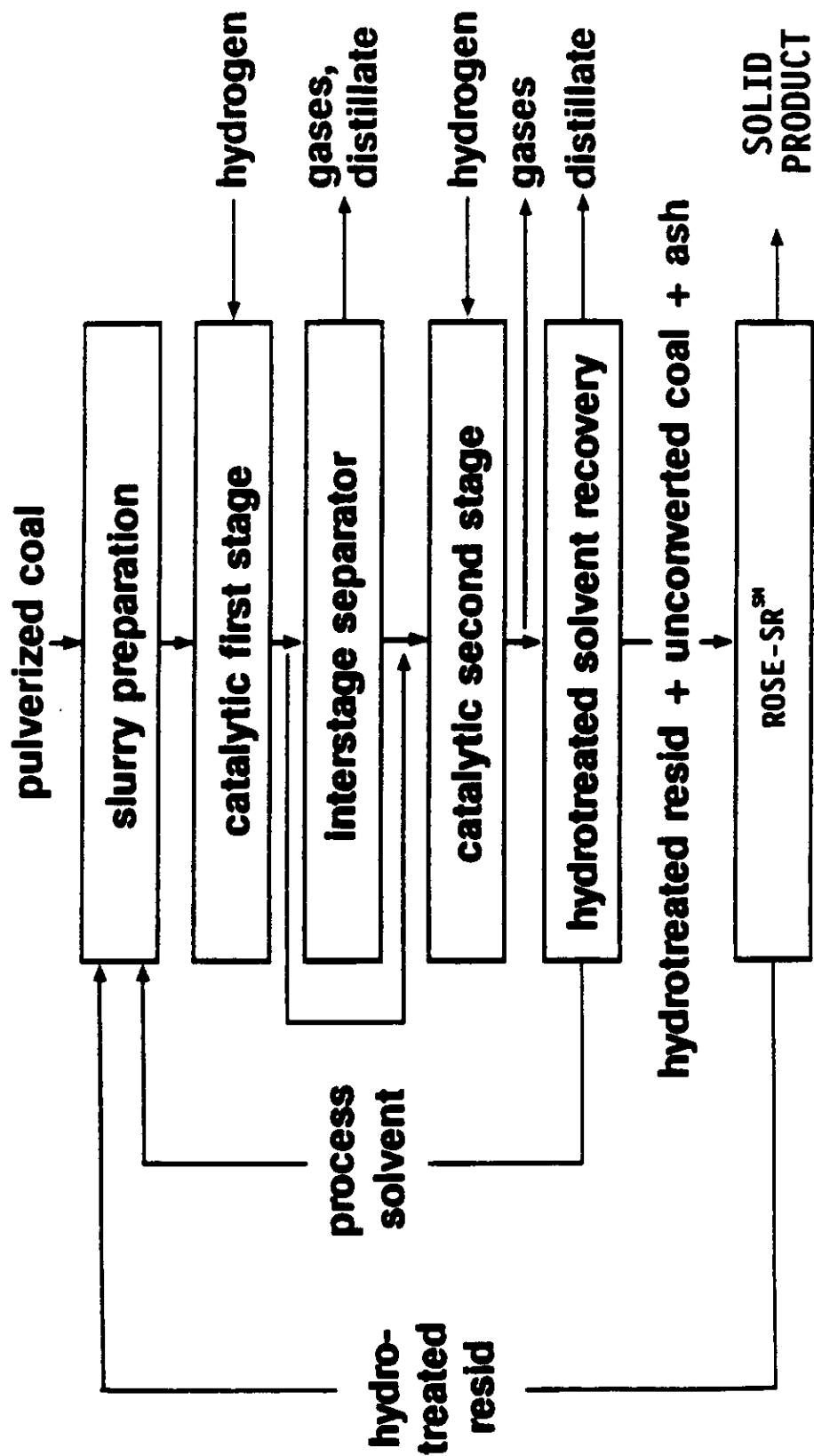


FIGURE 1. BLOCK DIAGRAM OF CATALYTIC-CATALYTIC CLOSE-COUPLED INTEGRATED TWO-STAGE LIQUEFACTION PROCESS (CC-ITSL)

COAL CONVERSION VS. SPACE VELOCITY

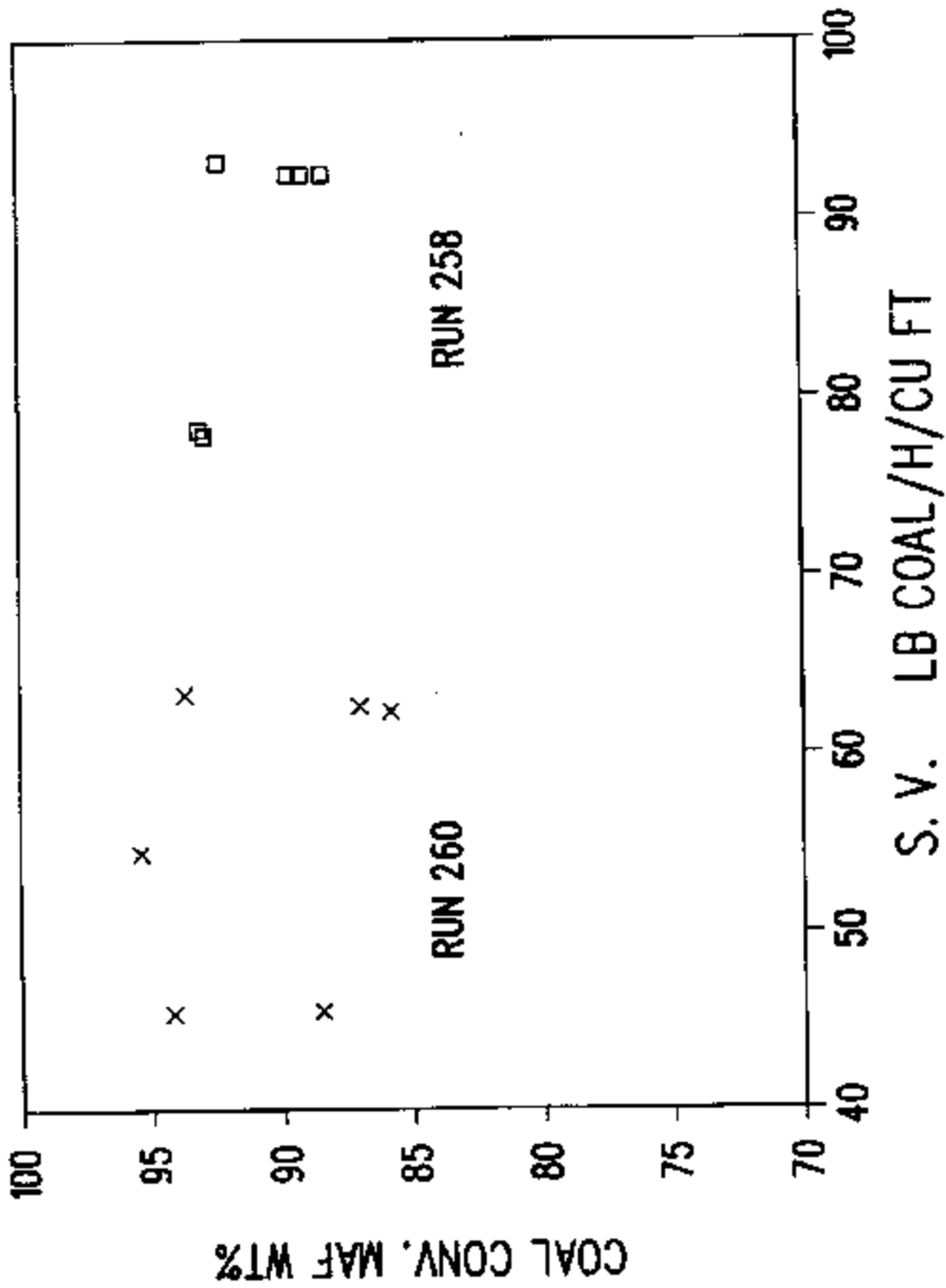


FIGURE 2. BLACK THUNDER COAL CONVERSION IN RUNS 258 AND 260 AS A FUNCTION OF CATALYTIC SPACE VELOCITY

COAL CONVERSION VS THERMAL SEVERITY

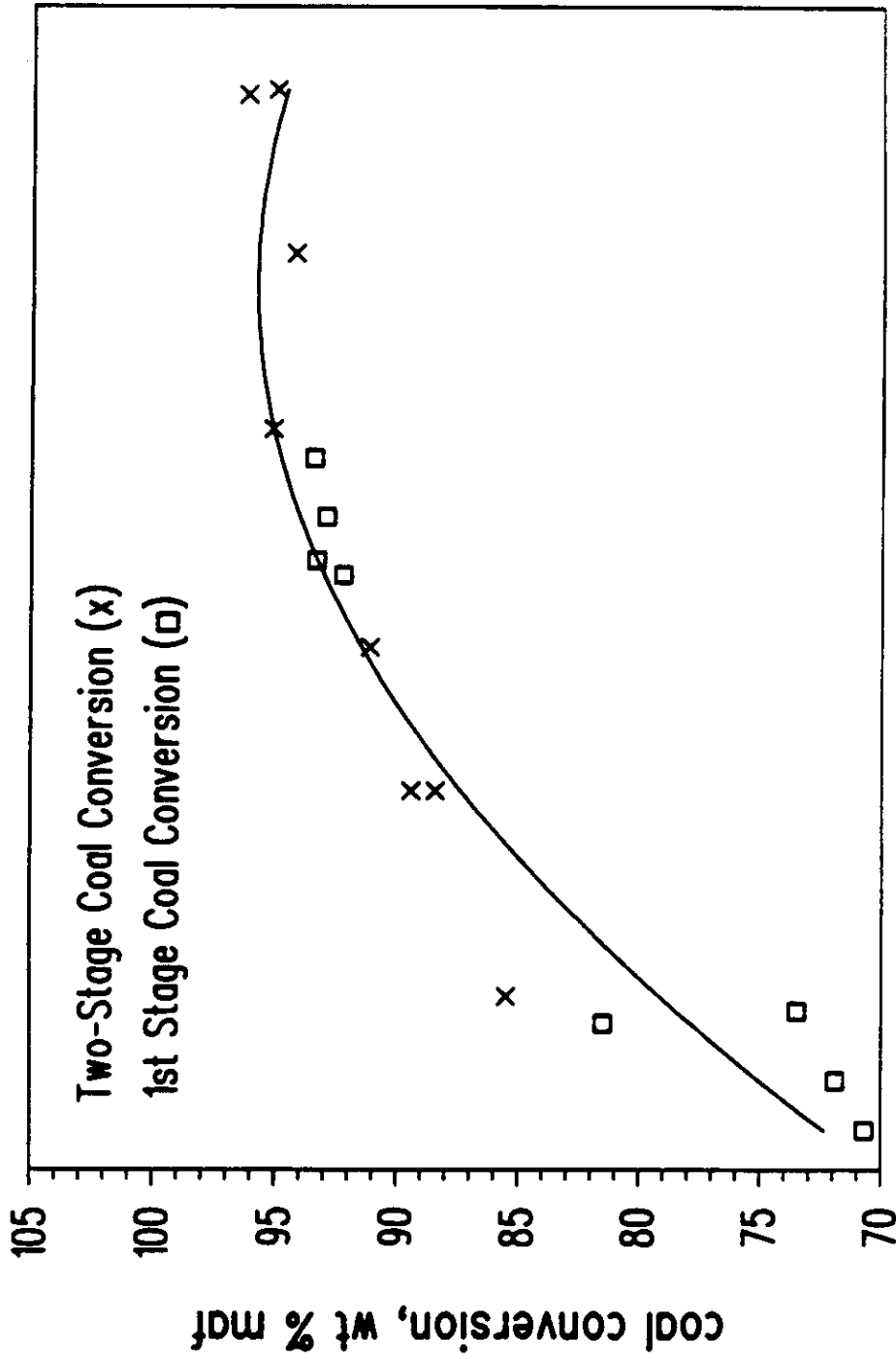


FIGURE 3. EFFECT OF THERMAL SEVERITY ON COAL CONVERSION (RUN 260)

R+UC CONVERSION VS THERMAL SEVERITY

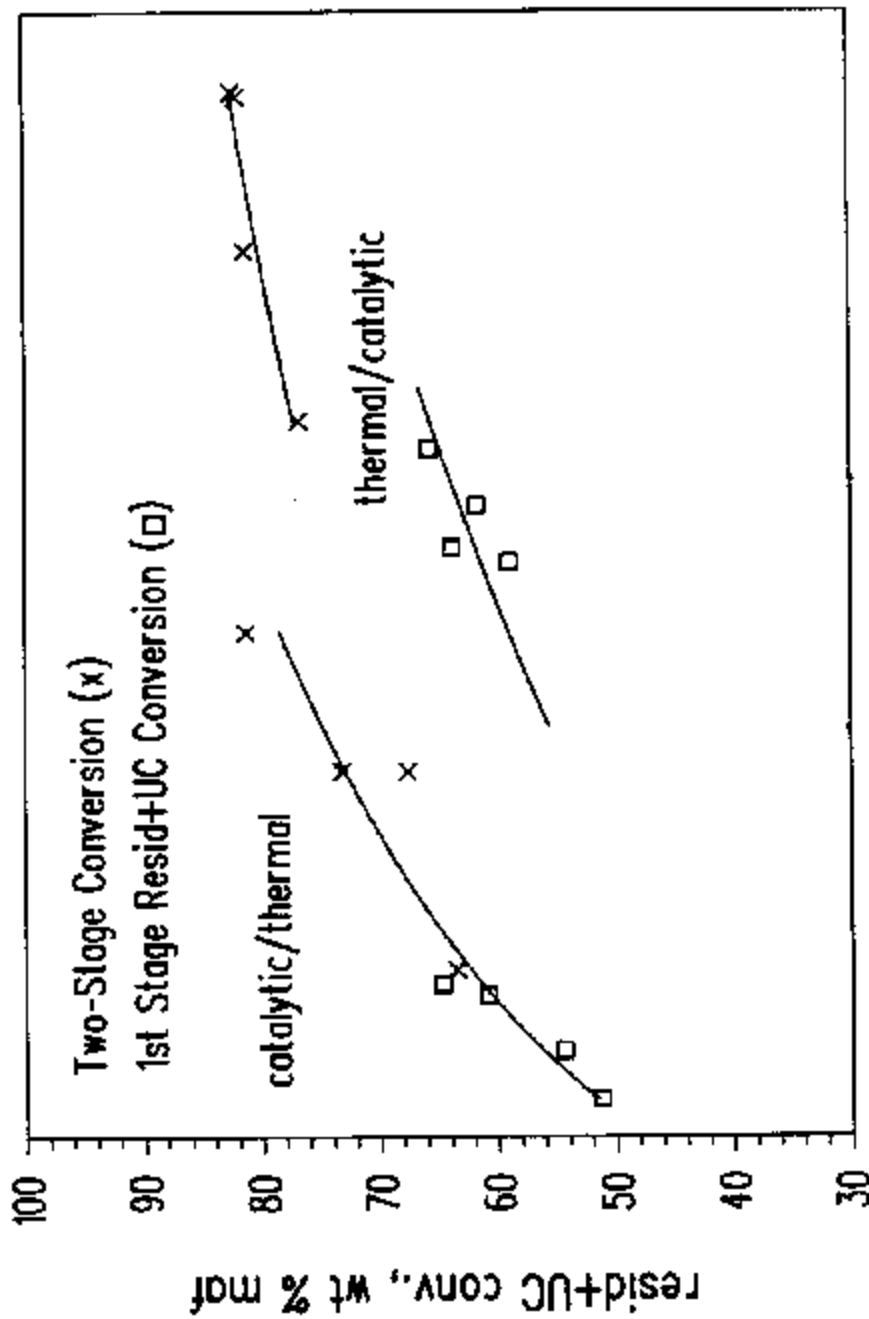


FIGURE 4. EFFECT OF THERMAL SEVERITY ON (RESID+COAL) CONVERSION (RUN 260)

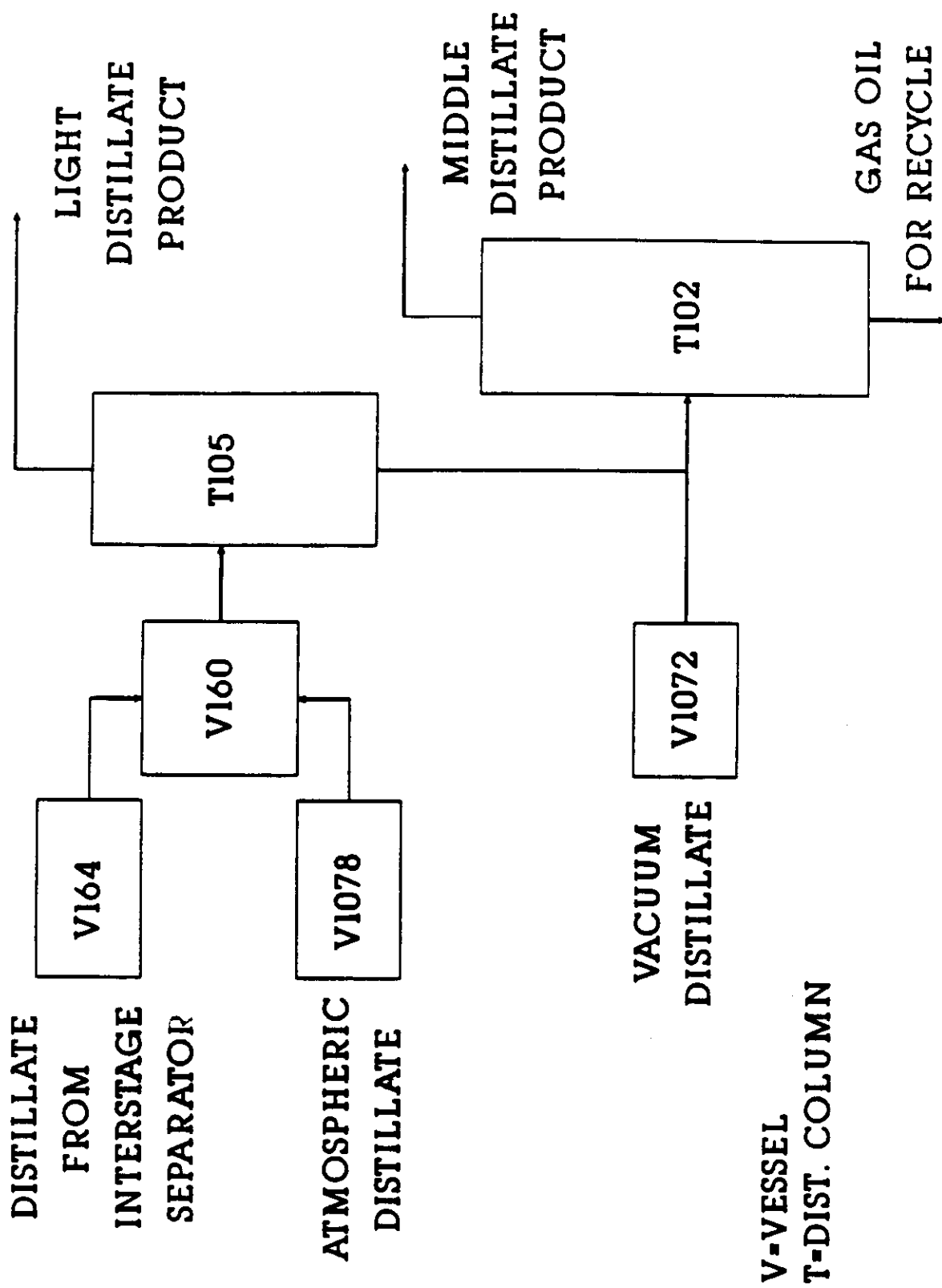


FIGURE 5. SCHEMATIC DIAGRAM OF DISTILLATE PRODUCT SEPARATION

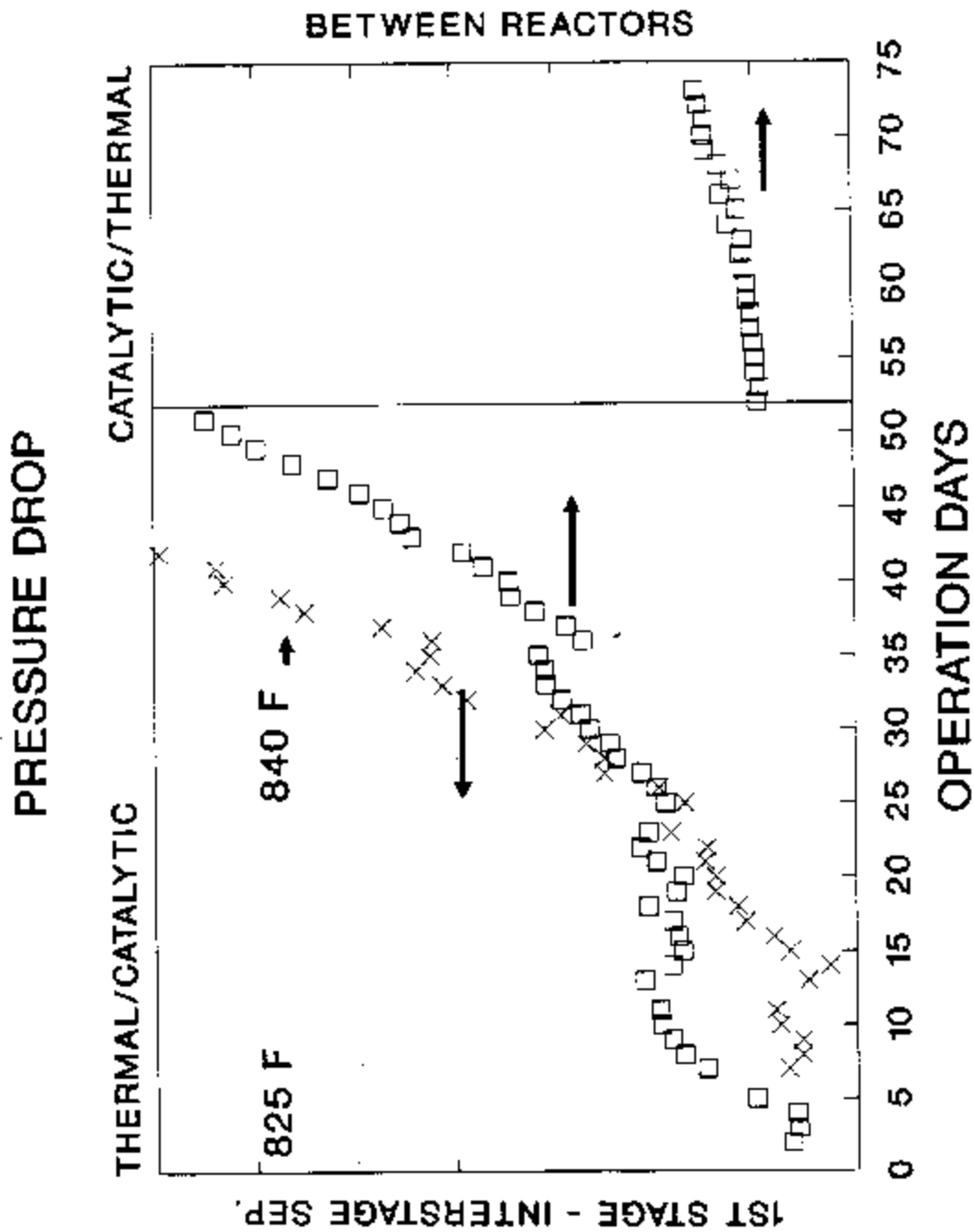


FIGURE 6. PRESSURE DROPS BETWEEN THE 1ST REACTOR AND INTERSTAGE SEPARATOR AND BETWEEN THE REACTORS (RUN 260)

WT% HYDROGEN IN PROCESS SOLVENT

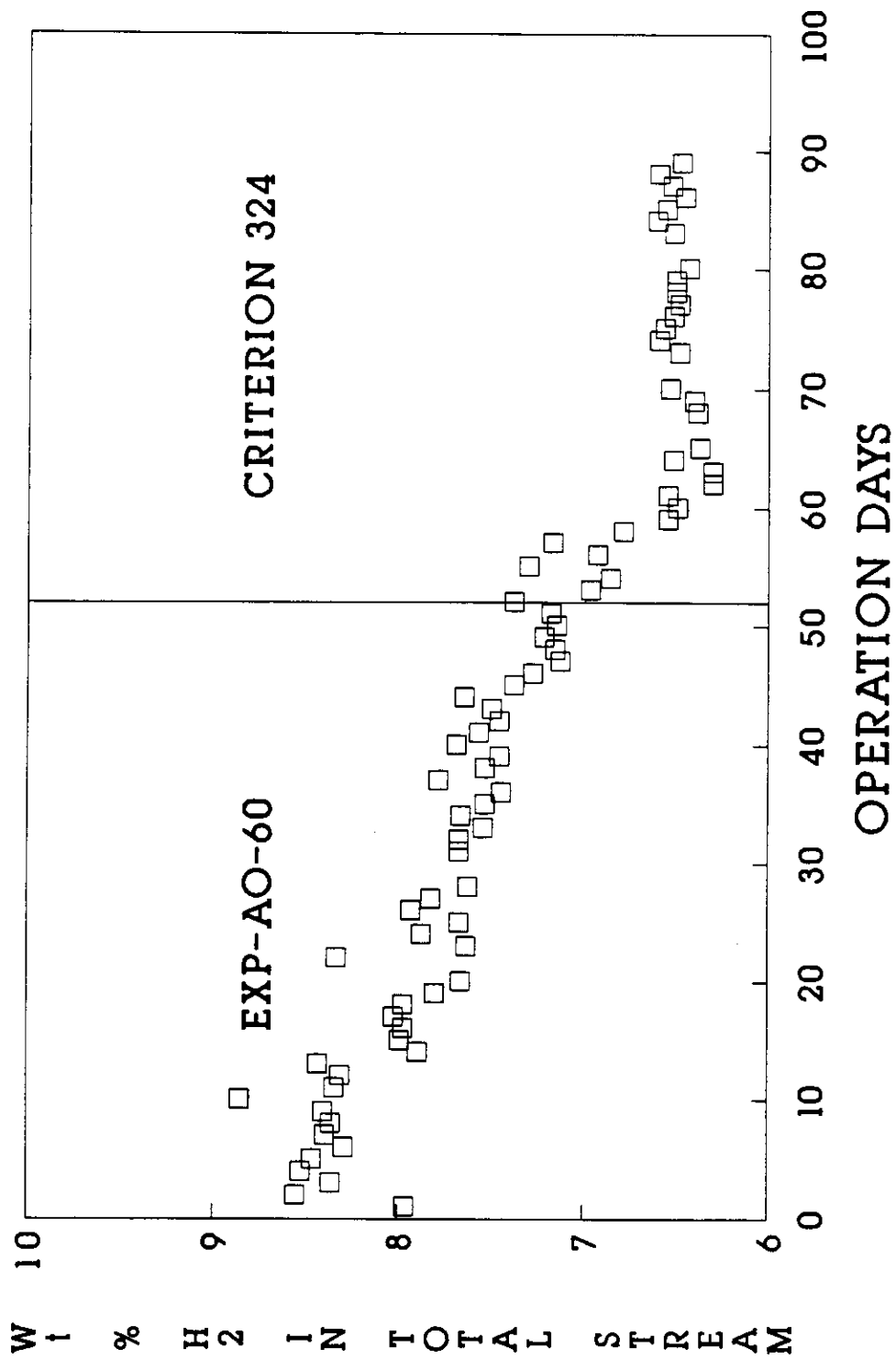


FIGURE 7. HYDROGEN WT% IN PROCESS SOLVENT IN RUN 261 WITH EXP-AO-60 AND CRITERION 324 CATALYSTS

CATALYST ACTIVITY (EXP-A0-60)

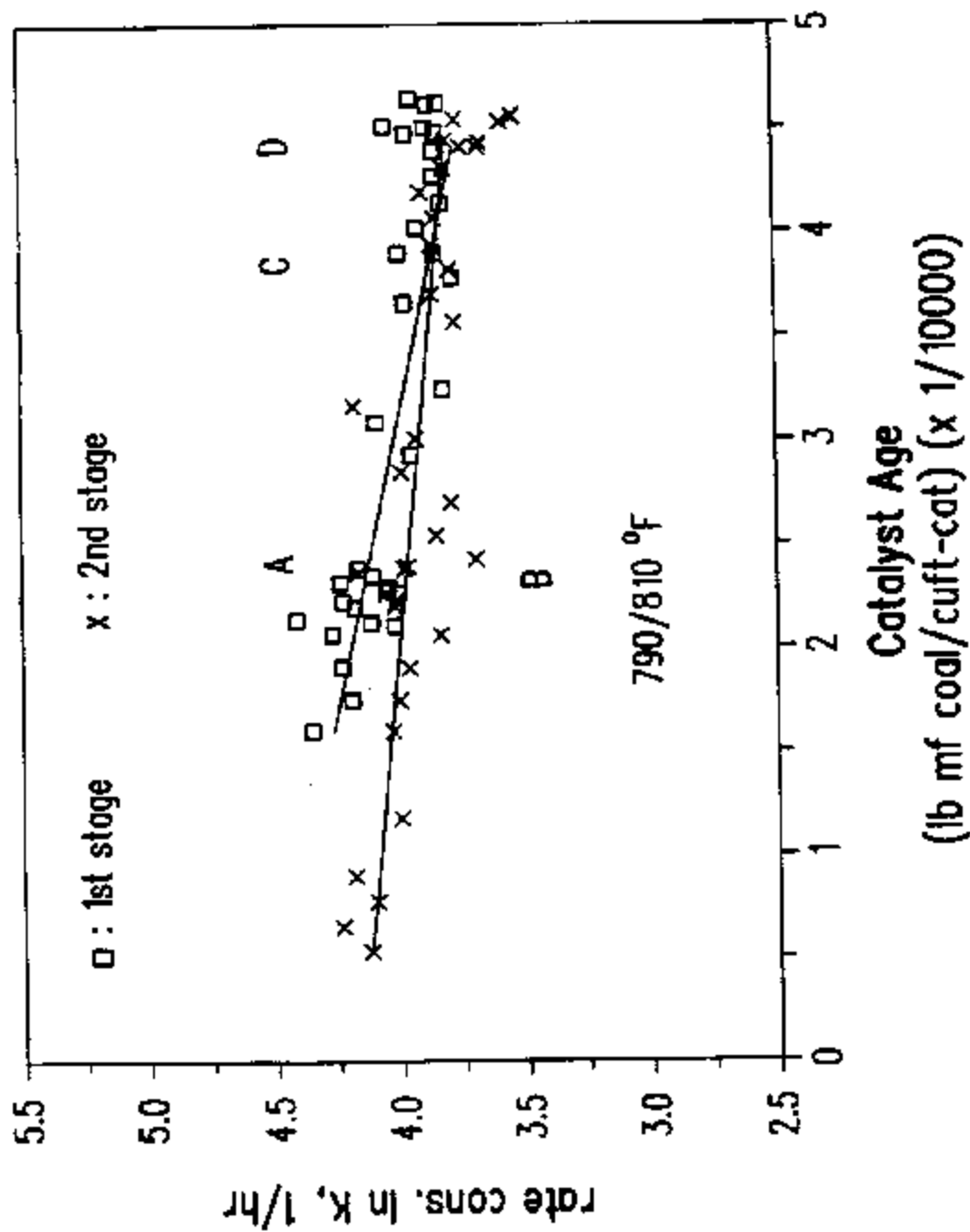


FIGURE 8. EXP-A0-60 CATALYST ACTIVITY AS A FUNCTION OF AGE
 (RUN 261)

CATALYST ACTIVITY (CRITERION 324)

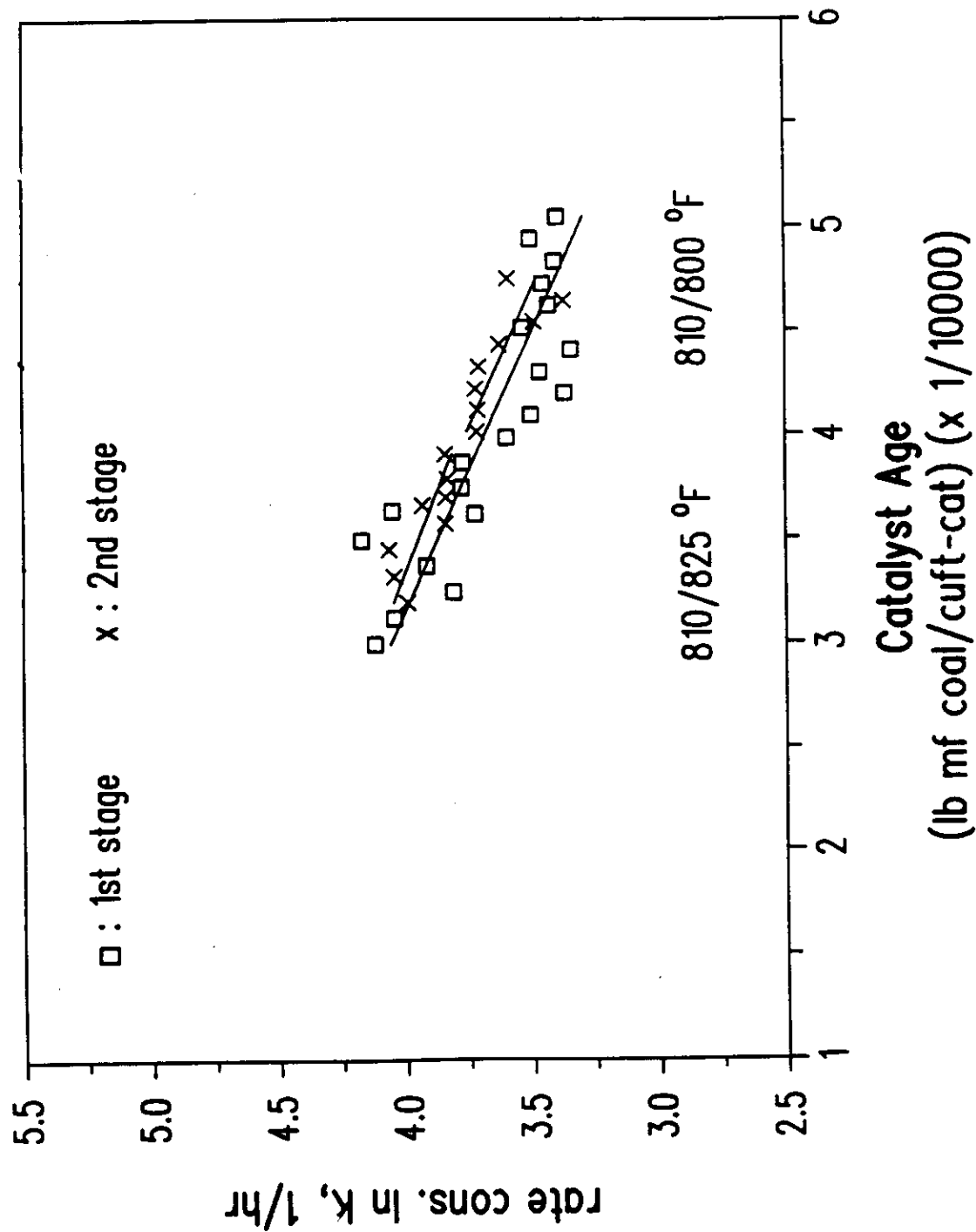


FIGURE 9. CRITERION 324 CATALYST ACTIVITY AS A FUNCTION OF AGE
 (RUN 261)

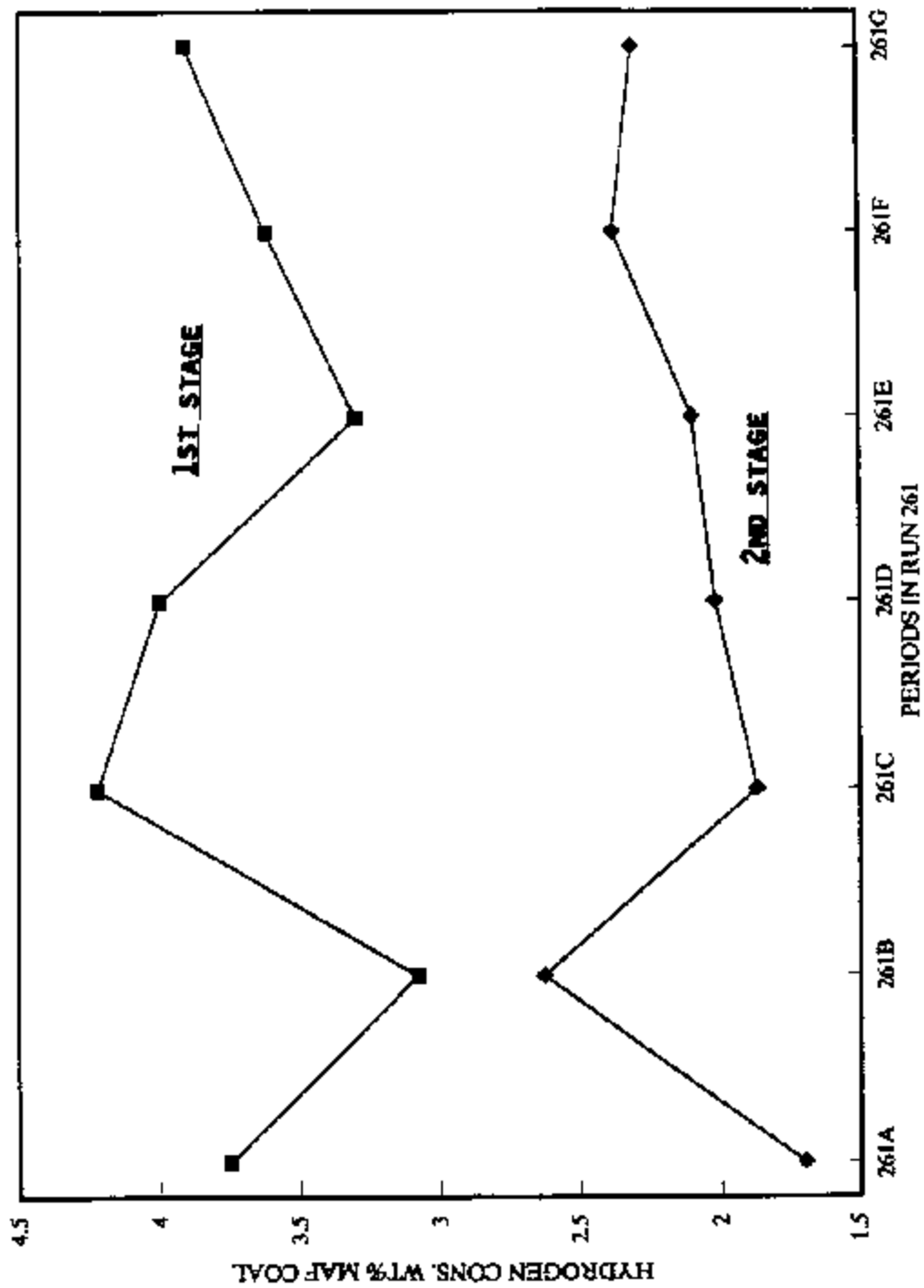


FIGURE 10. HYDROGEN CONSUMPTION IN EACH STAGE IN RUN 261 PERIODS