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CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS

Interim Report for the
Period March 1976 - May 1976

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OBJECTIVE

It is the object of this research to convert coal to clean distillate fuels. This program will be limited to research on the product from existing coal liquefaction processes. Liquefied coal will be converted by a catalytic hydrogenation at elevated temperatures and pressures. Samples of the products from PAMCO, H-Oil, COED and Cresap processes will be obtained. They will be heated and pumped, with and without solvent, into a catalytic reactor in the presence of hydrogen and other reducing gases. Variables to be investigated will include temperature, pressure, space velocity, hydrogen-to-oil ratio, chemical nature of the solvent. The catalysts to be studied will include nickel molybdate and sulfide, cobalt molybdate and sulfide, nickel tungstate and other combinations on carriers such as mordanites and other molecular sieve types.

ABSTRACT

COED Tar: The investigation of the hydrotreating of COED tar with a nickel-tungsten catalyst showed that this catalyst is an improvement over cobalt molybdate in the production of lighter boiling product, that more lighter boiling product is obtained at the longer residence time and that sulfur removal from the product does not increase as the hydrogen rate is increased.

SYNTHOIL: Two runs were made on the hydrotreating of SYNTHOIL with cobalt molybdate catalyst to establish a basis for comparison with other catalysts. One run was completed with a nickel tungsten catalyst giving product boiling slightly lower than that obtained from cobalt molybdate.

SRC: The hydrotreating of Solvent Refined Coal (SRC) was carried out in both continuous and batch reactors using the synthetic coal oil as a carrier solvent and employing a nickel tungsten catalyst. The higher pressure run gave a better conversion.

The work to date on these three feedstocks indicates that temperature is a critical variable and should be maintained in a narrow range. In order to determine more quickly what is the optimum temperature for each catalyst and set of conditions, a few batch runs in a rocking bomb autoclave are being carried out on all three feedstocks prior to running the continuous feed hydrotreaters.

THE CONVERSION OF COED TAR TO DISTILLATE FUELS - by S. Kujawa

I. Progress Summary

Previous progress reports have established that:

1. Increasing hydrogen flow relative to the flow rate of liquid feed increases the yield of light products.
2. Sulfur removal depends on hydrogen flow rate up to a point, then stays level.
3. A nickel-tungsten catalyst gives a better product than a cobalt-molybdate one.

The work presented in this progress report will show that:

1. At the pressures that have been tested, no significant increase in cracking or in desulfurization occurs by increasing the run pressure.
2. From batch autoclave runs, there is some evidence that very long residence times might be necessary to obtain high light product yields.
3. Sulfur removal seems to be independent of the flow rate of hydrogen; at least after a certain minimum flow of hydrogen is obtained.
4. The nickel-tungsten catalyst reported previously still gives the best light product yield.

II. Technical Progress

All data commented on hereafter is given in Table 3 at the end of this report. Table 3 includes run data, ASTM distillations and product sulfur analyses for runs number 5 through 10.

Experimental Results

The results first reported here are from runs done with a nickel-tungsten catalyst. The catalyst is Harshaw Ni4401 which has the composition 6% Ni, 19% W, 50% SiO_2, 25% Al_2O_3. The catalyst was presulfided by Harshaw. Runs 5, 6, 7 and 8 used this catalyst.

The results of run 5 were reported in the last progress report. In that run, which occurred at 450°C, and 800 psig., the COED tar was cracked to a greater extent than previous runs with Co-Mo catalyst; desulfurization occurred to similar extents. It was decided after this run that a more extensive test of this catalyst was in order to determine if higher pressures would give better yields.

Run number 6 used the Ni-W catalyst at 450°C and 1000 psig. Attempts were made to obtain space velocities and hydrogen flows similar to run 5. Figure 1 gives a comparison of sample 1 of run 5 and sample 3 of run 6, which were closest in LHSV and H_2 flow rates. As can be seen, the 800 psi run gave better cracking with slightly better sulfur removal.

After run 6, it was decided to make a run in a batch autoclave at a higher pressure. The first batch run (no. 7), reached a maximum H_2 pressure of 3880 psig at the run temperature of 450°C. The bomb was held at 450°C for 30 minutes by which time the pressure had fallen to 2570 psig. The sulfur content in the product was 0.21%, which was much less than any continuous run. The ASTM distillation of the product is shown in Figure 2. This product distilled very similar to the 1000 psi run.

The question was brought up after the first batch run whether maybe long residence times would be necessary to improve the distillate yield. Run 8 was made to check this, starting with the same initial pressure as Run 7 and with a 60 minute holding time at 450°C. As can be seen in Figure 2, the doubling of the residence time gave about a 7% increase in the amount of distillate, but this still had not equalled the performance of the 800 psig run; this is shown in Figure 3.

After the completion of run 8, it was then concluded that pressures above 800 psi would probably not be necessary for preliminary catalyst testing. The uncertainty in the pressure tests is that only one sample was collected during run 5 before the reactor was shut down by a blockage of the exit valve and that the favorable properties of the sample could be due to high catalyst activity during the start up.

The desulfurization that occurred in run 6 is illustrated in Figure 4 as weight percent sulfur in the product versus liquid hourly space velocity. The most important result shown is that the amount of sulfur does not depend strongly on the flow rate of hydrogen. Table I gives the data for the graph and as can be seen, although the amount of H_2 varied considerably, the graph in Figure 4 is monotonic, implying that the hydrogen in all cases was probably sufficient to react with the sulfur that was to be removed by the catalyst. This effect was reported in the last progress report for hydrogen flows above 10,000 scf/bbl but now it appears that this might have been a property of the Co-Mo catalyst tested there and that the necessary hydrogen for the Ni-W catalyst might be much less.

TABLE I. SULFUR CONTENT IN PRODUCT FROM RUN 6

Sample	LHSV	H_2SCF/bbl	wt. % S
2	3.12	8612	.78
3	1.69	10,700	.70
4	.52	34,700	.39
5	.84	5699	.56
6	3.3	23,651	.97

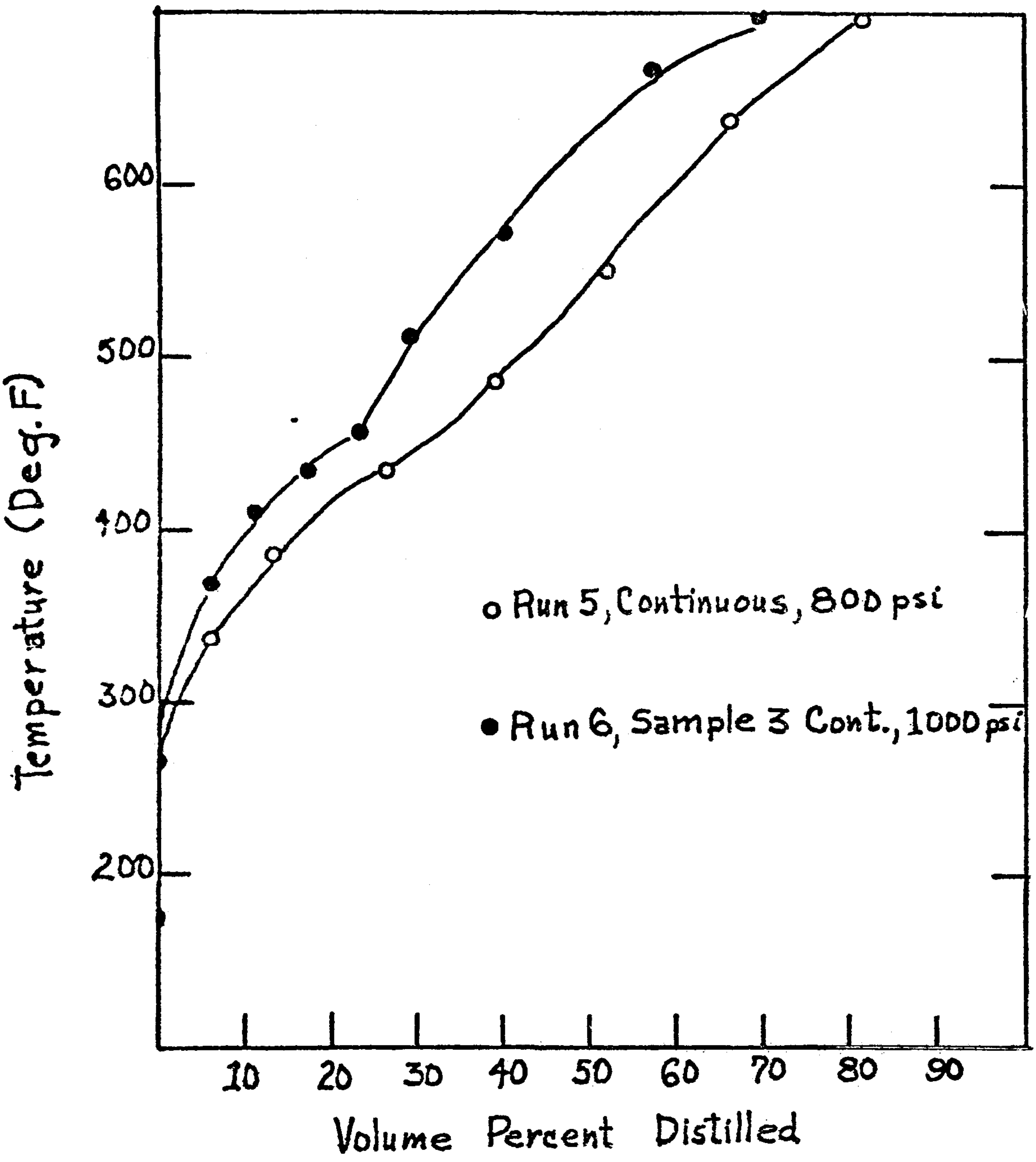
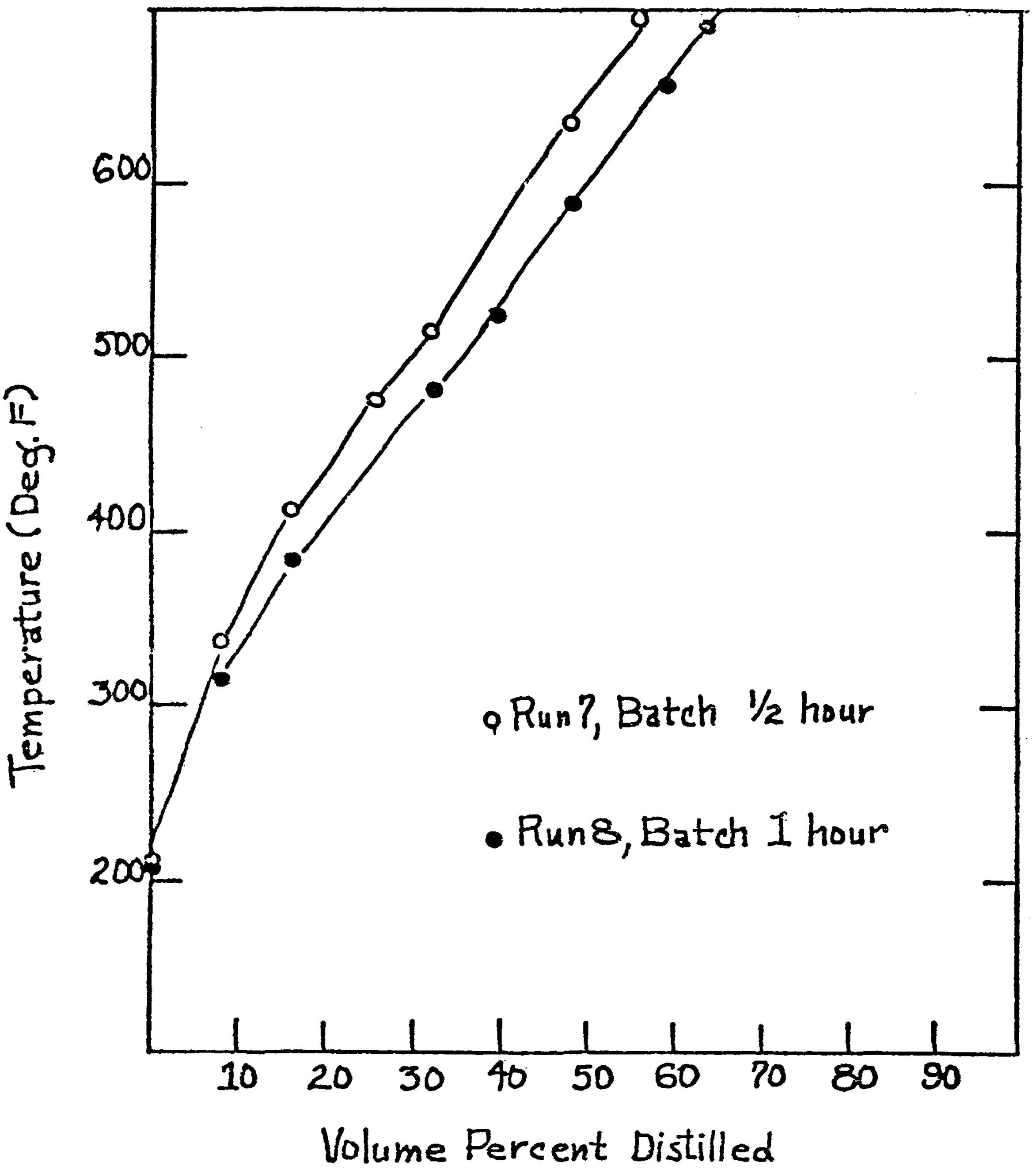

Temperature (Deg. F)
600
500
400
300
200
10
20
30
40
50
60
70
80
90
Volume Percent Distilled
○ Run 5, Continuous, 800 psi
● Run 6, Sample 3 Cont., 1000 psi

FIGURE 1



Temperature (Deg. F)
600
500
400
300
200
10
20
30
40
50
60
70
80
90
Volume Percent Distilled
○ Run 7, Batch ½ hour
● Run 8, Batch 1 hour

FIGURE 2

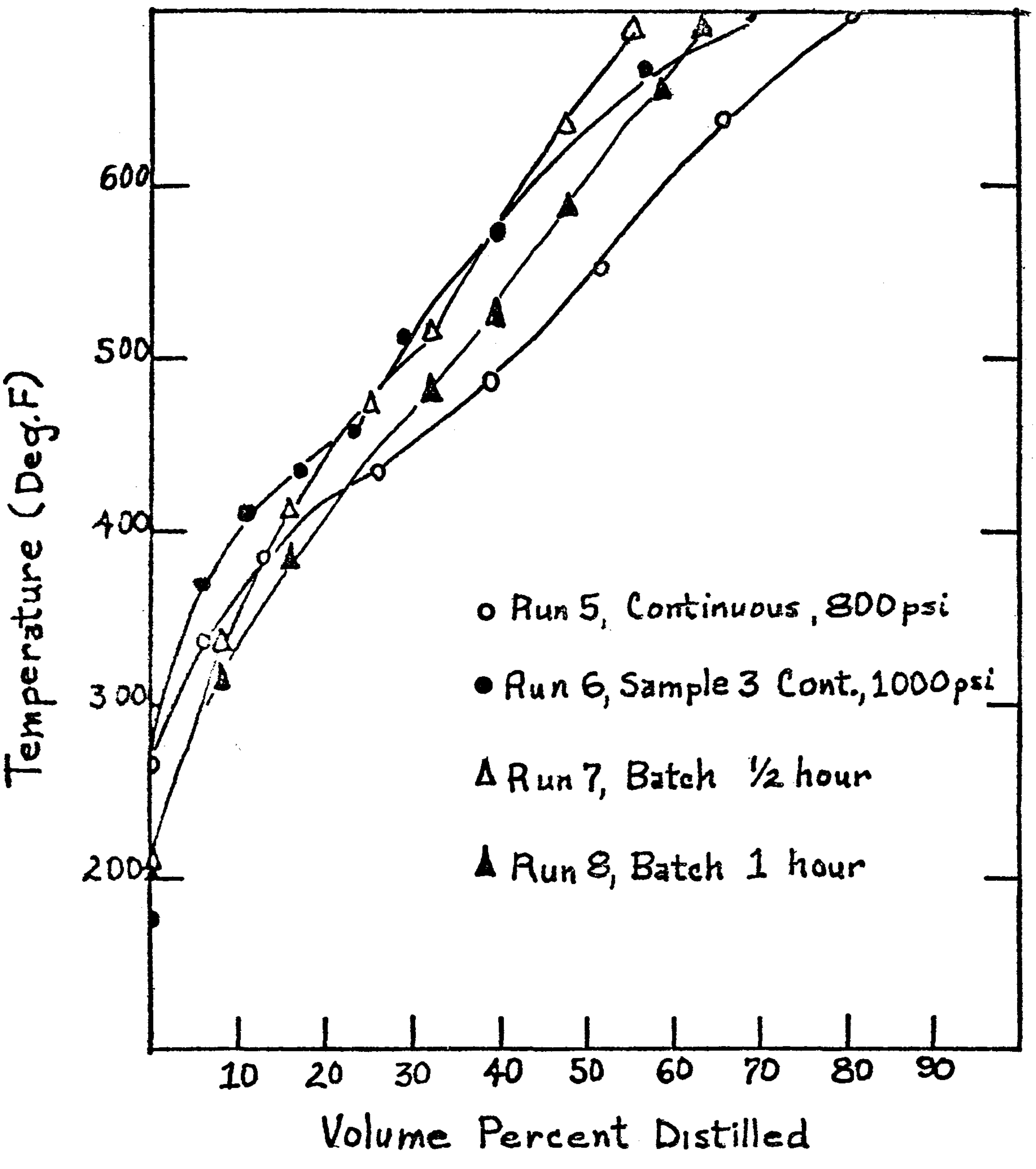

Temperature (Deg. F)
600
500
400
300
200
10
20
30
40
50
60
70
80
90
Volume Percent Distilled
○ Run 5, Continuous, 800 psi
● Run 6, Sample 3 Cont., 1000 psi
△ Run 7, Batch ½ hour
▲ Run 8, Batch 1 hour

FIGURE 3

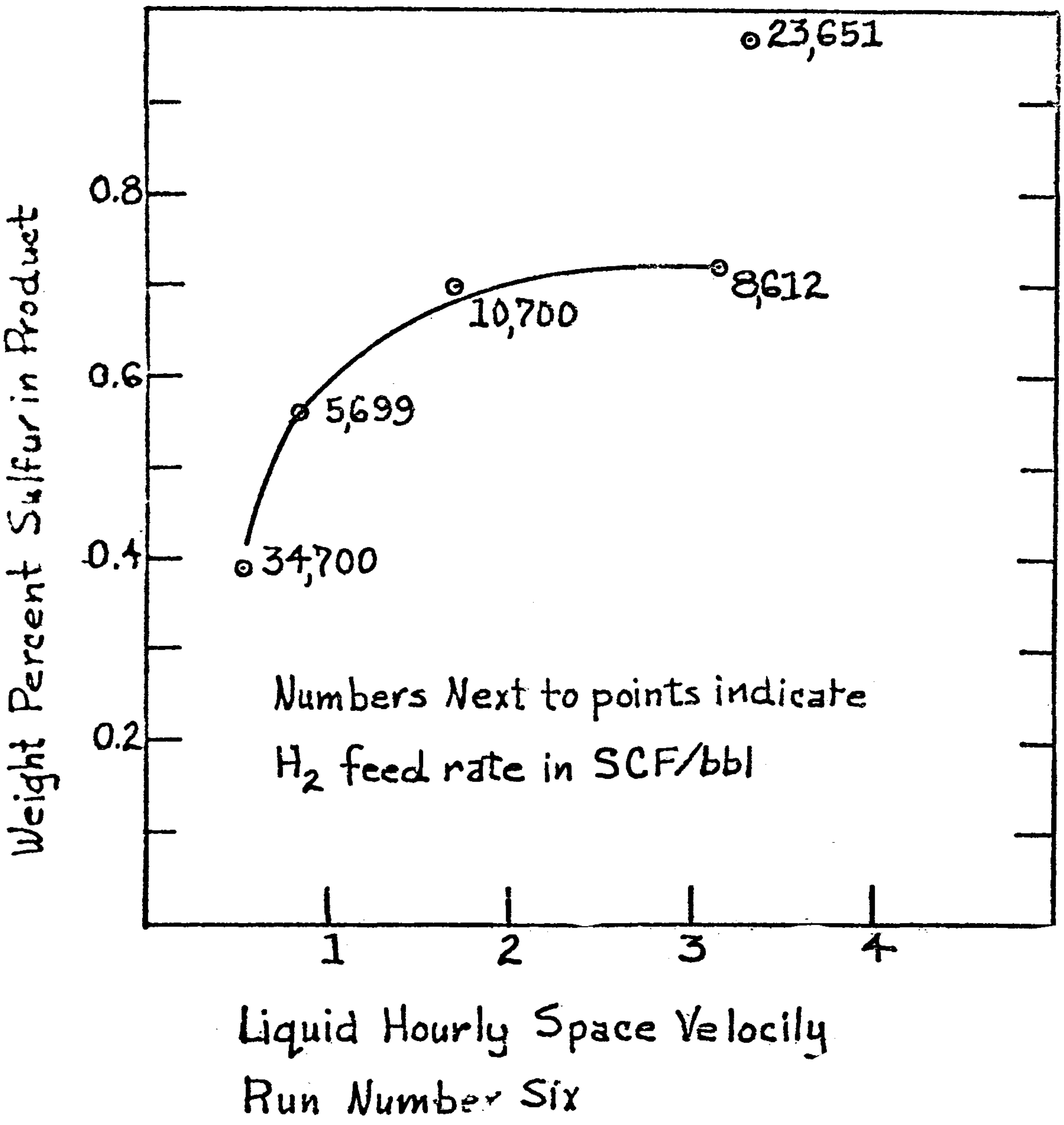

0.8
0.6
0.4
0.2
1
2
3
4
23,651
8,612
10,700
5,699
34,700
Numbers Next to points indicate
H2 feed rate in SCF/bbl
Weight Percent Sulfur in Product
Liquid Hourly Space Velocity
Run Number Six

FIGURE 4

The batch autoclave previously mentioned is a Parr Instrument Company rocking bomb of 500 ml capacity. It has been decided that this bomb can be used both to initially screen catalyt activity and initial reaction temperature. Catalyst activity will be determined by distillation and sulfur analysis as in continuous runs; initial temperature will be monitored by noting at what temperature the hydrogen pressure slows its increase and begins to decrease. It is felt that by first testing the catalyst by batch methods a lot of time now used to unplug reactors due to unsuitable catalyst can now be put to better use.

The last two runs made during this quarter were made with Harshaw Ni 1600 S¼, a catalyst described as "a decomposition catalyst containing 3 to 4 percent each nickel oxide, cobalt oxide and iron oxide mounted on inert alumina-silica spheres". Run 9 was a batch screening run which showed that cracking occurs, and run 10 was the continuous run on this catalyst. Run 9 was at 450°C with a half hour holding time; run 10 was at 450°C and 800 psig H_2.

An ASTM distillation of one of the samples from run 10 is shown in Figure 5 in comparison with a sample from run 6 of comparible space velocity. As can be seen, run 10 produced much less cracking. Also, as shown in Table II, desulfurization did not occur to a very great extent.

TABLE II. SULFUR CONTENT IN PRODUCT RUNS 9 and 10

Sample	LHSV	SCF H_2/bbl	Wt. % S
run 9	-	-	1.26
10-1	.28	34,300	1.2
10-2	.40	45,900	1.39
10-3	.83	28,400	1.51

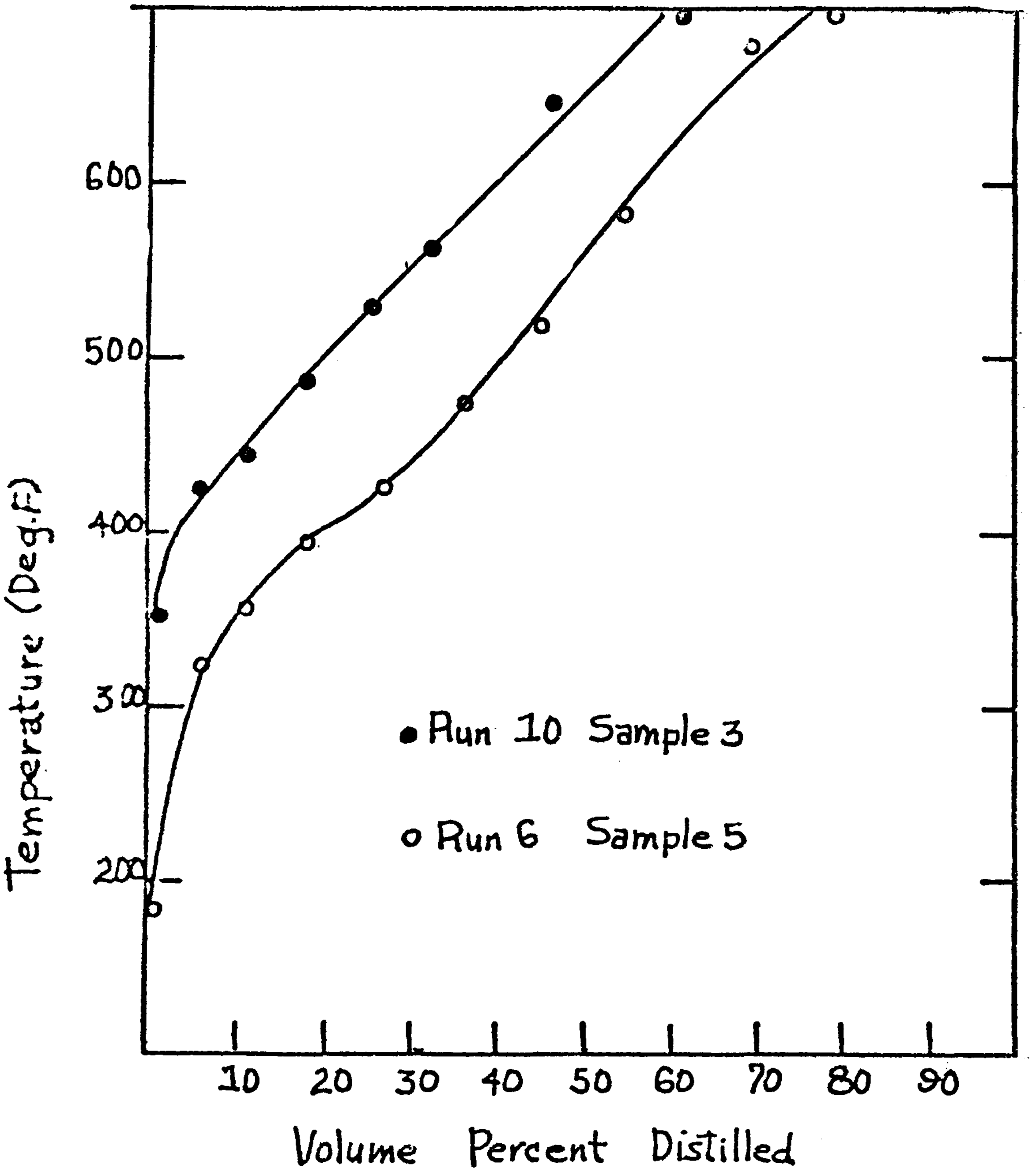
The hydrogen flow rates in run 10 were very high due to an error in calibration. It again appears that the amount of desulfurization that occurs is independent of H_2 flow above a certain minimum rate.

The product from runs 9 and 10 appeared to be much more syrup-like than that from all previous runs. After sitting for a time they appeared to grow darker in color from light, opaque brown to black, and seemed to flow less readily.

Observations on Reactor Operation and Design

Runs 5, 6 and 10 were all stopped by reactor blockage. It is felt that the reason this happened is that the product would build up around the orifice in the back pressure valve and cause it eventually to stick. For future runs, this problem will be prevented by going back to the reactor configuration used in the initial runs. This configuration is shown in Figure 6. Figure 7 shows the reactor outlet for runs 5, 6 and 10.

One of the problems with the reactor outlet shown in Figure 6 was that, after dumping the product, reopening the valve from the gas-liquid separator



Comparison of Run 10 product with Run 6 product

FIGURE 5

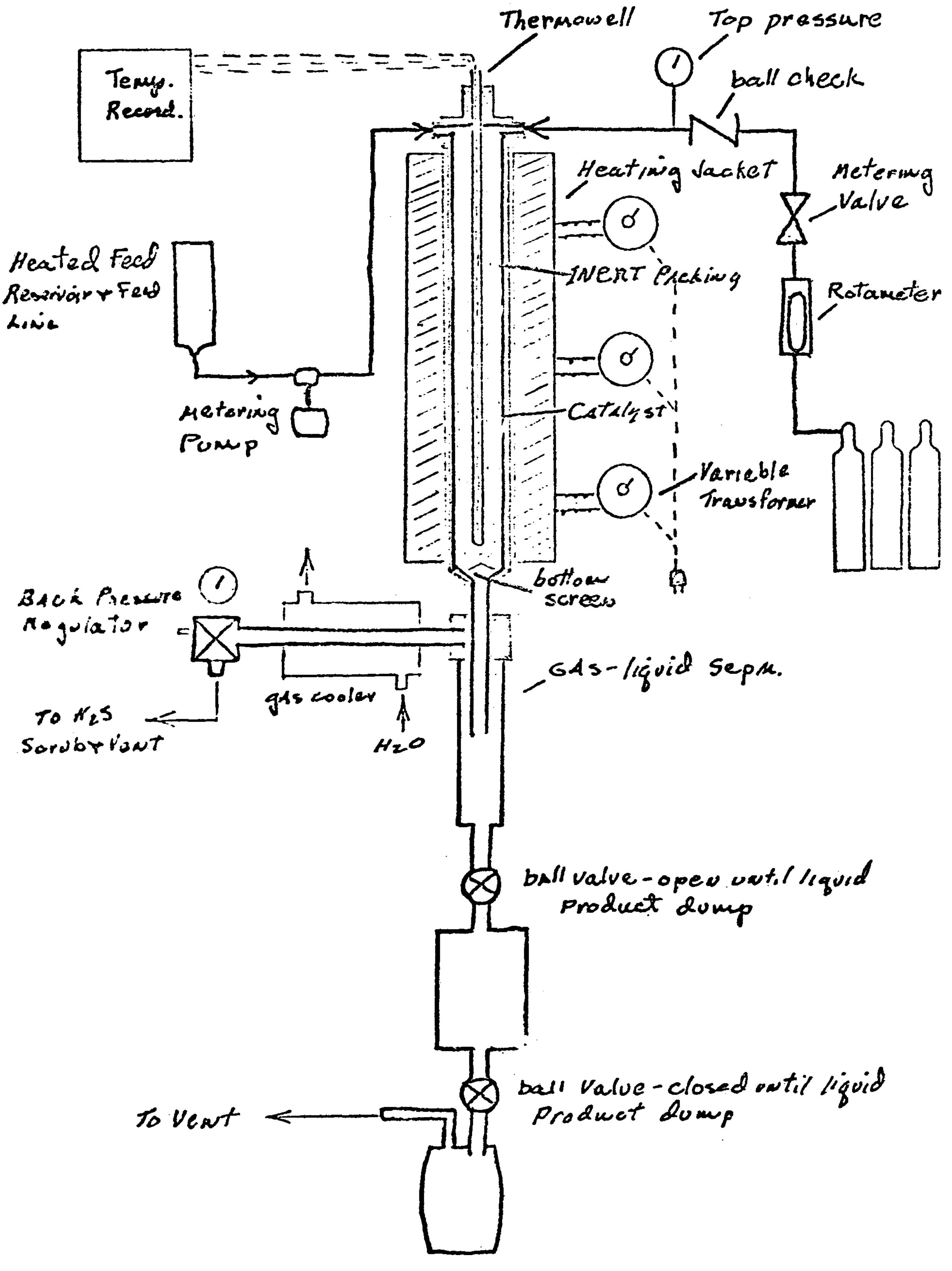
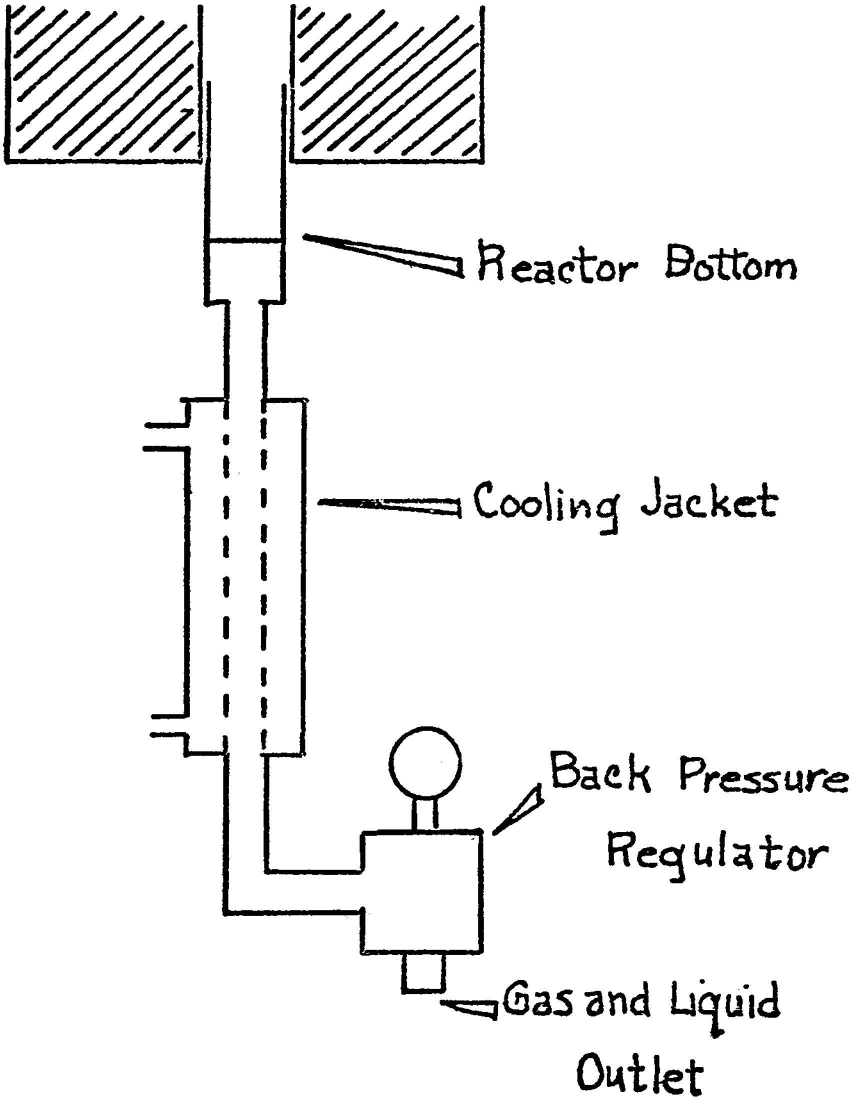

Thermowell
Top pressure
Temp. Record.
ball check
Heating Jacket
Metering Valve
Heated Feed Reservoir + Feed Line
INERT Packing
Rotameter
Metering Pump
Catalyst
Variable Transformer
Back Pressure Regulator
bottom screen
GAs-liquid Sepn.
gas cooler
To H2S Sorb + Vent
H2O
ball valve-open until liquid Product dump
ball Valve-closed until liquid Product dump
To Vent

FIGURE 6



Reactor Configuration for
Runs 5, 6, and 10

FIGURE 7

would cause the reactor to lose pressure until the hydrogen flow would again build up to the setting on the back pressure regulator. To prevent this, the catch pot will be modified as in Figure 8 to allow independent pressurization and depressurizing, thereby preventing a perturbation of the reactor pressure.

Following Quarter Work Forecast

Before any experimental work is attempted during this quarter, the reactor will be modified as in Figure 8.

It has been decided to build a separate reactor to sulfide catalysts for both batch and continuous runs. It is felt this will give better results with the batch runs and slow down component deterioration on the continuous reactor.

Catalyst testing will then continue. The following Harshaw catalysts will be tested during this quarter:

Ni 1601 - a catalyst promoted similar to run 10 with activated alumina support of high surface area.

Ni 1800 - 10% nickel oxide, 1% copper oxide on silica containing support.

Ni 3250 - an alkaline catalyst with 50% Ni.

Ni 4301 - 6% Ni, 19% W on silica alumina

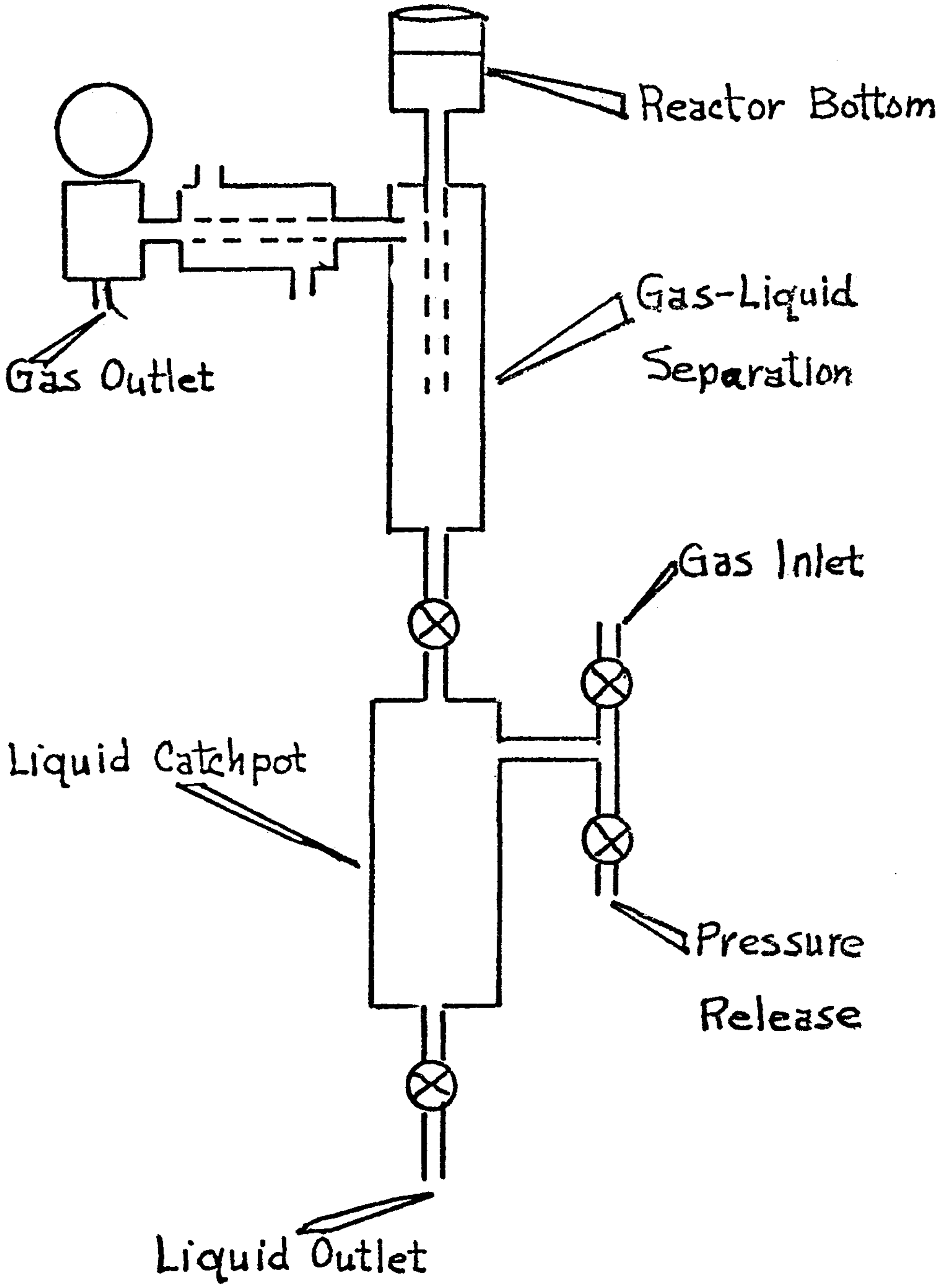
Co-Mo 0401 - 3% Ni, 9% Mo on silica.

III Conclusion From This Quarters Work

1. The Ni-W catalyst of runs 5-8 give the best cracking and desulfurization yet found.
2. Apparently, in the pressure range tested, pressure has little effect on cracking or desulfurization.
3. After a certain required amount, it seems that increasing hydrogen to liquid feed rate gives little product improvement.
4. From batch runs, it appears that long residence time might be necessary to get a better product.

IV Tables of Experimental Data

The following Table III gives all derived data from runs 5 through 10 for the COED Tar segment of this project.



Future Reactor Outlet Modifications

FIGURE 8

TABLE III. ACCUMULATED RUN DATA, RUN 5 through 10

Run # 5 - Continuous Reactor

Catalyst: Harshaw 4401, press: 800 psig, Temp. 450 C

Sample #1 LHSV: 2.25 H_2 flow: 10,000 scf/bbl

Weight % sulfur in product: 0.66%

ASTM Distillation:

Vol. %	Deg. F
IBP	266
6	336
13	387
26	435
39	487
52	552
66	637
81	698

Run #6 - Continuous Reactor

Catalyst: Harshaw 4401, press: 1000 psig, Temp: 450 C

Sample #2 LHSV: 3.12 H_2 rate: 8612 scfb

ASTM Distillation:

Weigth % Sulfur in Product: 0.78

Vol %	Deg. F	Vol %	Deg. F
IBP	180	30	514
5	333	40	538
10	390	50	606
15	415	60	662
20	450	70	698

Sample #3 LHSV: 1.69 H_2 rate: 10,700 scfb

Weight % Sulfur in Product: 0.70%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
IBP	176	20	513
6	370	40	572
11	412	57	667
17	435	69	698
23	459		

Sample #4 LHSV: .52 H_2 Rate: 34,700 scfb

Weight % Sulfur in Product: 0.39%

No ASTM Distillation possible due to insufficient product.

Sample #5 LHSV: .84 H_2 Rate: 5699 scfb

Weight % Sulfur in Product: 0.56%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
IBP	185	30	475
6	325	45	520
11	359	54	583
18	394	69	680
27	426	79	698

Sample #6 LHSV: 3.3 H_2 Rate: 23,651

Weight % sulfur in Product: 0.97%

No ASTM Distillation

Run #7 - Batch Reactor

Catalyst: Harshaw 4401 Run Temp. 450 C

Charge: COED Tar 100 ml, catalyst 25 ml; Pressure (cold):

initial 1900 psig, final 700 psig; at run temp: initial 3880; final 2570

Run time at temperature: 30 min. Max pressure at 450 C then drop

Weight % sulfur in product: 0.21%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
IBP	210	40	579
8	334	48	633
16	410	56	698
25	475	65	700
32	516		

Run #8 - Batch Reactor

Catalyst: Harshaw 440   Run Temp; 450 C   Charge COED Tar 100 ml

Cat: 25Ml, Pressure: cold, initial 1970, final: 600

at temp., initial: 3500, final: 2310   Max Pressure: 3780 at 398 c then drop

Run time at temperature: 60 minutes

Weight % sulfur in product: 0.13%

ASTM Distillation:

Vol. %	Deg. F.	Vol. %	Deg. F
IBP	203	48	584
8	320	59	657
16	386	63	691
32	482	73	700
40	523		

Run #9 - Batch Reactor

Catalyst: Harshaw Ni 1600   Run Temp. 450 C   Charge: COED Tar, 125 ml

cat: 30 ml H_2 Pressure: cold, initial: 2100, final: 1500,
hot, initial: 4190, final: 3850

Max. Pressure 4200 psi at 435 C

Run time at run temp: 30 minutes

Weight % sulfur in product: 1.26%

ASTM Distillation:

Vol. %	Deg. F.	Vol. %	Deg. F
IBP	200	42	633
1	202	60	700
13	390		
22	440		
33	542		

Run # 10 - Continuous Run

Catalyst: Harshaw Ni 1600   Pressure: 800 psig   Temp: 450 C

Sample #1   LHSV: 0.28 H_2 Rate: 34,300 scfb

Weight % Sulfur in product: 1.2%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
IBP	376	25	528
6	419	36	619
10	451	45	668
17	496	59	700

Sample #2 LHSV: .40 H_2 Rate: 45,900

Weight % sulfur in product: 1.39%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
IBP	220	30	587
7	438	39	627
15	498	42	640
20	522	56	700

Sample #3 LHSV: .83 H_2 Rate: 28,400

Weight % Sulfur in product: 1.51%

ASTM Distillation:

Vol. %	Deg. F	Vol. %	Deg. F
1	353	25	528
6	425	32	561
11	446	46	649
18	488	61	700

SYNTHOIL - by K. N. Runnion

Three continuous runs were made feeding Synthoil at different conditions to the reactor. One run was also made using a rocking bomb. Temperature, pressure and space velocity were varied for two different catalyst. The results of these runs, problems, conclusions, and future work will be discussed.

Progress

To determine if any hydrogenation and cracking have taken place and to give a quantitative comparison of the Synthoil feed and run products, an ASTM distillation is performed on the products.

ASTM distillation of Synthoil feed is used as a basis for comparison. Figure 9 is a cruve of these results. The percent Synthoil distilled is plotted vs. the temperature in degrees Fahrenheit up to 700 F which is the end point for ASTM distillation. Distillate starts coming off at 360 F and it increases gradually up to 45% at 700 F. The objective of this research is to shift this curve to the lower right.

Figure 10 is a comparison ASTM distillation of the Synthoil feed and the product from run 1. Synthoil was fed to the reactor at a space velocity of approximately 4. The run conditions were a temperature of 450 C and a pressure of 800 psig. The catalyst was sulfided Cobalt Molybdenum (Co-Mo) on silica activated Alumina (1). A hydrogen flow rate of 5000 scf per bbl of feed was used.

Product 1 had no improvement in cracking in the lower range of distillation. The slope of the curve, however, is not as steep and gives an endpoint of 53%. This shows improvement in the higher boiling fractions and is a step in the right direction.

The run was ended before more variables could be tested due to plugging of the back-pressure regulator valve with tar. It was theorized that uncracked synthoil tar was causing the plugging. So the run was repeated using a higher pressure and lower space velocity to try to increase conversion.

Run 2 was made using the same Co-Mo catalyst as in the previous run. Run conditions were 450 C and 1000 psig hydrogen pressure. A hydrogen flow rate of 10,000 scf per bbl of feed was used.

Product 1, run 2 is graphed in Figure 11. Synthoil was fed at a liquid hourly space velocity of 1.4. This product was very noticeably liquid compared to the feed stock and the product from run 1. Distillate started coming off at 250 F and 70% distilled off by the end point 700 F. This is a noticeable improvement over the Synthoil.

Figure 12 is a graph of product 2, from run 2. This is under the same conditions only with an increase in liquid hourly space velocity from 1.4 to 3. The graph shows no improvement over the Synthoil.

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(1) Catalyst and Chemicals Co. catalyst C-20-6 Cobalt Molybdenum, sample No. 1405, containing 3.5% CoO, 14% MoO_3.

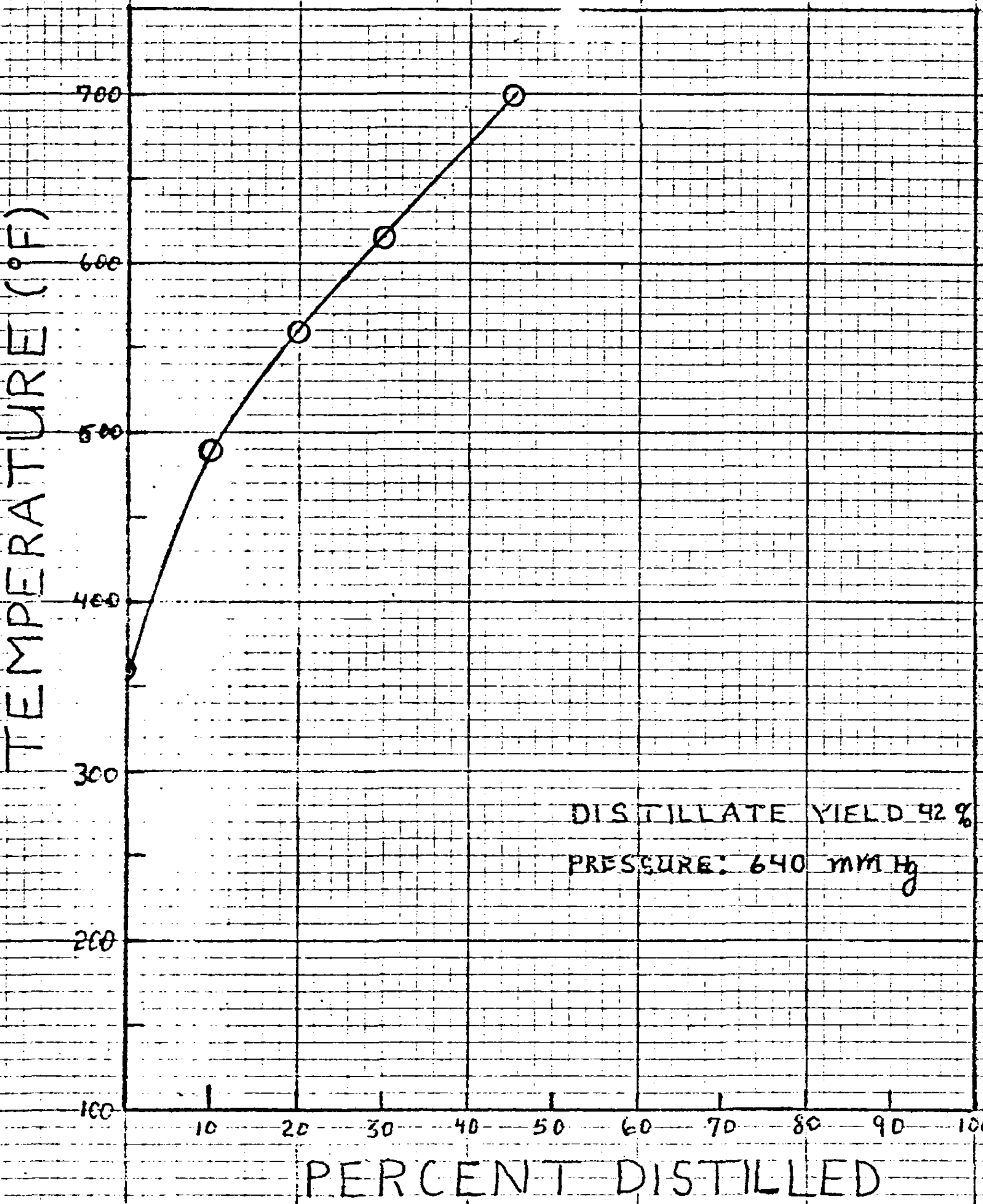

Fig 9. ASTM DISTILLATION OF SYNTHOIL

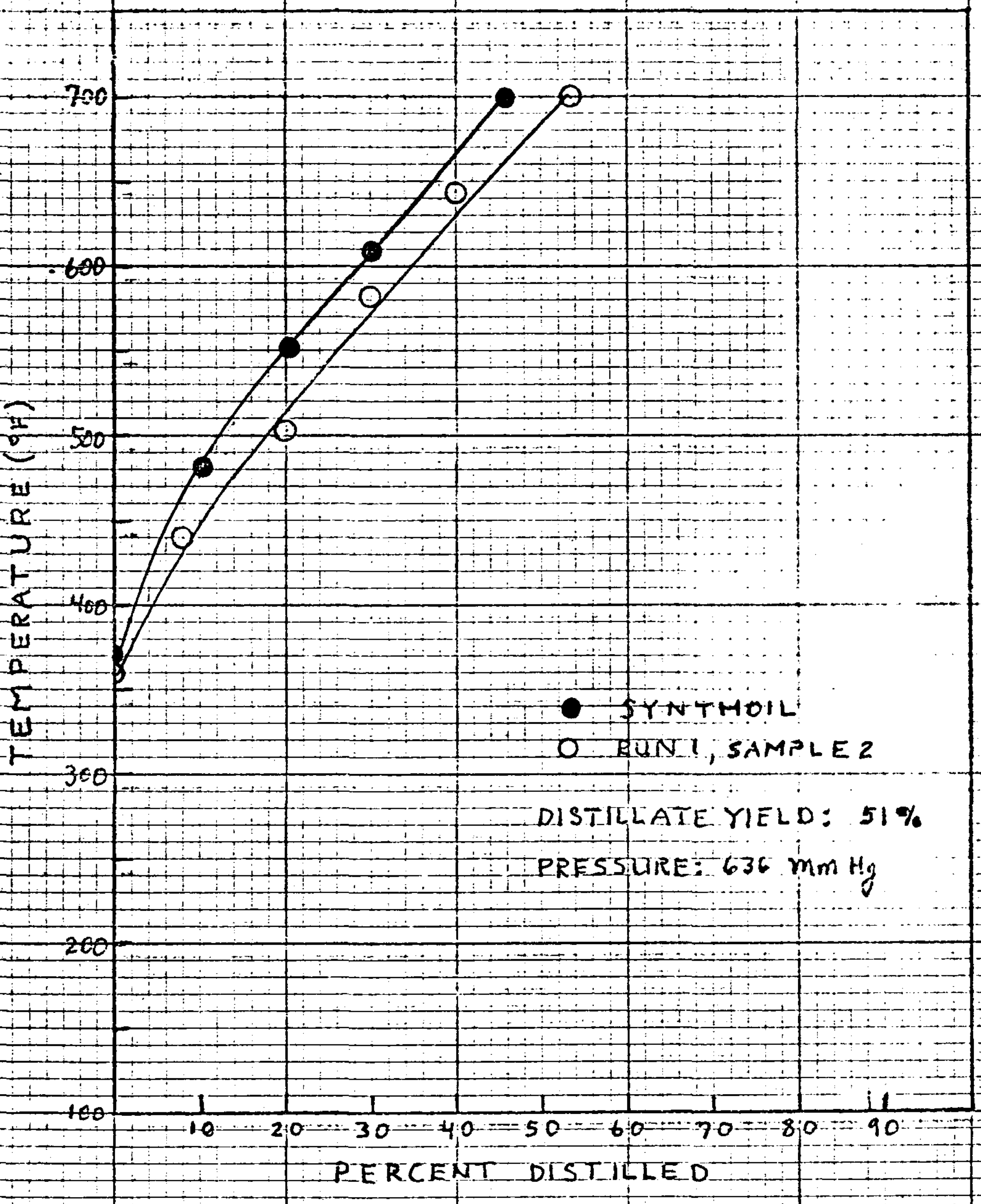

FIG 10 ASTM DISTILLATION OF RUN 1, SAMPLE 2

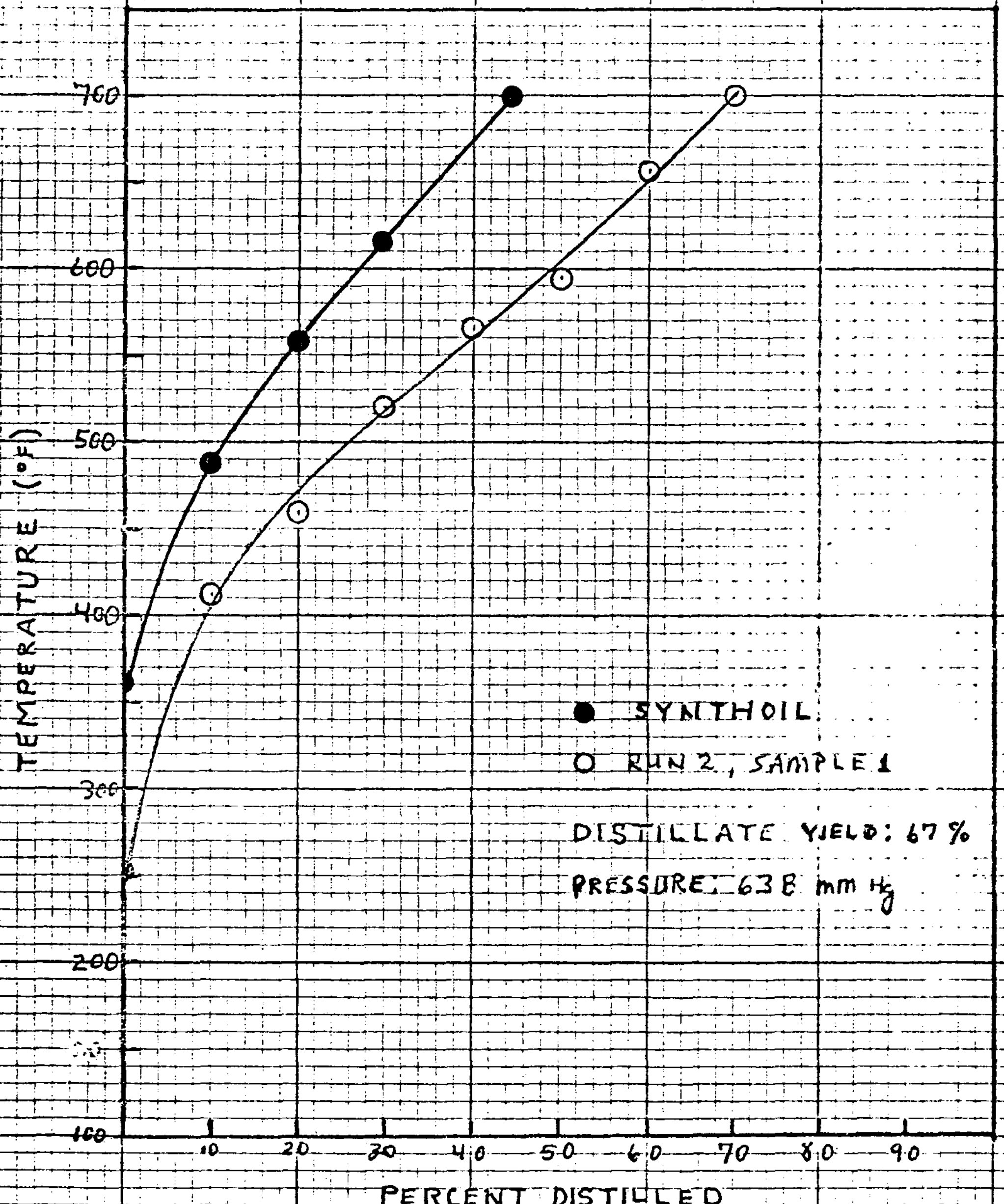

FIG 11. ASTM DISTILLATION OF RUN 2, SAMPLE 1

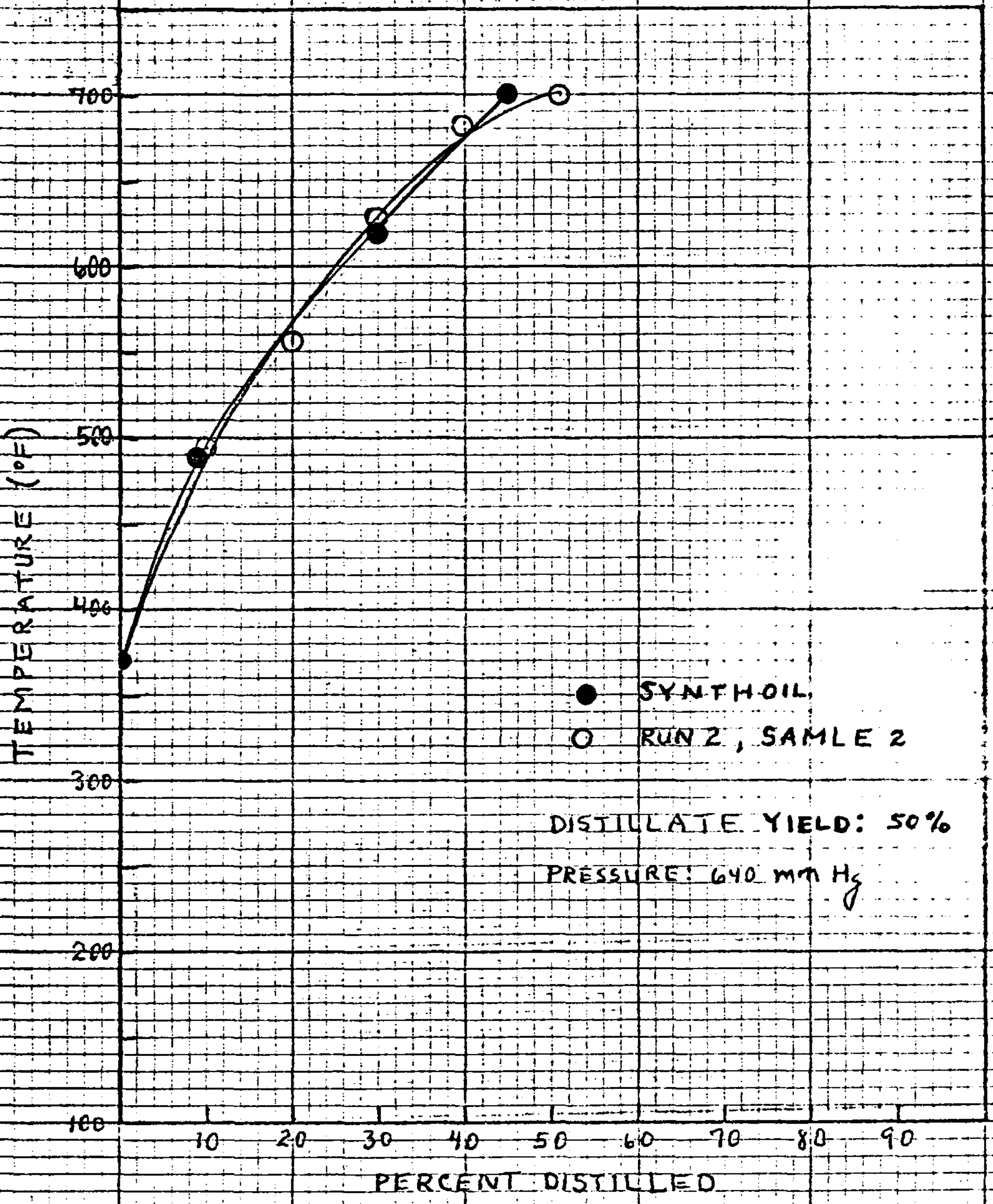

FIG 12 ASTM DISTILLATION OF RUN 2, SAMPLE 2

Again the run was ended due to plugging of the back pressure regulator valve. Since conversion seemed to drop off with time during the run, the unreacted Synthoil that was plugging the back pressure regulator might be due to carboning up of the reactor. To test this theory a temperature decrease from 450C to 400 C was decided on for the next run.

Run 3 was made using another catalyst, Nickel-Tungsten[2](Ni-W). Run conditions were a temperature of 400 C and a pressure of 800 psig. Hydrogen flow rate was 10,000 scf/bbl. Synthoil was fed at a liquid hourly space velocity of one. The product from run 3 and the feedstock are plotted on Figure 13. Distillate started coming off at a lower temperature, approximately 300 F. Endpoint for this distllation was 62% which is a definite increase over the untreated Synthoil.

Plugging of the back pressure regulator valve ended this run.

The results from S. T. Kujawa's bomb runs showed promise in predicting catalyst success. So it was decided that a bomb run should be made for each new catalyst tested. Data from the bomb runs would indicate if any improvement in the Synthoil is made, and at what temperature reaction starts.

Bomb run B1 was made using the same Ni-W catalyst as in run 3. The bomb was charged with 125 ml of Synthoil and 25 ml of Ni-W catalyst. Then the bomb was initially pressured to 2000 psig with H_2. The bomb was heated gradually to 450 C and held at this temperature for 30 minutes. A pressure drop from 4200 to 4000 psig was noted the last 15 minutes of the 30 minute run.

ASTM distillation results from run B1 are plotted in Figure 14. A slight improvement is noted over the Synthoil charged to the bomb. A longer residence time would probably have given a better product since no reaction was noted until 15 minutes into the 30 minute run.

Problems

The number one problem this quarter has been plugging of the back pressure regulator valve three to four hours into the run. This prevented any changing of parameters during the run which would have given more data. Down time between runs to clean and recharge the reactor and to sulfide the catalyst is time consuming and cuts down the number of runs that can be made.

My theory on the plugging problem is that the lighter fractions from the Synthoil feedstock are easily driven off and hydrotreated. Some of the heavier fractions are also cracked and hydrotreated, but the tar residue that is left is too thick and viscous to flow through the back pressure regulator valve. The tar accumulates during the run until it blocks the flow of even the lighter oils.

This theory is based on the observations of the product collection and the cleaning of the back pressure regulator valve and the piping from the reactor

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[2] Harshaw Catalyst, Nickel Tungsten, Ni 4401 E 1/10, sample No. 386A-1-12-1, containing 6% Ni, 19% W, 50% SiO_2, 25% Al_2O_3.

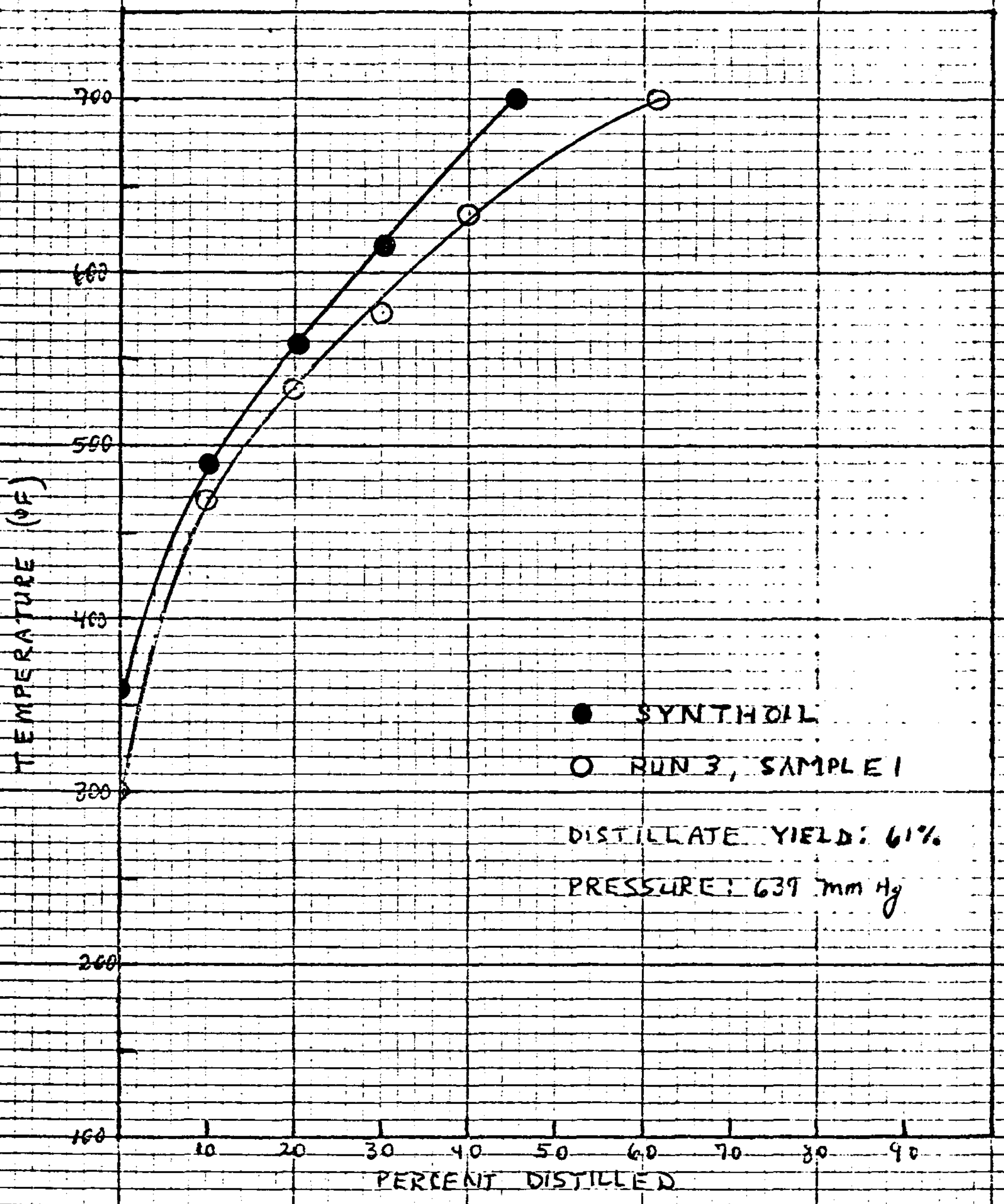


FIG 13 ASTM DISTILLATION OF RUN 3, SAMPLE 1

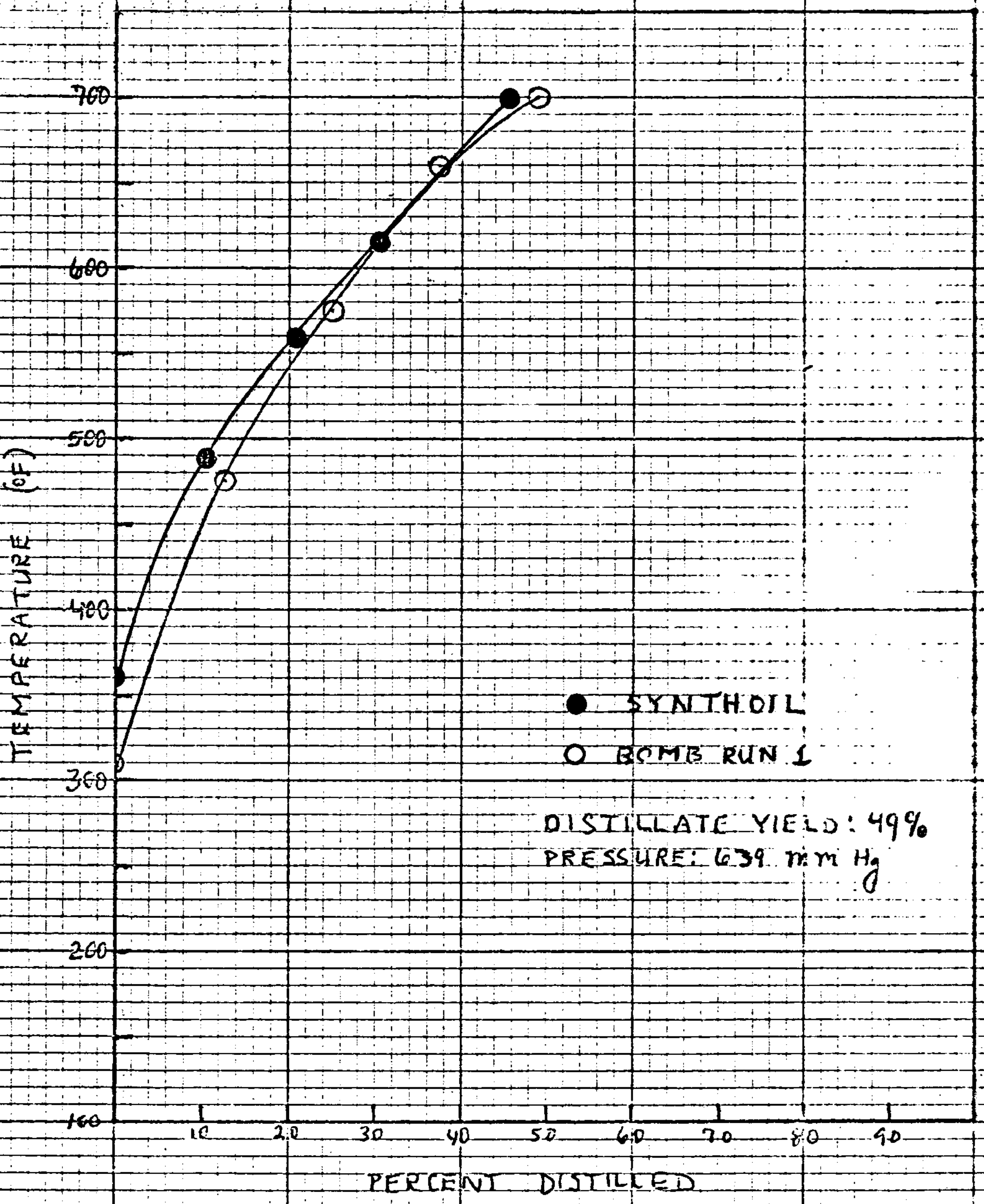


FIG 14 ASTM DISTILLATION OF BOMB RUN 1

to the valve. The first product that comes from the reactor is small continuous drops of oil. Gradually the drops change into spurts as the product surges out, then stops, then surges again. These spurts increase in intensity as they decrease in frequency. At the same time an increase in reactor pressure is noted from 10-15 psig between surges and then drops back to operating pressure with each surge of product. The run is ended when the reactor pressure increases 100-200 psig above the back pressure without any product coming off. When the reactor is taken apart for cleaning, the back pressure valve and piping from the reactor are full of tar which sometimes must be drilled out because it has solidified.

To get around this problem it has been decided to change the design of the piping coming from the reactor. Instead of running the gases and product through the back pressure valve and collecting them, only the gases will go through the valve. The gases and liquids will be separated before the back pressure valve. The liquid product will be collected at the bottom of the separator and product will be drawn off in batches.

At the end of each run a solvent will be pumped through the reactor to clean the tar off the catalyst particles and prevent any carbon laydown. This will allow the same catalyst to be reused and will decrease downtime between runs.

FUTURE WORK

Bomb runs will be made on each new catalyst before being run in the continuous reactor. This will indicate the run temperature and what kind of conversion can be expected. Bomb runs will also be made with catalysts previously tested to compare with results from any new catalyst tried.

A small reactor for reducing, drying, and sulfiding catalysts has to be built to prepare catalysts for the bomb runs.

Implementation of the new gas-liquid separator to alleviate the plugging problems and cleaning of the reactor after each run will allow runs to be long enough to vary parameters and decrease down time between runs.

Analytical analyses of the products for sulfur and nitrogen still has to be done. Sulfur analysis requires mastery of the Bico-Brown Shell design sulfur determination apparatus until duplicate results can be obtained. The Macro-Kjedahl method will be used to determine the nitrogen content of the products. This procedure needs to be set-up.

SUMMARY OF PROGRESS TO DATE

Two catalysts were tested this quarter, Co-Mo and Ni-W both on silica activiated alumina. Co-Mo was run at three different space velocities and two pressures. There was a decrease in conversion with an increase in liquid hourly space velocity from 1.4 to 3. No increase in cracking was noted with an increase in pressure from 800 to 1000 psig. The Co-Mo and Ni-W catalysts both achieved cracking of the Synthoil tar. The biggest problem in running the reactors was plugging of the backpressure regulator valve to end each run. A bomb run was also made using the Ni-W catalyst. Bomb runs will be made to test each new catalyst before they are evaluated in the continuous system.

CONCLUSIONS

The conclusions from the three runs are:

1. The Co-Mo and Ni-W catalysts gave noticable cracking of the Synthoil tar.

2. A decrease in cracking occurs with an increase in liquid space velocity.

3. No significant amount of cracking takes place with an increase in pressure from 800-1000 psig at approximately the same liquid hourly space velocities.

PAMCO SOLVENT REFINED COAL - by Lee M. Henton

SUMMARY OF PROGRESS

Additional information was gleaned from the runs and analyses this quarter. Both apparatus design and experimental approach have been modified.

Two continuous and two batch runs were attempted; the coal solvent, the run feedstock, and products from the three completed runs were analyzed by a modified ASTM petroleum products distillation test.

Runs 1 and 2 were conducted in the continuous reactor at 450 C and 1000 psia of hydrogen pressure with space velocities of 2 and 3/4 respectively. Run 1 was successful, but Run 2 was discontinued before steady state samples were obtained. The reactor plugged necessitating shutdown.

The coking and cleaning required in the continuous reactor indicated that the continuous reactor is unsuitable for initial temperature dependency tests. Batch runs are more suitable to find the lowest reaction temperature and catalyst activity.

Runs 3 and 4 were conducted in a heated bomb agitated by a rocker mechanism. Temperature and pressure were recorded during the heat-up period and the half-hour steady temperature run. A decrease in pressure at approximately 400 C suggested that this is the minimum reaction temperature for hydrogenation of the SRC coal.

The effect of higher hydrogen pressure was determined in Run 3. Initial cold hydrogen pressure was 2100 psig and run temperature was 430 C; the maximum pressure of 4075 psig occurred at a temperature of 401 C. Final cold pressure was 1000 psig, indicating quite a bit of the charge of hydrogen was consumed. The product easily poured at room temperature and yielded the highest percentage of distillate of any runs so far. Thus higher hydrogen pressure favors reaction.

The effect of lower hydrogen pressure was investigated in Run 4. The run temperature was 415 C and initial cold hydrogen pressure was 500 psig. Maximum pressure was 1100 psig at 418 C and final cold pressure was approximately 275 psig. The product again easily poured. Distillation analysis revealed that this product has fewer distillates than the high pressure product.

Distillation of the solvent alone and of the feedstock (7:2 solvent-to-SRC coal wt %) gave curves to which the other distillation can be compared.

Figures 15 to 19 are the distillation analyses.

Discussion of Work and Experiments

The first thing to be determined this quarter was a practical set of conditions for solution of solvent-refined coal (SRC). An ERDA contintors standard synthetic coal oil is used; it contains 43% tetralin, 38% 2-methylnaphthalene, 17% para-cresol and 2% gamma-picoline.

The use of as little solvent as possible made elevated temperatures necessary. But preparation of a solution at atmospheric pressure limits the practical temperatures. Substantial fuming of the solvent at temperatures above approximately 120 C meant that some of the solvent was being lost. If the most volatile component, gamma-picoline was lost during stirring, then the nitrogen characteristics of the synthetic solvent would be altered. This necessitated using a fairly large solvent-to-coal ratio to obtain solution at atmospheric pressure. The conditions of 100 C (230 F), 7:2 solvent-to-coal (wt % ratio), and 15 minutes of stirring are necessary to prepare 1500 ml of feedstock.

A modification of the continuous reactor was necessary to handle the hot solution. The feed reservoir, pump, valves, and lines to the reactor are now heated by flexible heating tape. A higher temperature pump was obtained and calibrated using an oil at 230 F.

Run 1

The first series of runs were planned originally to survey the range of space velocities from 2 to 1/4; the space velocity found to give the best results would be used in subsequent runs. The temperature, pressure, and catalyst were 450 C, 1000 psig, and 100 ml of Harshaw Ni-W catalyst (Ni-4401 E 1/10 368 A-1-12-1). Hydrogen flow rate was 10,000 scf/bbl; S. Kujawa found this to be sufficient to overcome mass diffusion limitations using FMC taf feed. It was assumed that this is sufficient for my feedstock also. The temperature, pressure and catalyst were chosen because S. Kujawa and K. Runnion had used similar conditions.

Run 1 was conducted at a space velocity of 2. 475 ml of product was collected during approximately 2 hours of steady-state run.

Run 2 was conducted at a space velocity of 3/4. No steady-state product was collected. The hydrogen rate and pressure varied drastically during the unsteady period. Product sometimes came out as black foam. The gas rate was never established at the steady necessary value. Run 2 was abandoned and clean-up procedure was initiated.

Cleaning the reactor by pumping toluene under pressure was attempted, but was unsuccessful. Cleaning by pumping SRC solvent was initiated but abruptly stopped when the system plugged and the pressure rapidly rose to 1600 psig. Reactor was immediately shut down.

Preliminary results from these two runs are as follows:

1) A hard carbon block was set up in the reactor. We speculated that the product was cracked too far by excess temperature. Therefore future runs will be confined to lower temperatures.

2) The hydrogen rate will have to be set by wet-test meter before any liquid is pumped. Once set, the H_2 rate should not be adjusted.

3. The reactor should not be heated if the thermowell is stuck in it. Heating sets up the carbon even harder in the pipe reactor.
4. A thick heating oil will be pumped through the reactor to clean it out at the end of a run (Toluene is unsuitable until reactor cools).
5. The thermowell should be pulled while the reactor is still warm from the run.
6. The low space velocity may have contributed to the coking. A space velocity of 2 will probably be used for future work.
7. The gas check valve was gummed up - a stronger one will be used in the future.
8. Batch bomb runs should be used to search for activity since bombs are simpler and faster to prepare, operate and clean.

Runs 3 and 4

The plan for these runs was to evaluate the activity of the same Ni-W catalyst used before to find reaction temperature, and to determine the effect of pressure. The reaction temperature can be determined during the heat-up period in a bomb (batch) run by noting the temperature at which the hydrogen pressure decreases.

Batch runs are made by charging a quantity of solvent, SRC coal, and catalyst into a pressure bomb. A gauge on the top of the bomb indicates pressure and a thermocouple inserted in the base of the bomb indicates temperature. The bomb is mounted in a heater and agitated by a rocker mechanism.

Conditions for Run 3 were as follows: charge of 125 ml of feedstock, 20 gr of Ni-W catalyst, and initial hydrogen pressure of 2100 psig. The run was one-half hour long at a temperature of 430 C. 430 C was picked because it was below the coking temperature of 450 C but above the reaction temperature observed by S. Kujawa with FMC tar. The half hour run time was strictly arbitrary.

The pressure reached a maximum of 4075 psig at 401 C at about 1 hour 10 minutes into the heat-up perid. After a half hour run at the planned temperature the bomb was pulled from the heater and allowed to cool overnight. The final cold pressure (at room temperature) was 1000 psig.

The product from Run 3 was a black, easily poured liquid at room temperature. A pungent smell was present upon opening the bomb. Figure 18 shows the distillation curve.

Run 4 was similar to Run 3, but was conducted at a maximum pressure of approximately 1000 psig, which is the same pressure the continuous unit ran at. 125 gr of feedstock and 20 gr of Ni-W catalyst were charged; initial hydrogen pressure was 500 psig. The run was planned to last one-half hour at 415 C.

The pressure reached a maximum of 1100 psig at 418 C at about 50 minutes into the heat-up period. The final cold pressure of hydrogen was approximately 275 psig, and a pungent odor was present when the bomb was opened. The product was a black, easily-poured liquid; it wet some of the sides of the beaker, but not all. Figure 19 shows the distillation curve of the Run 4 product.

Preliminary results from Runs 3 and 4 are as follows:

1. The products are completely liquid at room temperature.

2. The minimum reaction temperature appears to be about 400 C.

3. Both low and high pressure runs have consumed hydrogen.

4. A larger charge of feedstock should be made to the bomb since some product is lost to entrainment on the catalyst particles. (Distillation test calls for 100 ml of material).

Distillation Analyses

The object of this project is to hydrogenate coal compounds to useful distillate fuels, so a distillation analysis of the materials before and after is important. The ASTM Petroleum Products distillation test D-86-72 is used, with modification. Usually it takes more time than specified to distill the coal liquids without excess bumping and boil overs. Also, a foil cup around the bottom of the distillation flask serves to distribute the heat better and allows a better distillation.

The feedstock used in all runs is a 7:2 (wt %) ratio of solvent-to-SRC coal. The distillation curve of the solvent alone is shown in Figure 15 and the curve of the complete feedstock is shown in Figure 16.

Figure 15 shows that 98% of the solvent will distill below 470 F and 2% decomposes above this temperature.

Figure 16 shows the distillation curve of the 7:2 feedstock solution. This curve can be used as a base to compare other curves. The charge to the still flask is always 100 ml; the amount of distillate from the feedstock solution is 79 ml. with the endpoint at 475 F. The undistilled material begain decomposing at that point - there are 21 ml of non-distillables from a 100 ml charge.

The distillation curve of Run 1 product shows that a bit of improvement was made. Figure 17 compares the feedstock curve to the product curve. The solvent is essentially uncharged, since the two curves nearly match along their length. The product had more distillate, though: 81.5 ml came off by 490 F. The 81.5-79/21 approximately 12% conversion into distillates. The comparison rests on the assumption that if the solvent was hydrogenated, no volume charge occurred. One other favorable observation can be drawn from Figure 17 - most of the product curve matches the feedstock curve (except on the low end). Therefore the coal was hydrogenated and not the solvent.

Figure 18 compares the Run 3 curve with the feedstock curve. Run 3 was the high pressure half-hour bomb run. A considerable amount of distillate came off (85.5 ml by 442 F).

This distillation was difficult to accomplish - the charge bumped excessively at about 350 F and the distillation had to be done three times before it was successful.

The percent conversion for Run 3 is 85.5-79/21 = 31%. The spread of the curve in Figure 18 indicates that the solvent was partially hydrogenated in this run. The largest difference between feed and product is at the initial boiling point, consistent with Run 1.

Perhaps several things could be done to improve the product from Run 3. If less solvent were used, more coal might react. In batch bombs this would be entirely feasible - the separate coal and solvent can be charged with the catalyst and heated under hydrogen pressure. The coal would probably dissolve at temperatures below 400 C, then react when it reaches 400 C. Another variable which could change conversion is residence time in the bomb. If the catalyst survey finds some good prospects, those two factors could be optimized.

Run 4 was a low pressure ½ hour bomb run. In Figure 19 the distillate curve is compared to the feedstock curve. The product line is almost uniformly below the feedstock line - this suggests that the solvent was highly hydrogenated. An endpoint of 81.5% was observed at 427 F. This is again a yield of 12%; though the initial boiling point and amount of distillate obtained are the same. The curve of Run 4 differs considerably from the curve of Run 1. The solvent was much more hydrogenated in the bomb run.

Design Changes

Due to S. Kujawa's observations of his continuous reactor, it was decided that a modification of the reactor outlet system would help prevent coking. S. Kujawa deduced that the back-pressure regulator valve is a bottleneck in the system; since the valve has small clearances on its moving parts, it is suseptible to gumming and backing up of material. This may lead to coking.

To alleviate the bottleneck, the liquids will be collected batchwise in a pressurized pot, while the gases may be passed continuously through the back-pressure regulator.

Conclusions

1. Solvent refined coal will dissolve at atmospheric pressure at a ratio of 7:2 wt% solvent-to-coal and 230 F.
2. The 7:2 feedstock solution has a definite temperature range for operation; a temperature of 450 C will coke the reactor, but the lowest reaction temperature is 400 C.
3. Batch reactors are more suitable for initial catalyst screening then continuous reactors; batch bombs will be used initially in the future.
4. A liquid hourly space velocity of 2 is practical for continuous runs.
5. The continuous reactor should be cleaned immediately after a run to help prevent coking.
6. High hydrogen pressure favors the converison reaction.
7. Harshaw's Ni-W catalyst Ni-4401 E 1/10 368 A-1-12-1 will yield a conversion of 12% at 415 C and 1000 psig; it yields a conversion of 31% at 430 C and 4000 psig.
8. Continuous reactors hydrogenate the coal solvent less than batch reactors under similar conditions.
9. Future runs should be made at about 1500 psig since hydrogen pressure favors reaction and 1500 psig is attainable in the continuous reactors.

Future Experiments

The next two catalysts to be evaluated will be Co-Mo and NiS. A bomb run of solid SRC particles and powdered catalyst particles, without solvent, is also considered. Bomb runs using various amounts of solvent are also being considered.

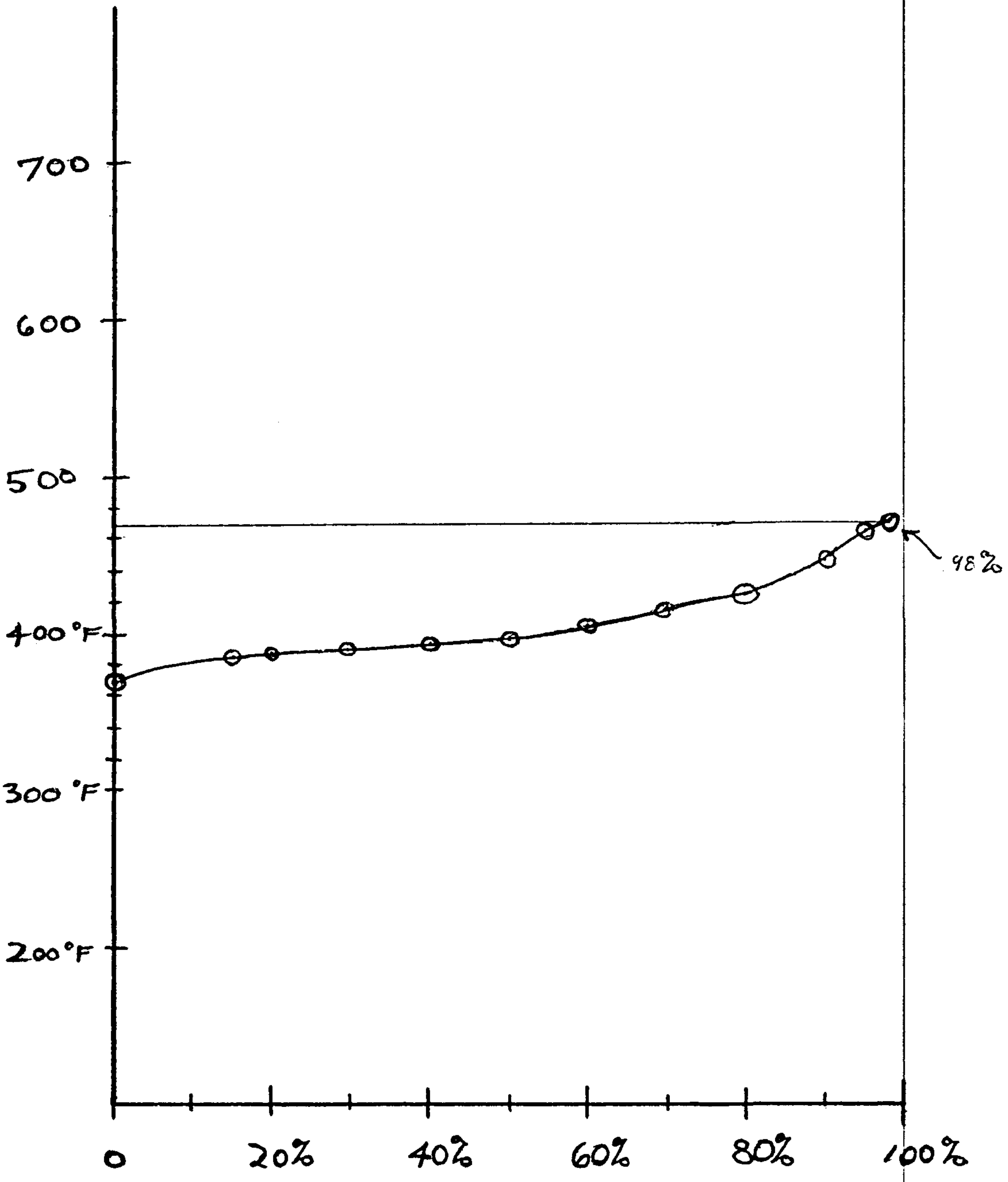


Figure 15 DISTILLATION OF SOLVENT ALONE

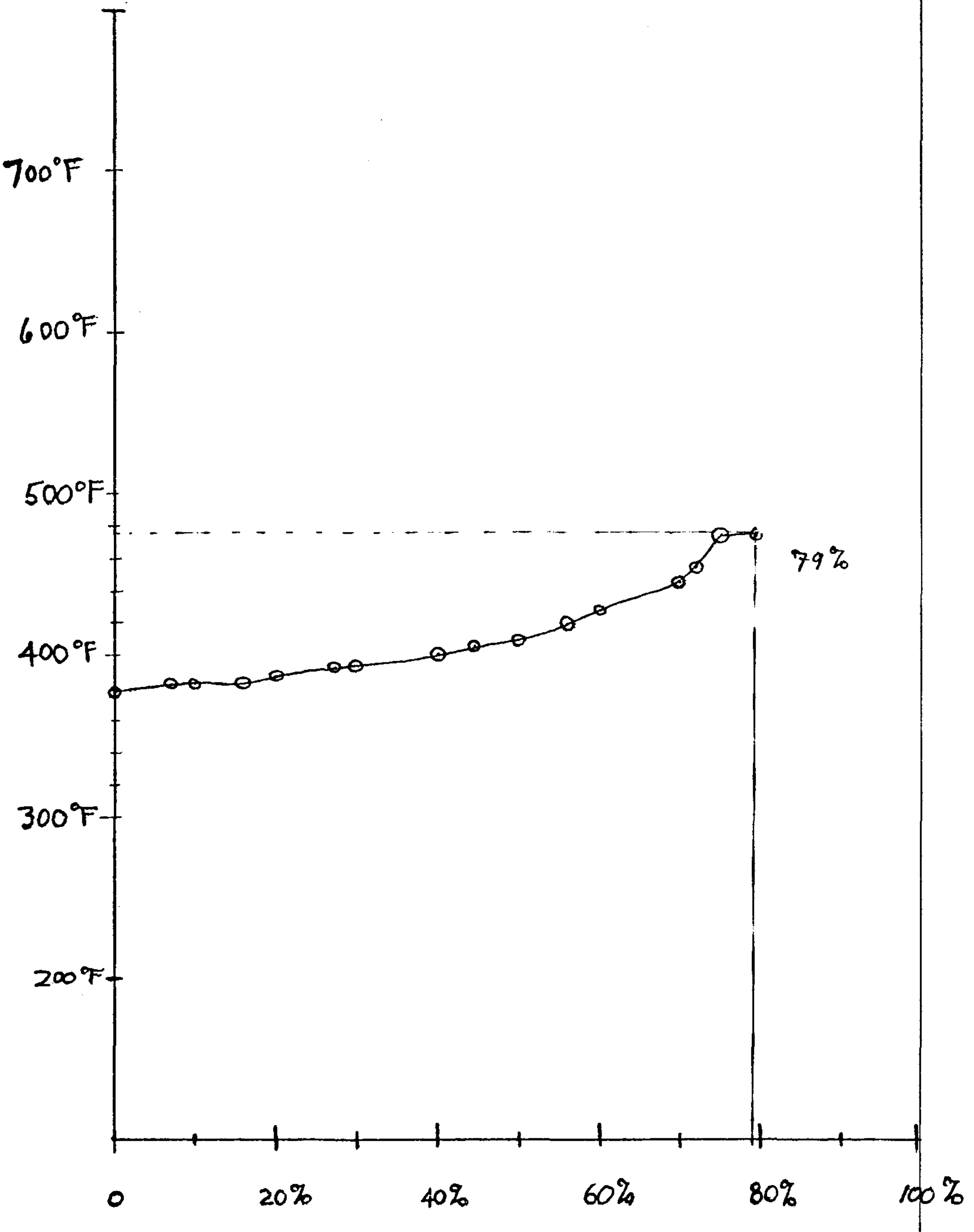


Figure 16 FEEDSTOCK DISTILLATION CURVE
7:2 Solvent - To - SRC Coal (WT %)

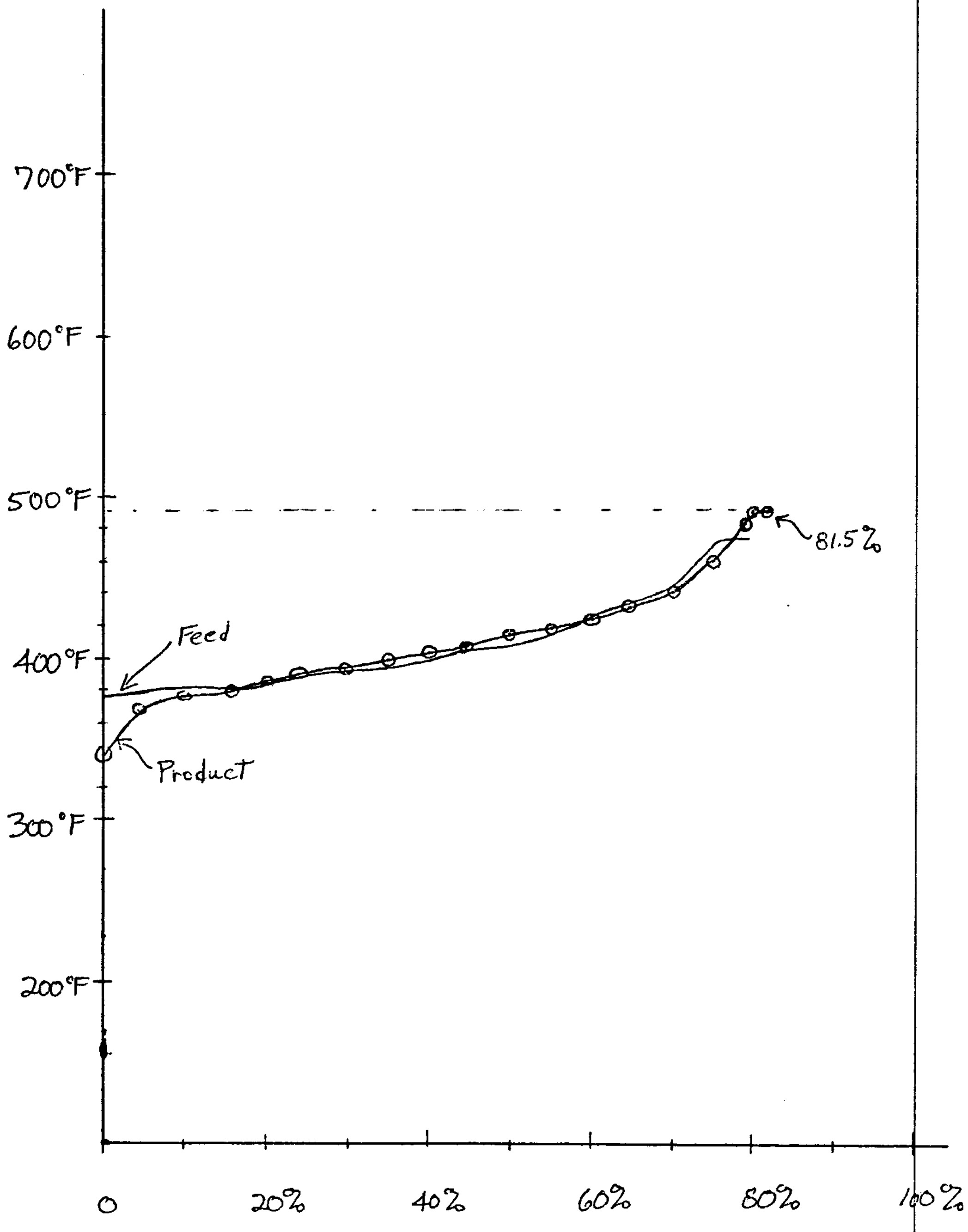


Figure 17 RUN #1 PRODUCT DISTILLATION CURVE

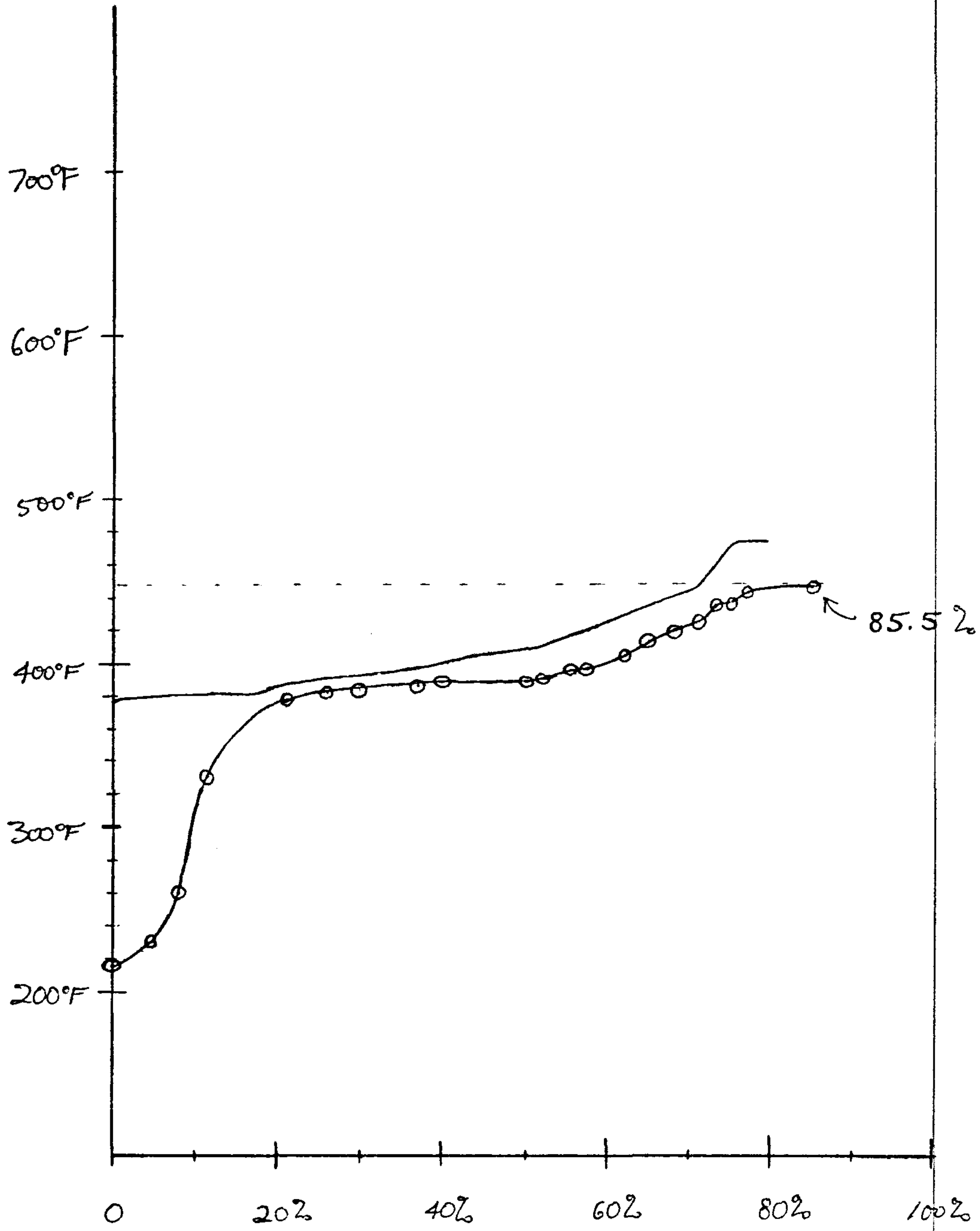


Figure 18 RUN #3 PRODUCT DISTILLATION CURVE

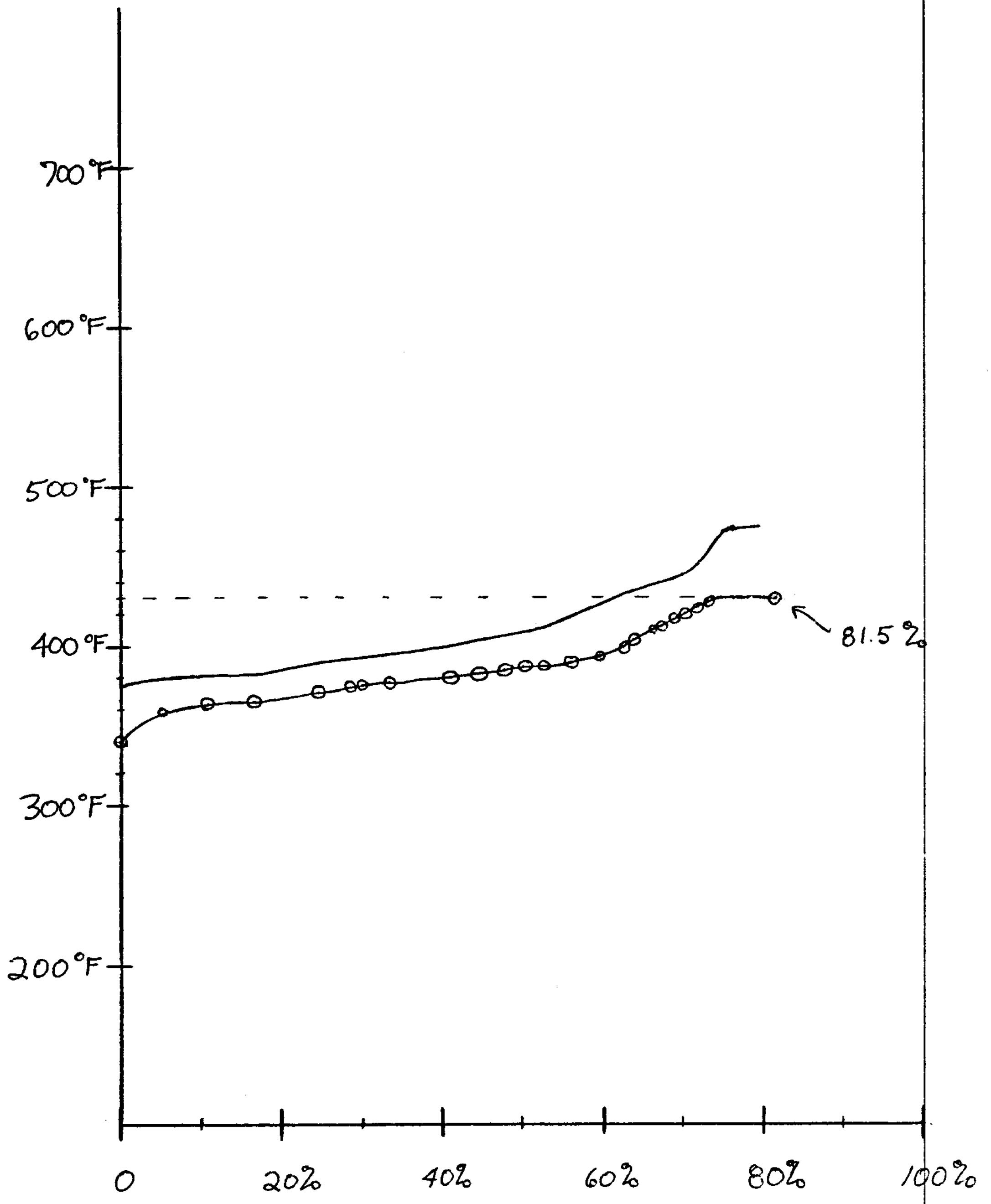
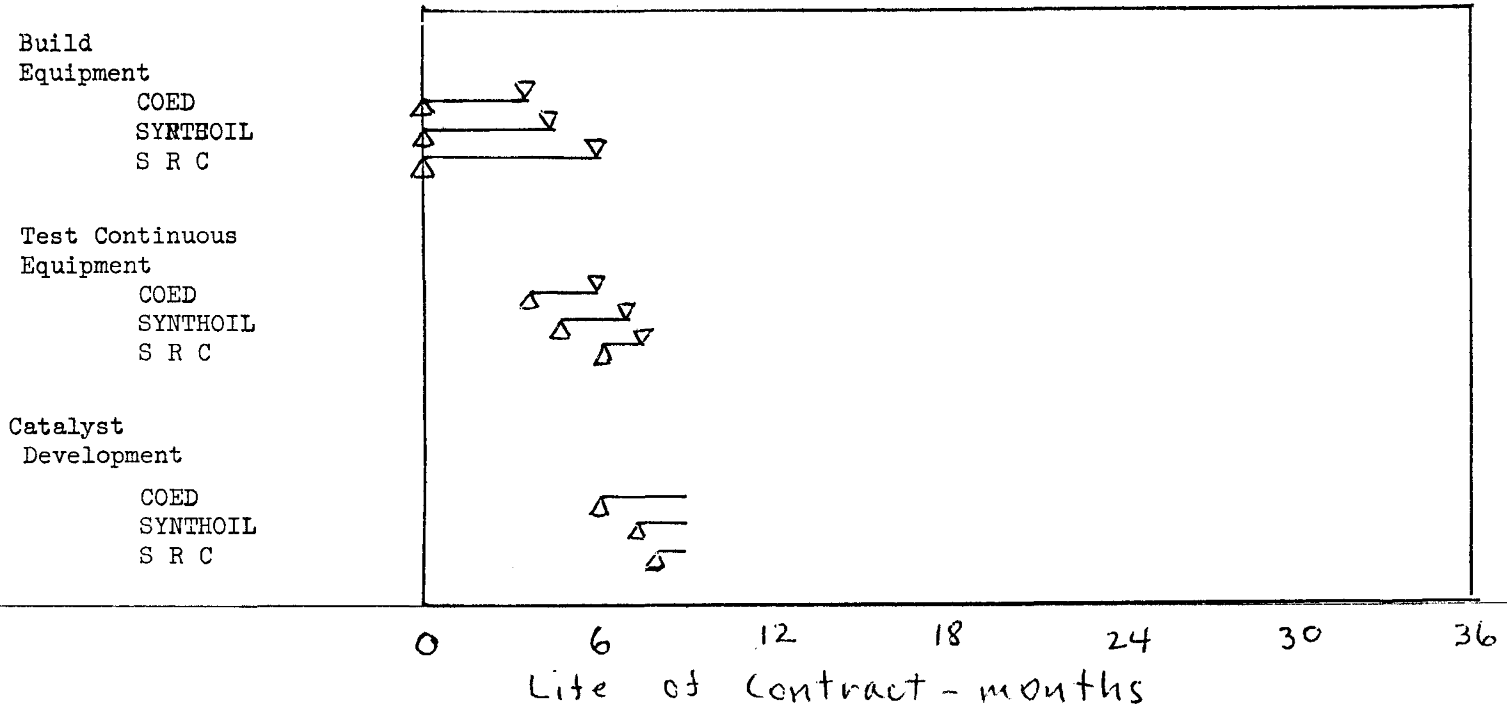


Figure 19 RUN #4 PRODUCT DISTILLATION CURVE

PICTORIAL PROGRESS REPORT



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G & C              PROJECT FINANCIAL REPORT               NO. 789              MARCH 31, 1976

DEPT 6131    BERG          DISTILLATE FUELS            BEGIN DATE 07-01-75   END DATE 01-01-76

                       CURRENT MO.          TOTAL TO DATE                AMT. AUTH.

RECEIPTS                         .00                  .00                155932.00


                                                      ENCUMBRANCES   TOTAL COMMITTED     BUDGET
EXPENDITURES
  SALARY AND WAGES        1550.00             11320.00     4650.00        15970.00          68657.
  BENEFITS                 117.68               511.16                      511.16           4255.
  TRAVEL                                        322.50                      322.50           3000.
  COMPUTER                                                                                   3000.
  SUPPLIES                 559.88              3214.21      752.88         3967.09          12750.
  EQUIPMENT                                    1310.86       13.49         1324.35          12700.
  AWARDS                                        684.55                      684.55           6000.
  INDIRECT CHARGES                                         45570.00        45570.00          45570.

TOTAL                     2227.56             17363.28     50986.37       68349.65         155932.

  BALANCE           CASH -17363.28                       FREE BALANCE     87582.35


DETAIL                 DATE          NUMBER       DESCRIPTION                  AMOUNT        TOTAL
TRANSACTION            -  -7                     BERG LLOYD                   570.00
                       -  -7                     RUNNION KENNETH N            300.00
                       -  -7                     KUJAWA STEPHAN T             350.00
                       -  -7                     MCCANDLESS FRANK P           330.00
                                                                                            1550.00
                     03-03-76       J600376      FEB MT UCC                     1.80
                     03-03-76       J600377      FEB SOCIAL SECURITY           52.64
                     03-03-76       J600378      FEB MT I A                     2.26
                     03-03-76       J600379      FEB TRS                       56.24


                                                        NO. 789               PAGE  1 OF  2
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G & C PROJECT FINANCIAL REPORT NO. 789 MARCH 31, 1976

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	03-03-76	J600381	FEB GROUP MED INS	4.74	
					117.68
	03-04-76	4604549	IDAHO VALVE&FITTING	140.93	
	03-04-76	4604582	VWR SCIENTIFIC	16.43	
	03-17-76	4604926	B S & B INC	164.88	
	03-18-76	4605153	DEPT CHEM STORES	69.82	
	03-19-76	4605191	SARGENT-WELCH SCI	77.14	
	03-25-76	4605387	CHEMISTRY STORES	15.38	
	03-30-76	4605495	SARGENT-WELCH SCI CO	23.18	
	03-30-76	4605496	BROOKLYN THERMOMETER	52.12	
					559.88
ENCUMBRANCE	03-31-76		SALARY ENCUMBRANCE	4650.00	
					4650.00
	01-06-76	17492	COASTAL ENGINEERING	588.00	
	03-11-76	17611	BLACK SIVALLS & BRY	164.88	
					752.88
	12-17-75	17454	MINE SAFETY APPLIAN	13.49	
					13.49

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G & C                   PROJECT FINANCIAL REPORT            NO. 789            APRIL 30, 1976

DEPT 6131   BERG          DISTILLATE FUELS             BEGIN DATE 07-01-75   END DATE 01-01-76

                        CURRENT MO.         TOTAL TO DATE               AMT. AUTH.

RECEIPTS                        .00                 .00                155932.00


                                                      ENCUMBRANCES   TOTAL COMMITTED     BUDGET
EXPENDITURES
  SALARY AND WAGES          1550.00            12870.00      3100.00        15970.00      68657.
  BENEFITS                   117.68              628.84                        628.84       4255.
  TRAVEL                     300.84              623.34                        623.34       3000.
  COMPUTER                                                                                  3000.
  SUPPLIES                  1033.90             4248.11       588.00         4836.11      12750.
  EQUIPMENT                                     1310.86        13.49         1324.35      12700.
  AWARDS                                         684.55                        684.55       6000.
  INDIRECT CHARGES                                          45570.00        45570.00      45570.

TOTAL                       3002.42            20365.70     49271.49        69637.19     155932.

  BALANCE            CASH -20365.70                      FREE BALANCE       86294.81


DETAIL               DATE          NUMBER     DESCRIPTION                AMOUNT           TOTAL
TRANSACTION         -  -7                     BERG LLOYD                 570.00
                    -  -7                     RUNNION KENNETH N          300.00
                    -  -7                     KUJAWA STEPHAN T           350.00
                    -  -7                     MCCANDLESS FRANK P         330.00
                                                                                       1550.00
                  04-08-76      J600446     MAR MT UCC                     1.80
                  04-08-76      J600447     MAR SOCIAL SECURITY           52.64
                  04-08-76      J600448     MAR MT IA                      2.26
                  04-08-76      J600450     MAR GROUP MED INS              4.74



                                                  NO. 789                 PAGE  1 OF  2
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DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	04-08-76	J600451	MAR TRS	56.24	
					117.68
	04-01-76	4605560	COASTAL ENGR CORP	502.40	
	04-08-76	4605938	HARSHAW CHEMICAL CO	62.40	
	04-14-76	4606162	MATHESON GAS PROD	35.76	
	04-22-76	4606312	MSU BOOKSTORE	5.35	
	04-23-76	4606417	CHEMISTRY STORES	120.20	
	04-27-76	4606524	GENERAL DISTRIBUTING	268.91	
	04-29-76	J600491	4605153 CHEM STORES	38.88	
					1033.90
	04-14-76	4606130	LLOYD BERG	300.84	
					300.84
ENCUMBRANCE	04-30-76		SALARY ENCUMBRANCE	3100.00	
					3100.00
	01-06-76	017492	COASTAL ENGINEERING	588.00	
					588.00
	12-17-75	017454	MINE SAFETY APPLIAN	13.49	
					13.49

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G R C                  PROJECT FINANCIAL REPORT                    NO. 789                  MAY 31, 1976

DEPT 6131    BERG              DISTILLATE FUELS                    BEGIN DATE 07-01-75   END DATE  6-19-78

                             CURRENT MO.          TOTAL TO DATE                     AMT. AUTH.

RECEIPTS                           .00                    .00                     155932.00


                                                                   ENCUMBRANCES   TOTAL COMMITTED      BUDGET
EXPENDITURES
   SALARY AND WAGES          1550.00              14420.00           1550.00          15970.00        68657.
   BENEFITS                   117.68                746.52                              746.52         4255.
   TRAVEL                                           623.34✓                             623.34         3000.
   COMMUNICATIONS              16.87                 16.87                               16.87
   COMPUTER                                                                                            3000.
   SUPPLIES                   281.22               4529.33                             4529.33        12750.
   EQUIPMENT                                       1310.86✓                            1310.86        12700.
   AWARDS                     181.00                865.55✓                             865.55         6000.
   INDIRECT CHARGES          9234.56               9234.56✓         36335.44          45570.00        45570.

TOTAL                       11381.33              31747.03          37885.44          69632.47       155932.

   BALANCE           CASH -31747.03                             FREE BALANCE    86299.53


DETAIL                 DATE            NUMBER       DESCRIPTION                      AMOUNT            TOTAL
TRANSACTION           6 -7                         BERG LLOYD                       570.00
                      6 -7                         RUNNION KENNETH N                300.00
                      6 -7                         KUJAWA STEPHAN T                 350.00
                      6 -7                         MCCANDLESS FRANK P               330.00
                                                                                                  1550.00
                    05-30-76          J600514      APR SOC SEC                       52.64
                    05-30-76          J600516      APR TRS                           56.24
                    05-30-76          J600517      APR MT IA                          2.26
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Adjustment to costs to date $1140.86 by JV

G K C PROJECT FINANCIAL REPORT NO. 789 MAY 31, 1976

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	05-30-76	J600518	APR UCC	1.80	
	05-31-76	J600524	APR GROUP MED INS	4.74	
					117.68
	05-06-76	4606870	DEPT CHEM STORES	15.32	
	05-06-76	4606870	DEPT CHEM STORES	23.93	
	05-06-76	4606870	DEPT CHEM STORES	6.12	
	05-06-76	4606871	DEPT CHEM STORES	8.00	
	05-06-76	4606871	DEPT CHEM STORES	21.99	
	05-12-76	4607067	DEPT CHEM STORES	13.62	
	05-12-76	4607067	DEPT CHEM STORES	33.43	
	05-18-76	4607317	HARSHAW CHEMICAL CO	21.60	
	05-19-76	4607444	CHEMISTRY STORES	55.75	
	05-26-76	4607641	CHEMISTRY STORES	19.77	
	05-17-76	J600557	G K C XEROX MAY 76	46.50	
	05-21-76	J600561	XEROX LIBR COPY SVC	15.19	
					281.22
	05-04-76	J600562	LONG DISTANCE TEL	16.87	
					16.87
	05-30-76	J600560	INDIRECT COSTS T0999	8093.70	
					8093.70
	05-12-76	4607065	MONT STATE UNIV	82.30	
	05-12-76	4607065	MONT STATE UNIV	98.70	
					181.00
ENCUMBRANCE	05-31-70		SALARY ENCUMBRANCE	1550.00	
					1550.00