

II. EXPERIMENTAL WORK

A. Equipment and Method of Operation

1. Synthesis Gas Generation

The synthesis gas mixture of carbon monoxide and hydrogen was the product of the uncatalyzed reaction between natural gas and oxygen at 425 psig and at temperatures in the 2300°F. range. The natural gas contained approximately 85 per cent methane, 2.0 per cent CO₂, 9.0 per cent ethane, 3.5 per cent propane, and small amounts of butane and nitrogen. The generator product gas was composed of hydrogen and carbon monoxide in the ratio of 1.5-1.7:1 and normally contained less than 2.5 per cent unconverted methane, 3 per cent carbon dioxide, and less than one per cent nitrogen.

During Run 48 before the synthesis gas entered the reactor, it was scrubbed and cooled by passing through a water-wash tower. This tower contained an 18" by 25' bed of one-inch, carbon raschig rings kept moist by a cold water spray. The temperature of the effluent gas was approximately 70°F., and the water content corresponded to saturation at 70°F. instead of saturation at 140-150°F. as had existed before the scrubbing tower was used.

The generator system has been described in detail in previous reports¹ and since it serves only as a utility unit for the reactor, no further details are included in the present report.²

2. Catalyst Pretreatment and Reduction

The base material for the catalyst was Alan Wood run-of-the-mine magnetite concentrate, on which a sieve analysis showed the following results:

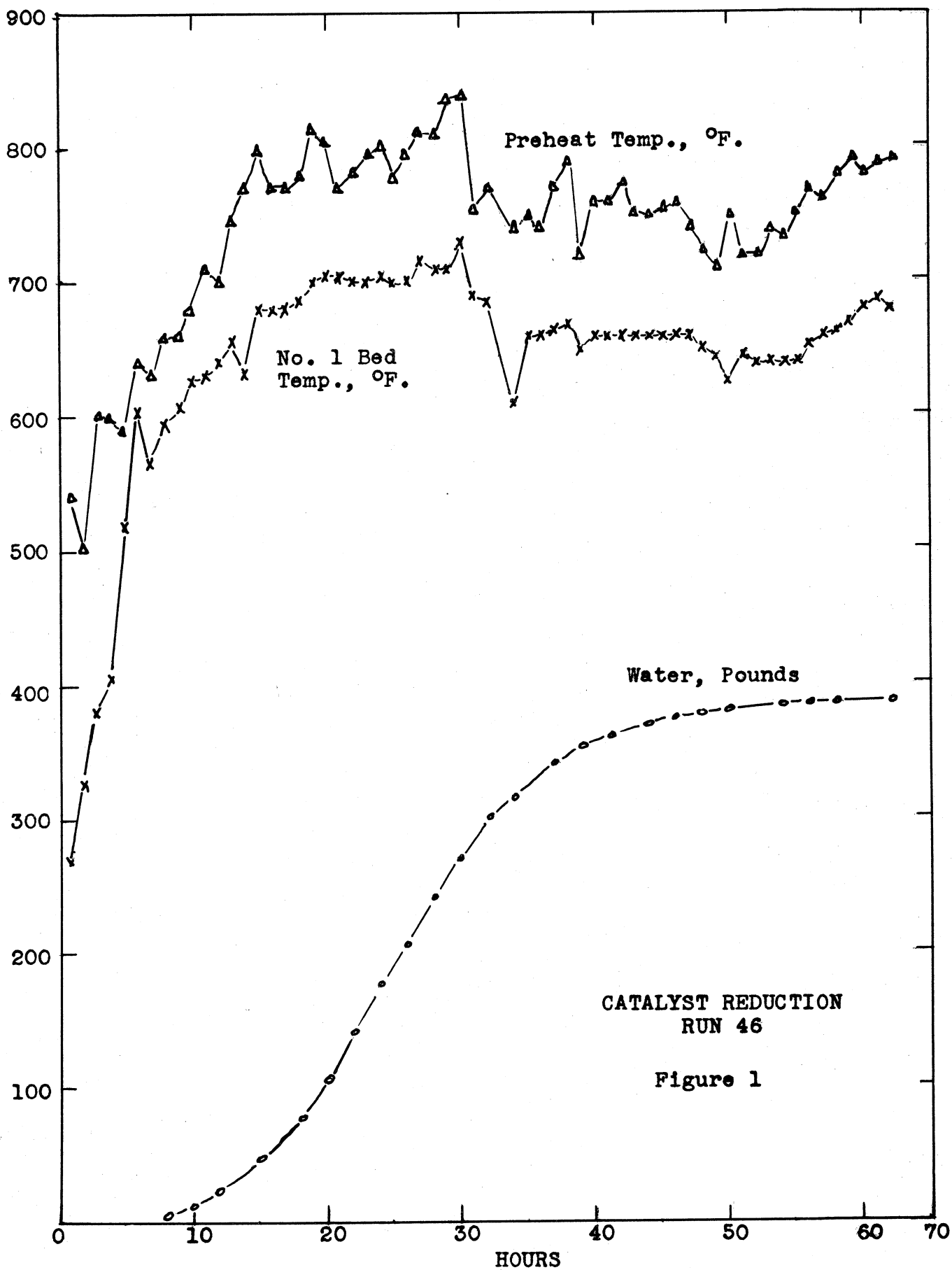
<u>A.S.T.M. NO.</u>	<u>WEIGHT PER CENT</u>
On 40	26.3
100	46.0
140	8.3
200	7.3
230	2.6
325	0.8
Thru 325	8.7

This material was used as received for Runs 46 and 48, but for Run 47 it was ground by Twining Laboratories of Fresno, California, so that 98.8 per cent passed through a No. 325 ASTM sieve. For all three runs the magnetite was impregnated with K_2CO_3 to give 0.6 part of K_2O per 100 parts of Fe. The impregnation was carried out in the normal manner as described in previous reports.³ The original charges of catalyst to the reactor amounted to approximately 1800 pounds of unreduced magnetite which was reduced in situ by circulating hot hydrogen through the catalyst bed at approximately 1 foot-per-second velocity, 640-710°F. bed temperature, and 200 psig pressure. During reduction the steam cooling tubes were dry. The operating procedure was almost identical to that used when reducing catalyst in the special reducer.

¹Partial Report Nos. 5, 10, and 13, Experiment No. TDC-802.

²Data on synthesis gas generations appear in the Appendix.

³Partial Report Nos. 31 and 32, Experiment No. TDC-802.



All make-up catalyst used during the runs was prepared in the usual manner in the reducer which has been described in detail in previous reports.

To illustrate a typical reduction in the reactor, a graphical presentation of the data from Run 46 is shown in Figure 1, facing. Over a period of 62 hours, a total of 388 pounds of water was obtained from an initial charge of 1800 pounds of magnetite. The maximum water rate was 16.7 pounds per hour.

When the reduction in the reactor was complete, the circulation of hot hydrogen was continued while water was put into the cooling tubes and the pressure in the steam system was raised to about 500 psig. Synthesis gas was then introduced after which the pressure in the entire reactor system was raised to 400 psig within three hours.

3. Synthesis System

a. Description of Synthesis Reactor

The reactor used in Run 46 was the same 19 ft. by 12-inch vessel that was used in Runs 44 and 45², except that suitable changes in materials and fittings were made to allow for safe and trouble-free 400 psig operation.³

For Runs 47 and 48, a catalyst return line was installed between the bottom of the first cyclone separator and the lower part of the reactor. This line was made of 2-inch pipe and entered the reactor at a point 2 feet above the bottom steam header. The only obstruction in the line was a 2-inch cock which remained in an open position during normal operation, the theory being that the head of catalyst in the cyclone and return line would be

¹Partial Report Nos. 31 and 32, Experiment No. TDC-802.

²Partial Report No. 32, Experiment No. TDC-802.

³A more complete discussion of equipment may be found on pp. 63 through 71, Appendix.

greater than in the reactor and would create a constant return of catalyst fines to the bottom of the reactor. A pressure connection was installed below the cock in the return line so that in case of a minor obstruction in the line, the cock could be closed and recycle-gas pressure or nitrogen-cylinder pressure could be utilized to clear the line.

All of the other operations remained the same as in Runs 44 and 45.

b. Methods of Sampling and Analysis

Gas samples were taken every four hours in dry aluminum bombs, but normally only every other sample was analyzed and a 24-hour average made of these three analyses.

The liquid product samples were drawn directly from the product separator into glass bottles at 12-hour intervals.

The catalyst samples were obtained through a one-inch line located two feet from the bottom of the catalyst bed. The sample was blown directly into 5-gallon buckets containing about two pounds of "dry ice" and was immediately transferred to glass jars containing small pieces of "dry ice". Since the magnetite was not very pyrophoric except when freshly reduced, it was not deemed necessary to use sealed bombs to obtain the samples.

All gas analyses, including those for carbon dioxide, were made with a Consolidated Engineering Corporation mass spectrometer. Orsat analyses using the explosion technique were made periodically of the synthesis gas from the generator but these were only for control purposes.

Except as stated otherwise below, the tests made on

catalyst and product were by methods found in either The Texas Company Standard Methods of Test Book or Special Methods of Test Book. The specific surface of the catalyst was determined by ammonia adsorption. This method was devised and calibrated using F.C.C.U. cracking catalyst and does not give absolute values for specific surface of iron catalyst. It may, however, give an indication of the change in specific surface of iron catalysts.

The specific gravity of the catalyst was determined by the displacement of carbon tetrachloride in a picnometer.

The water-soluble chemicals content of the water was determined by salting out with potassium carbonate at 40-50°F.¹ These chemicals were predominantly alcohols since the test does not indicate the light organic acids content.

c. Methods of Calculation

The data used in this report were obtained by forcing the weight balances on the assumption that any losses were in wet gas flow measurements. Overall weight balances varied between 90 and 99 per cent. The yields of separated oil and water were based on actually measured quantities. The term "C₃ plus" has been used in this report as in the past to denote all hydrocarbons having three or more carbon atoms to the molecule, plus the water-soluble chemicals as determined by the salting out test mentioned above.

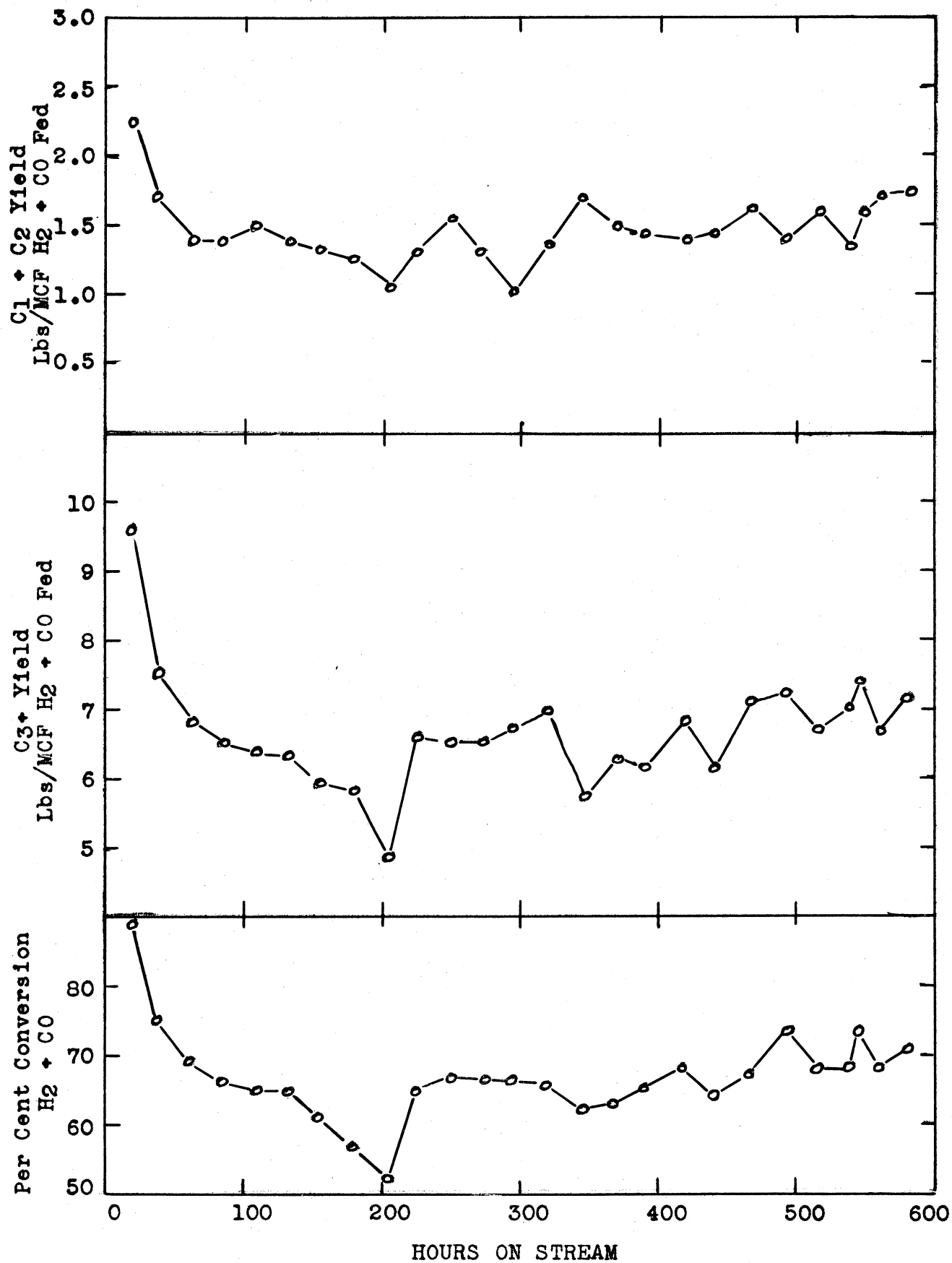
B. Experimental Results

1. Run 46

Except that the initial charge of catalyst was reduced in the reactor, the operating technique was the same as in Run 45.²

¹This method is not in The Texas Company Standard Method of Test Book or Special Method of Test Book, but is discussed fully in Partial Report No. TDC-101-33.

²Partial Report No. 32, Experiment No. TDC-802.



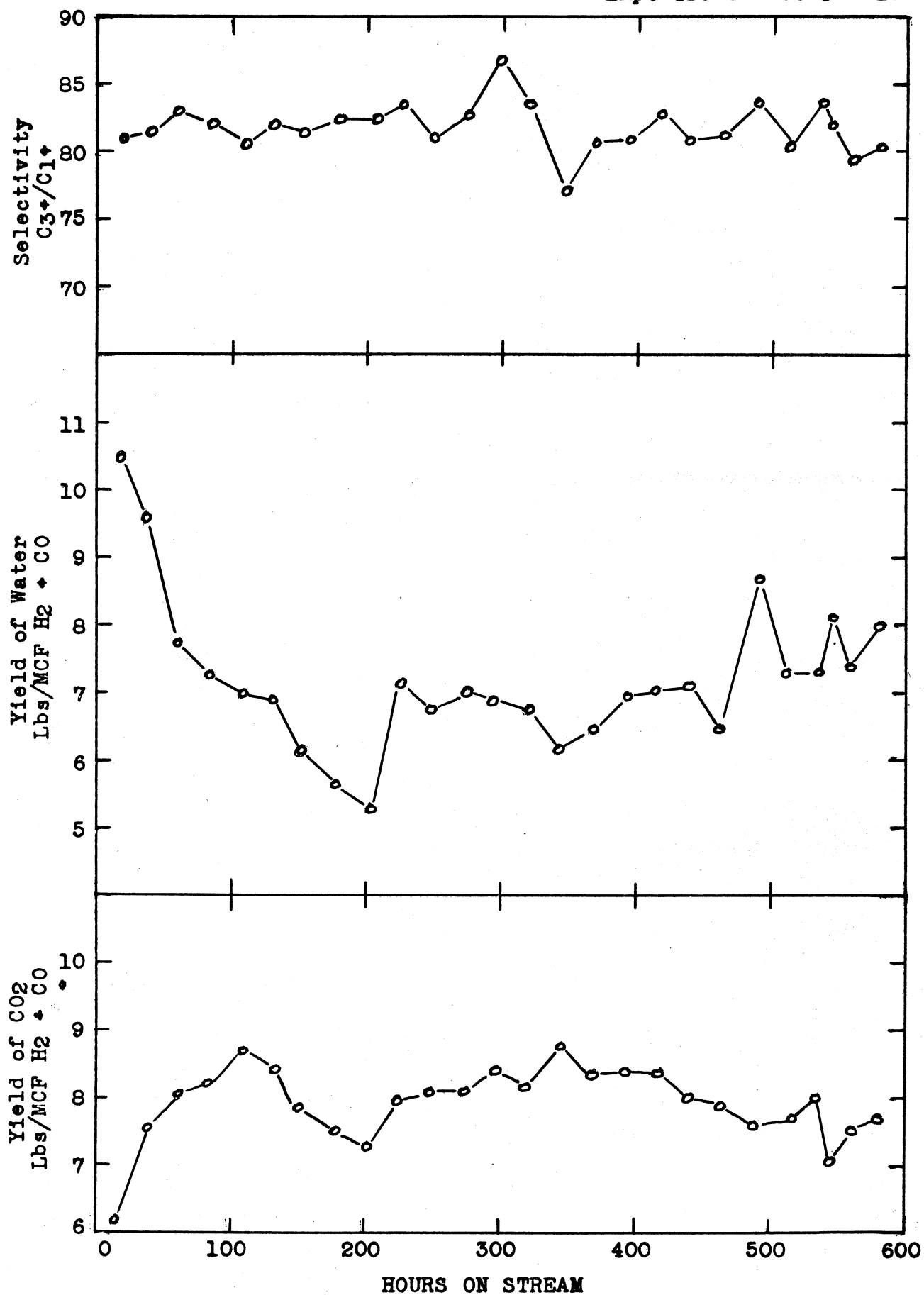
CONVERSION AND HYDROCARBON YIELDS
RUN 46

Figure 2

For the first 19 hours of operation, the fresh feed rate was only 10,254 SCFH, because of the limitation of the orifice in the meter run. After the orifice plate had been changed, the fresh feed rate was raised to 16,000 to 17,000 SCFH for the remainder of the run. There was no addition of catalyst during the first 206 hours of operation, during which time the conversion of $H_2 + CO$ declined from an initial 88.8 per cent to 51.7 per cent. The yield of C_3+ followed a similar pattern, going from 9.6 lbs/MCF $H_2 + CO$ to 4.9 lbs/MCF.

The decision was then made to load fresh catalyst in an effort to increase the conversion rate. Addition of 257 pounds of reduced catalyst brought the conversion of $H_2 + CO$ up to 65 per cent and increased the C_3+ yield to 6.5 lbs/MCF. A 50 pound-per-day addition rate for the next 164 hours maintained the conversion and C_3+ yield almost at these levels. Beginning with Period 46-Q (390 hours) the addition rate was raised to about 160 pounds a day average and was held there until the end of the run. This caused the C_3+ yield and conversion to increase slowly to 7.0 lbs/MCF and 70 per cent respectively.

The conversion of $H_2 + CO$ and the yields of hydrocarbons are shown chronologically in Figure 2, facing. The selectivity and yields of carbon dioxide and water are shown in Figure 3, following. Usually the CO_2 yield varied inversely with the water yield except during a short general decline in all yields just prior to the time when the addition of catalyst was initiated. The water yield was consistently of the same magnitude as the C_3+ yield. The selectivity (yield of C_3+ /yield of C_1+) did not vary much and usually was between 80 to 85 per cent.



SELECTIVITY AND YIELDS OF CARBON DIOXIDE AND WATER

Figure 3

A bad leak in the high pressure steam system and mechanical failure of the recycle compressor terminated Run 46 after 580 hours on stream.

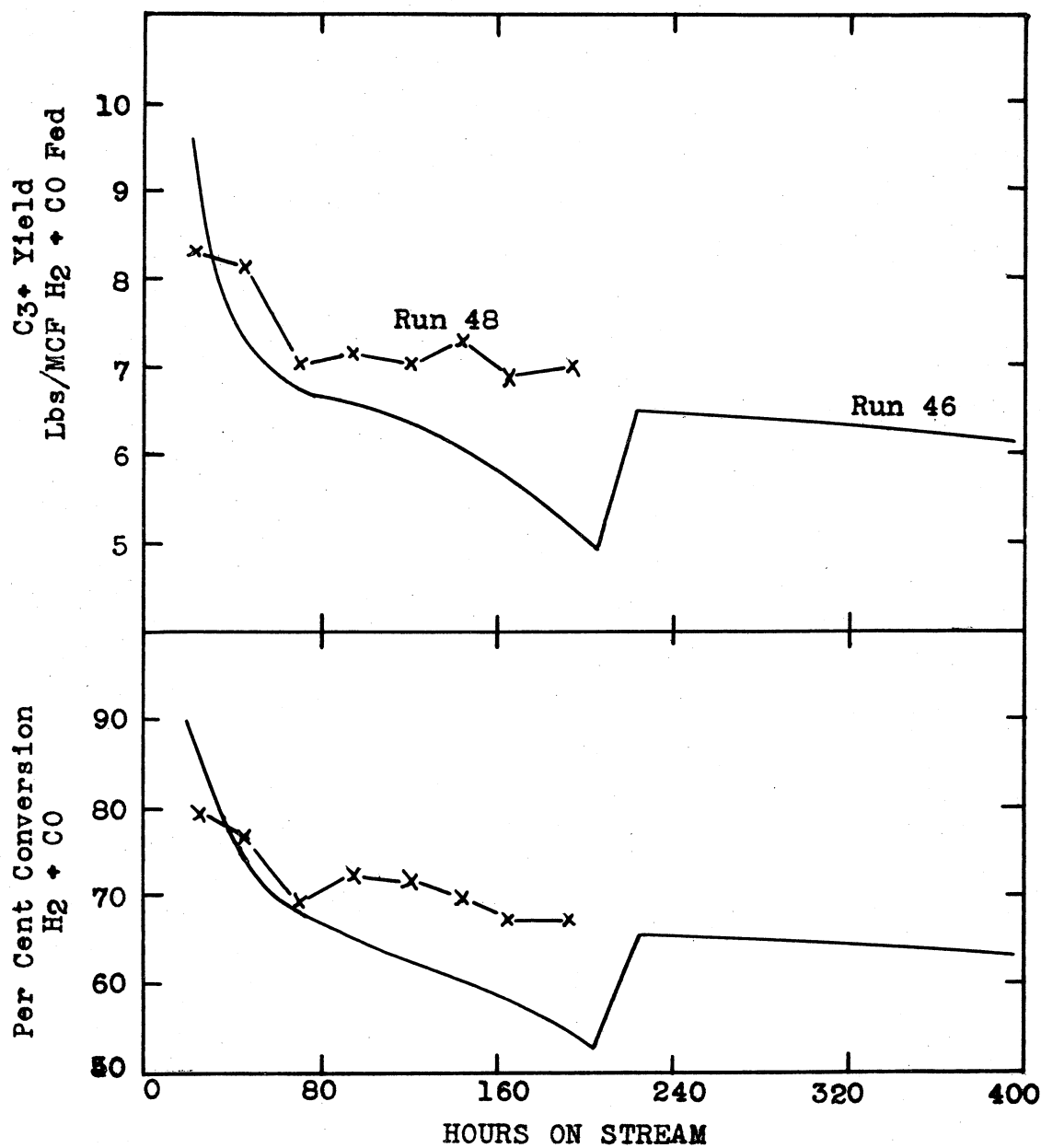
2. Run 47

Run 47 was an attempt to operate the Montebello Reactor with finely ground magnetite to determine whether a catalyst of smaller particle size would effect better conversion. It was intended that the magnetite be ground so that it would be predominantly in the 100-325 mesh size range, but the type of grinding facilities available resulted in a grind of 98.8 per cent through a 325-mesh sieve. The run lasted only 14 hectic hours and was shut down because of plugs in the cyclones, catalyst loader, and product condenser. It was impossible to control the bed temperatures and operation, and no significant data were obtained.

3. Run 48

It was suspected that there might have been a trace amount of some unidentified catalyst poison in the fresh feed because Runs 42, 45, and 46 all showed declines in yield down to similar levels even though different catalysts, flow conditions, and reactors were involved. For this reason a water-wash scrubbing tower was installed to determine whether or not the suspected poison could be scrubbed by this means. The Brownsville system similarly includes a water scrubbing of the generator product gas.

A catalyst return line from the first cyclone was installed with the idea that this might make possible operation with a higher bed height. Previously the highest bed height which could be maintained was of the order of 11 to 12 feet in the 19-foot reactor indicating that a disengaging space of at least 7 feet



CONVERSION AND HYDROCARBON YIELDS
RUN 48

Figure 4

above the dense phase level was necessary.

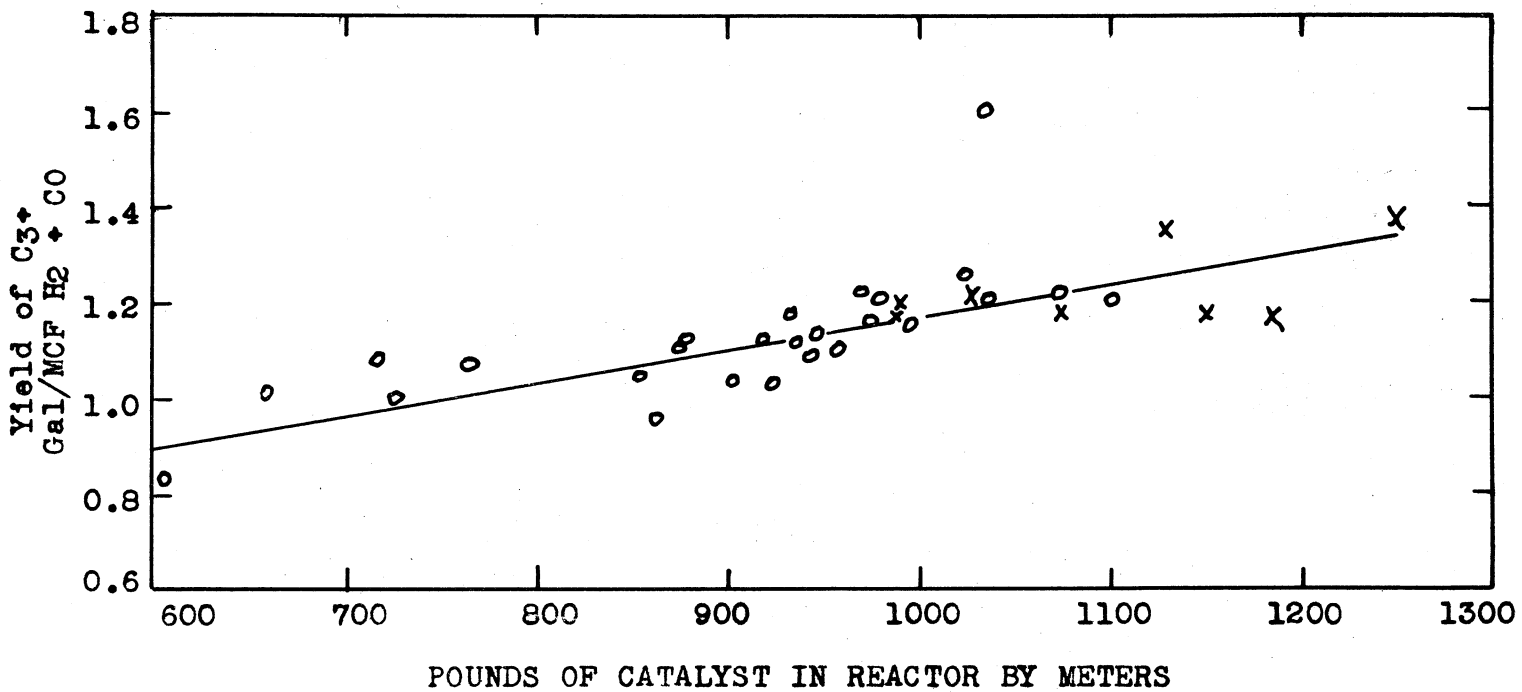
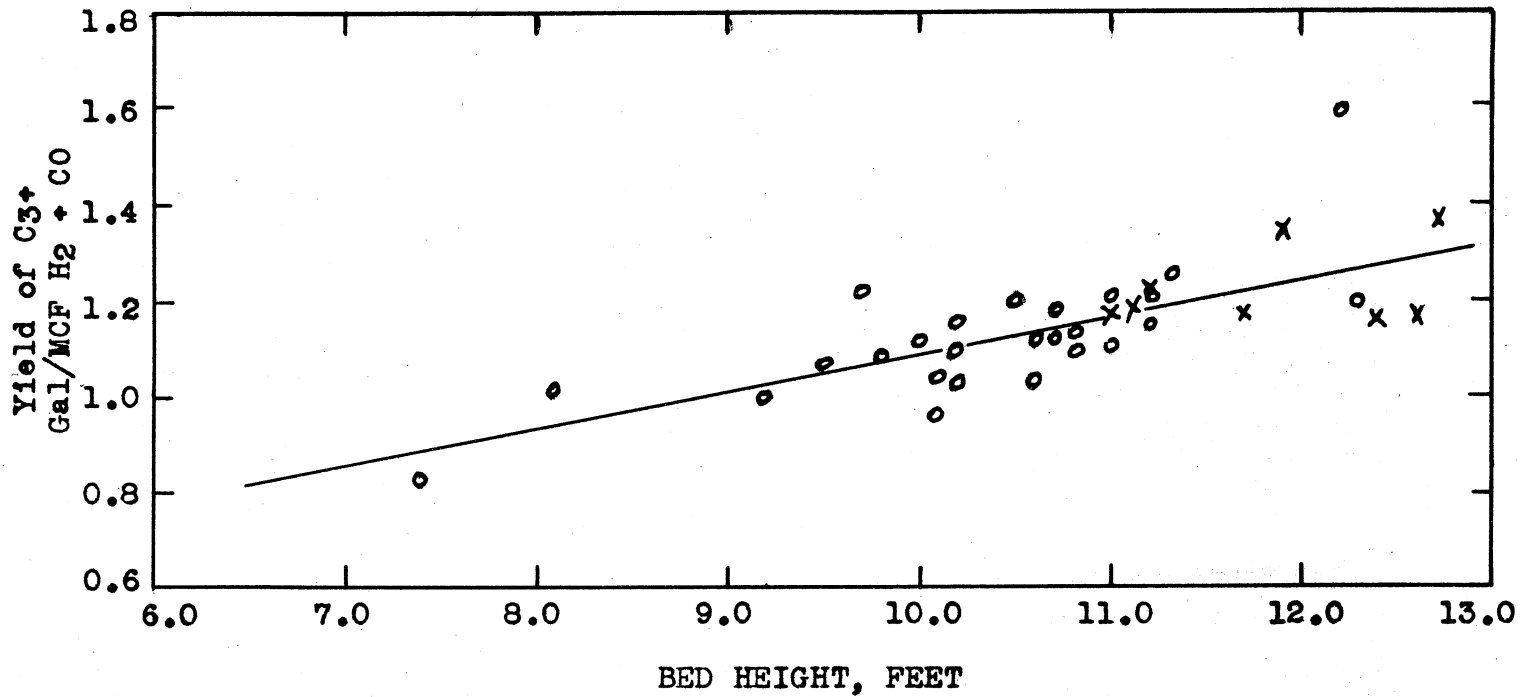
Despite these changes, Run 48 appeared to be only a confirmation of Run 46. The flow rates were approximately the same, but the catalyst make-up was started sooner. After 70 hours, freshly reduced catalyst was loaded at an average rate of 58 lbs/day for the remaining 120 hours. The catalyst return system operated for only the first 58 hours at most and may have become plugged sooner than was realized.

Another leak in the high pressure steam system caused the shut-down of the reactor after 190 hours. The run was not continued after the repairs were made since it was apparently only duplicating Run No. 46.

The conversion and C₃+ yield data for Run 48 are shown in Figure 4, facing. The corresponding data from Run 46 are also shown for comparison. It may be recalled that during the first portion of Run 46 no catalyst was added to the reactor whereas in Run 48 an addition rate of 58 lbs/day was used. Examination of the curves for conversion and C₃+ production shows that the data from Run 48 fall along a line that would probably represent data obtained from Run 46 had the bed level been maintained by catalyst addition from the start. It can be seen that extrapolation of the Run 48 curves would make them coincide with the Run 46 curves for the periods during which catalyst was added.

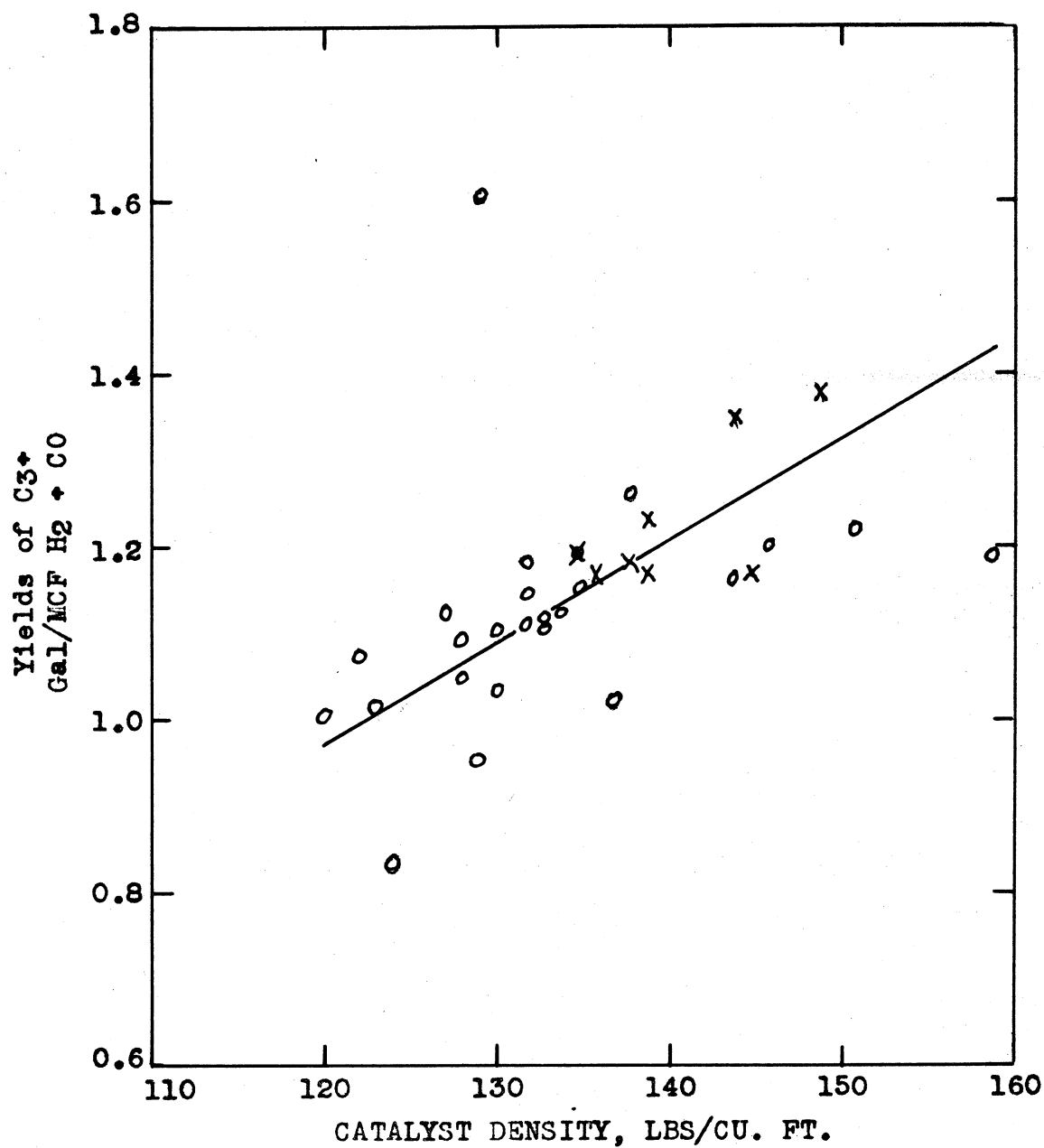
4. Effect of Bed Height and Catalyst Inventory on Yield of C₃+

The yield of C₃+ has been plotted against catalyst bed height and weight of catalyst in the reactor as shown in Figure 5, following. There was an increase in C₃+ yield with both bed



EFFECT OF CATALYST BED HEIGHT
AND INVENTORY ON YIELD OF C₃⁺

Figure 5



VARIATION OF CATALYST DENSITY WITH
YIELD OF C₃+

Figure 6

height and catalyst inventory. This was to be expected because the bed height was dependent on catalyst inventory, but it was observed that the bed height affected the yield more than did the inventory. The first supposition was that the real factor was only the bed height but this was made doubtful when the yield of C₃+ was plotted against catalyst density as shown in Figure 6, facing. These data indicate that an increase in catalyst density of 10 lbs/cu. ft. was accompanied by about the same increase of C₃+ yield as when the bed height was raised a foot. It is possible that the variation of the catalyst density was a resultant factor rather than a causative one with the C₃+ yield.

5. Comparison of Yields on Straight-Run and Polymer Bases

The ultimate yield of marketable product has been calculated on the assumption that in a commercial plant the propylene (4.32 pounds per gallon) will be polymerized to a product of 6.25 pounds per gallon with 90 per cent recovery. It is likewise expected to polymerize the butylenes (5.00 pounds per gallon) to a product of 6.10 pounds per gallon with 95 per cent recovery. The propane has not been included in the calculation of the ultimate yield. Water soluble chemicals have been considered in both cases as marketable product.

The yields on both straight-run and polymer bases are compared in Table I, page 17. The data have been averaged for those periods during which the catalyst make-up rates were similar. The yield on the polymer basis varied between 87.4 and 89.7 per cent of the straight-run yield of C₃+, this percentage being higher when the yields in general were higher.

COMPARISON OF YIELDS ON STRAIGHT-RUN AND POLYMER BASESTABLE I

Run No.	Catalyst Make-up Rate lbs./day	C3+ Yield Straight-Run gal./MCF H ₂ +CO	Ultimate Yield Polymer basis gal./MCF H ₂ +CO	Polymer/ Straight-Run Per Cent
46A-I	0	1.125	0.983	87.4
46J-P	50	1.090	0.953	87.4
46Q-Y	160	1.142	1.018	89.1
48A-H	58	1.232	1.105	89.7

6. Product Quality

Distillations of the recovered oil indicated that it was usually 70 per cent in the gasoline boiling range and 15 per cent in the gas-oil range with 15 per cent residue. The acid content of both water-soluble and oil-soluble product was high as was reflected by neutralization numbers normally in the range of 40 to 50. The saponification numbers of the oil were only about 4 to 5 points higher than the neutralization numbers. Bromine numbers in the range of 80 to 90 gave evidence that the recovered oil was highly unsaturated.

The water-soluble chemicals, as determined by salting out with K₂CO₃, almost always constituted 10 per cent of the total water product.

7. Comparison of Yields of Montebello Reactor with Brownsville Design

Brownsville Case VI design is based on a C₃+ yield of 1.6 gals/MCF H₂ + CO. With comparable flow conditions, the yield of C₃+ from the Montebello Reactor was about 1.2 gals/MCF H₂ + CO with a 10 to 12-foot bed height. This was only 75 per cent of Brownsville design. The Brownsville reactor is considered capable of operating with a catalyst bed height of about 20 feet, and this higher bed height may make it possible to obtain a better yield of C₃+ than 1.2 gals/MCF H₂ + CO.

8. Properties of Used Catalyst

Analytical facilities at Montebello are not adequate for making extensive tests on the synthesis catalyst. Routine tests are made to obtain particle-size distribution, bulk density, specific gravity, and ammonia adsorption number.

Spot samples of catalyst from Run 46 were sent to Beacon Laboratory for more complete analyses, such as distribution of iron compounds by x-ray diffraction, specific surface by nitrogen adsorption, and elemental analysis. A summary of the analyses of the catalyst is shown in Table II, following.

The distribution of the iron was consistently about 30 per cent carbide, 60 per cent oxide, and 10 per cent or less metallic iron. It is interesting to note that a sample of magnetite catalyst used at Beacon under Montebello conditions¹ showed an iron distribution of 60 per cent carbide, no oxide, and 40 per cent metallic iron.

Carbon deposition on the Alan Wood magnetite has not presented any problem when used in the Montebello Reactor. As shown in Table II, the maximum total carbon content of the used catalyst was less than 10 per cent by weight.

The impregnation of the raw catalyst was made to give 0.6 parts K_2O per 100 parts by weight of Fe and chemical analysis showed that the reduced catalyst contained 0.66 parts K_2O . The K_2O content dropped abruptly, however, after synthesis gas had been introduced, and remained at about 0.3 parts per 100 of Fe for the remainder of the run. It is hard to believe that the K_2O was stripped off mechanically with the catalyst fines after

¹Run 28-SF-11026 reported in Partial Report TDC-101-56.

TABLE II

ANALYSES OF CATALYST

RUN NO.	X-Ray Analyses Weight Per Cent			Specific Surface by N ₂ -M ² /g.	NH ₃ Adsorption No.	Chemical Analyses Weight Per Cent				K ₂ O/100 Fe
	Fe ₂ O ₃	Fe ₃ O ₄	Fe			K ₂ O	Fe	C	H	
46 Reduced			100 ¹	3.7		0.56	84.7			0.66
46-A	30	60	10	1	1.6	0.25	66.9	3.6	0.20	0.37
46-C					6.8			4.7	0.31	
46-E					8.0			8.63	0.45	
46-G					6.7			8.63	0.38	
46-I	30	65	5	1	5.4	0.12	65.6	9.7	0.63	0.18
46-K					6.4			6.65	0.37	
46-M					8.4			7.87	0.32	
46-N	30	60	10	1	9.4	0.20	68.9	6.45	0.22	0.29
46-P	40	55	5	2.7	9.4	0.17	63.7	7.7	0.36	0.26
46-T	30	60	10	1		0.23	71.3	6.18	0.26	0.32
46-Y	30	65	5	1	8.6	0.24	68.1	7.38	0.25	0.35

¹Chemical Analysis showed 73.5% metallic iron

synthesis gas was introduced when it was not removed by the same process when the catalyst was being reduced. A sizable proportion of the catalyst fines were removed during reduction but this did not affect the K_2O content. This indicates that the K_2O is removed by some mechanism related to the synthesis reaction; perhaps by formation of potassium iron acetate.