II. EXPERIMENTAL WORK

A. EQUIPMENT AND METHOD OF OPERATION

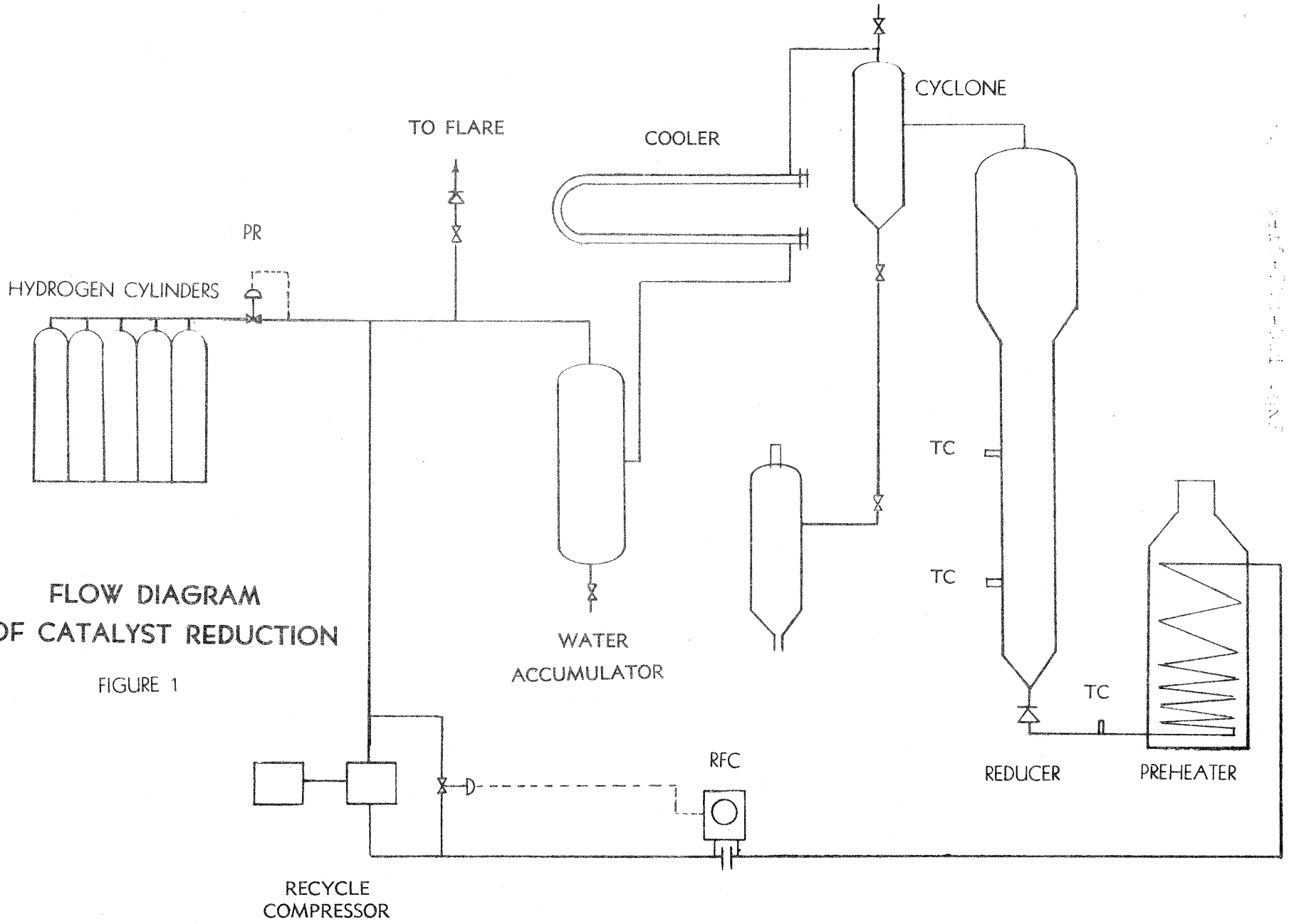
1. Synthesis Gas Generation

The synthesis gas mixture of carbon monoxide and hydrogen was the product of the uncatalyzed reaction between natural gas and oxygen at 280 psig and at temperatures in the 2300°F. range. The natural gas normally contained approximately 85 per cent methane, 1.5 per cent CO_2, 9.5 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 contained 4 per cent unconverted methane, two per cent carbon dioxide and less than one per cent nitrogen. The generator system has been described in detail in previous reports(1) and since it serves only as a utility unit for the reactor, no further details are included in the present report.

2. Catalyst Pretreatment and Reduction

Mill scale resulting from the rerolling of steel railroad rails served as the base material for the catalyst used in the present work. The scale was obtained from the Finkelstein Supply Corporation of Los Angeles, California, and sent to the Twining Laboratories of Fresno, California, for drying and grinding

(1) Partial Reports 5, 10, and 13, Experiment No. TDC-802



FLOW DIAGRAM OF CATALYST REDUCTION

FIGURE 1

A sieve analysis of the ground material gave the following results:

A.S.T.M. Sieve No.	Weight Per Cent
On 40	21.2
100	37.3
140	8.6
200	9.8
230	2.6
325	5.7
Through 325	14.8

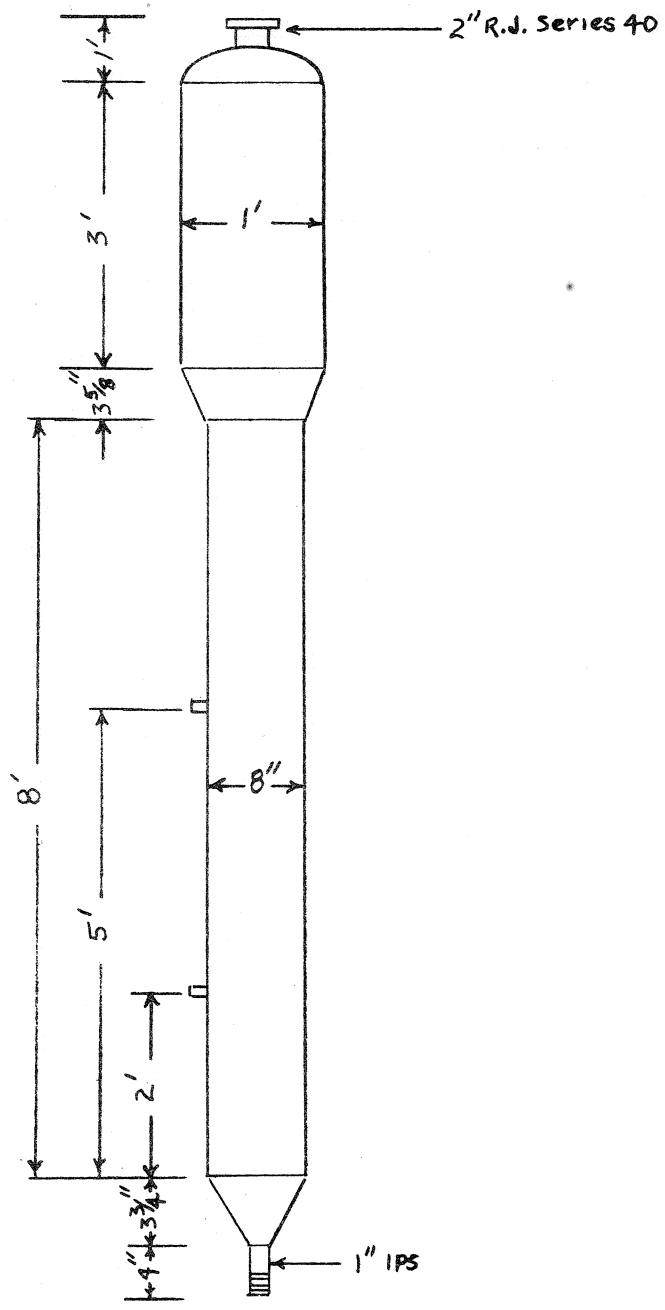
The impregnation of the mill scale with potassium carbonate was conducted in a rectangular steel gas-heated tray in batches of 250 to 1000 pounds. An amount of carbonate sufficient to provide 1.0 part K_2O/100 Fe was dissolved in steam condensate and poured over the mill scale in the tray. Additional condensate water was added to make a thick slurry, after which the mixture was stirred thoroughly. While being dried by the heat of the gas burners it was raked frequently to prevent caking.

The dried catalyst was transferred to the reduction system, shown in Figure 1 facing, and Figure 2 following, and treated with Linde cylinder hydrogen at 200 psig and at temperatures varying from 625 to 725°F. During the reduction the hydrogen was recycled after being cooled to approximately 80°F. to remove the bulk of the water. Make-up hydrogen was added to the system as required to maintain operating pressure.

The catalyst was considered sufficiently reduced when water production decreased to approximately one-tenth pound per hour. After reduction and prior to use the catalyst was kept blanketed and handled in an atmosphere of carbon dioxide obtained by the evaporation of "dry ice" furnished by Pure Carbonic, Inc., of Los Angeles, California.

CATALYST REDUCER

FIGURE 2



Natural gas was used as a purging medium to remove air from the reactor system. The reduced catalyst was then charged to the reactor and bed temperatures brought to the desired level by circulating hot natural gas before introducing the synthesis gas. In previous work with the unstirred reactors hydrogen had been used prior to the synthesis gas, but the heat loss from the Stratco Reactor was so great that it was impossible to preheat the catalyst bed to a sufficiently high temperature with hot hydrogen.

3. Synthesis System.

a. Description of Synthesis Reactor

The synthesis vessel, known as the Stratco Reactor or Stratco Contactor, made use of a mechanically-stirred catalyst bed cooled by oil jackets containing Regal Oil K (R & O). The overall height was 29 feet and the height of the reaction zone was 21 feet. The outside diameter of the uninsulated vessel was 16 inches.(1)

The synthesis gas entered the bottom and was carried along with some catalyst by the impellers on the center shaft. When the catalyst and gas got near the top, most of the catalyst dropped down into a chamber (annulus)(2) surrounding the stirring chamber, while the gas and catalyst fines continued upward. The catalyst that dropped down was recirculated. At the top of the reactor there was a multi-vaned spinner arrangement which rejected most of the fines entrained in the gas and returned this catalyst back down into the reactor.

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(1)Stratford Engineering Corporation Drawing No. 1814C1.

(2)A glossary of terms used with the Stratco Reactor System is in Appendix I, page 29.

The effluent gas left the reactor and passed through an external cyclone, then to a product condenser, and finally to a product separator. The non-condensable gas was used for recycle gas, the excess having gone to the flare as wet gas.

Flow diagrams are shown in Figures 3, 4, 5, 6, and 7, pages 8 through 12.

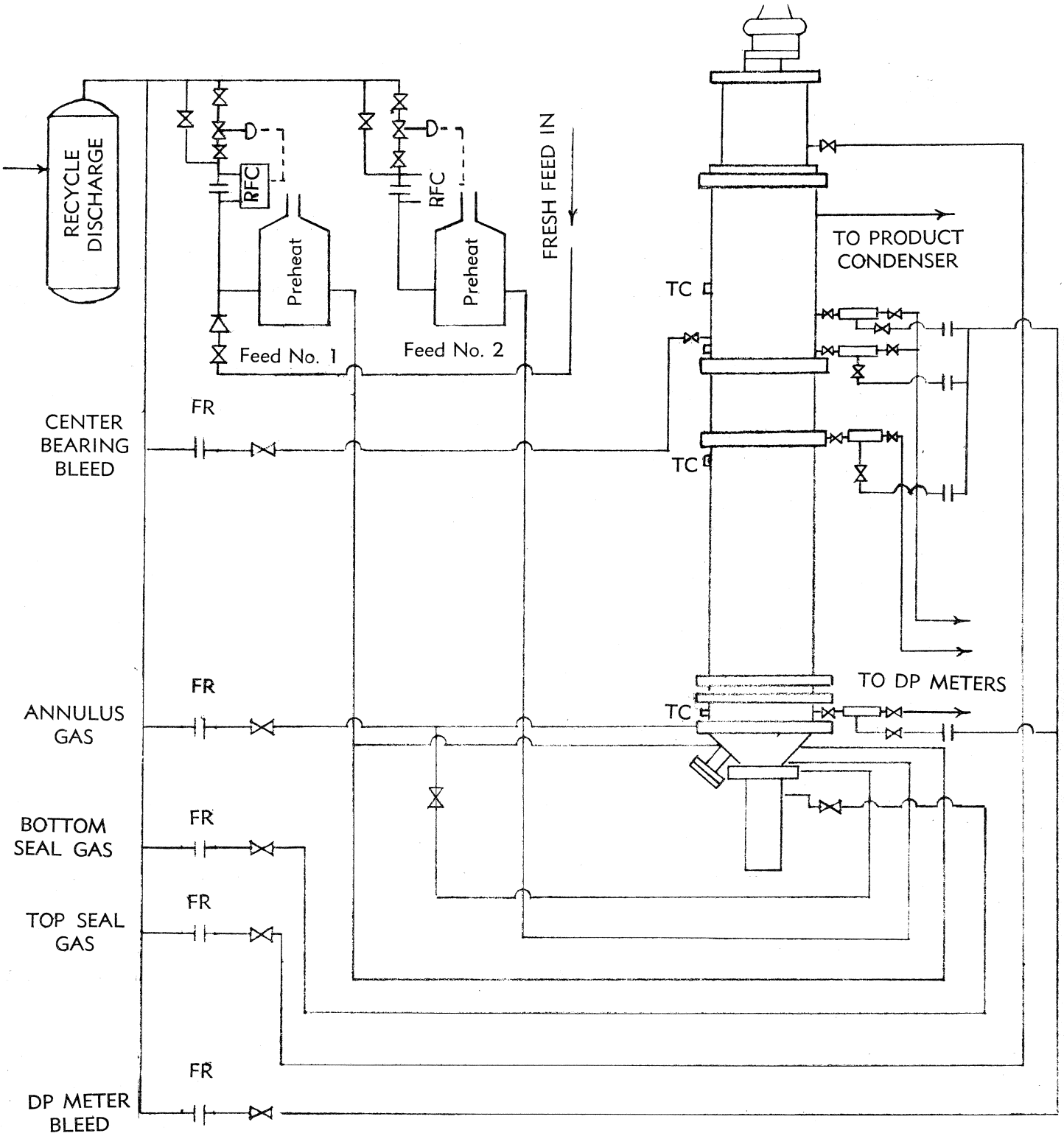
b. Methods of Sampling and Analysis

Prior to Run 42-C, 24-hour composite gas samples were collected by displacement of 0.1 per cent sulfuric acid solution. There was some indication that the wet-gas samples were being affected by the acidified water solution so that, beginning with Run 42-C, spot gas samples were taken in dry aluminum bombs and no composites were made. The 24-hour composite samples had been composed of samples of gas taken at two-hour intervals. The bomb samples were taken every four hours, but normally only every other bomb sample was analyzed and a 24-hour average made of these analyses.

The liquid product samples were taken directly from the product separator into glass bottles.

The catalyst samples were taken in bombs which were cooled with "dry ice" before being opened. The cooled catalyst was removed to jars containing pieces of "dry ice" to keep a blanket of carbon dioxide on the pyrophoric material. After the catalyst had been stored in the presence of the carbon dioxide, it usually lost its pyrophoricity.

All gas analyses, including those for carbon dioxide, were made with a Consolidated Engineering Corporation mass spectrometer. Orsat analyses were made of the synthesis gas from

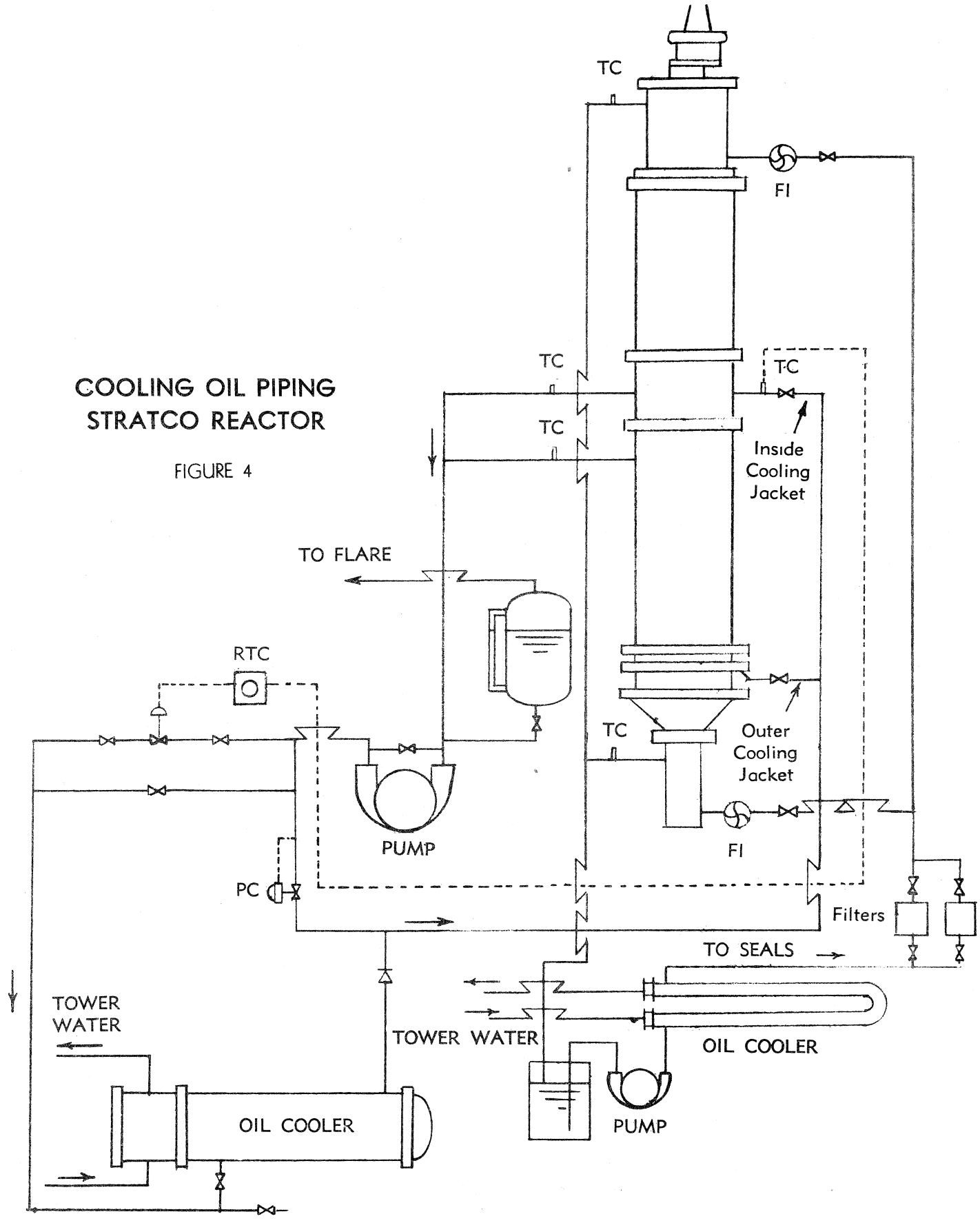


PIPING LAYOUT FOR GAS FLOW
STRATCO REACTOR

FIGURE 3

COOLING OIL PIPING STRATCO REACTOR

FIGURE 4



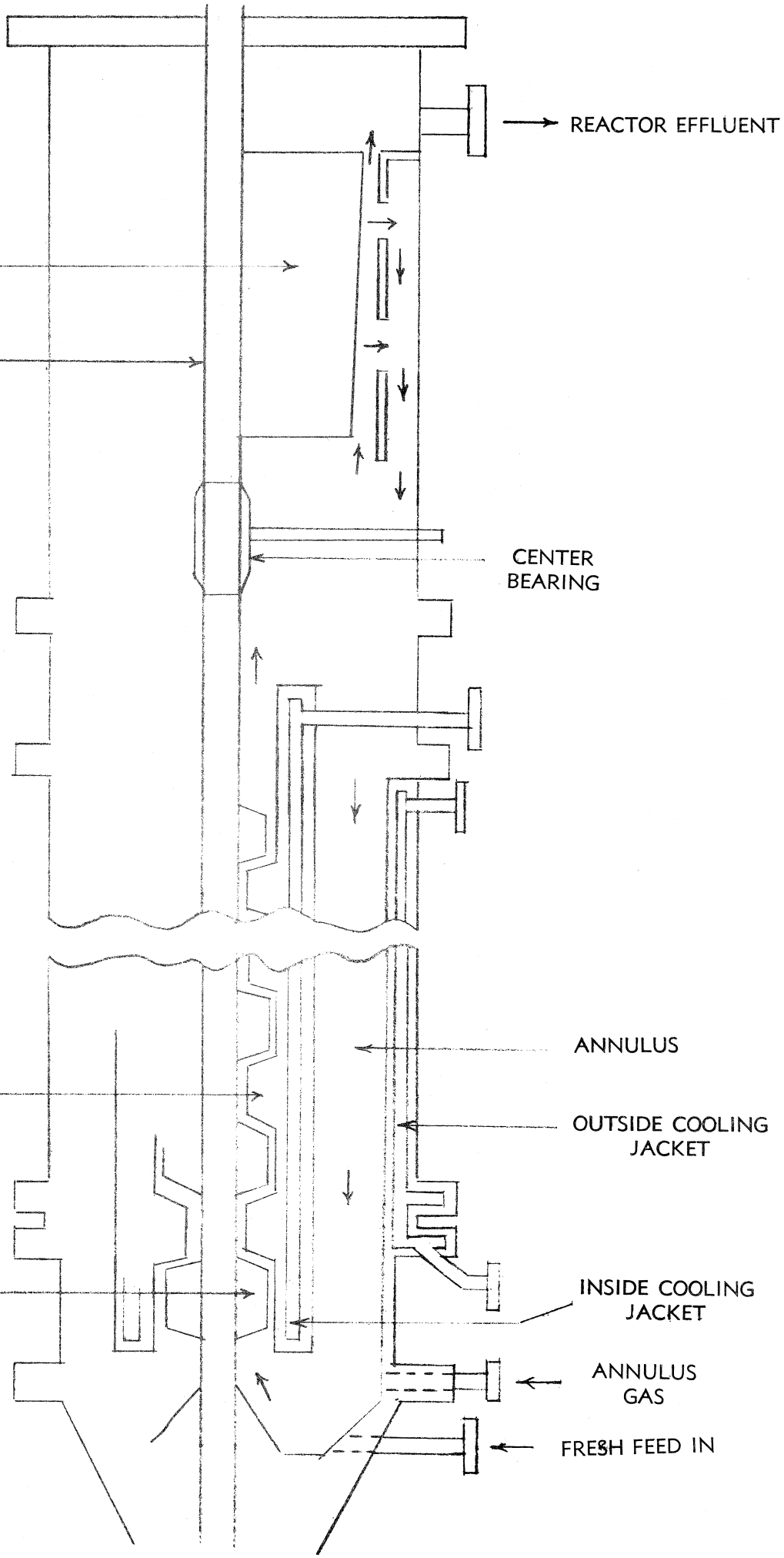


DIAGRAM OF STRATCO REACTOR

FIGURE 5

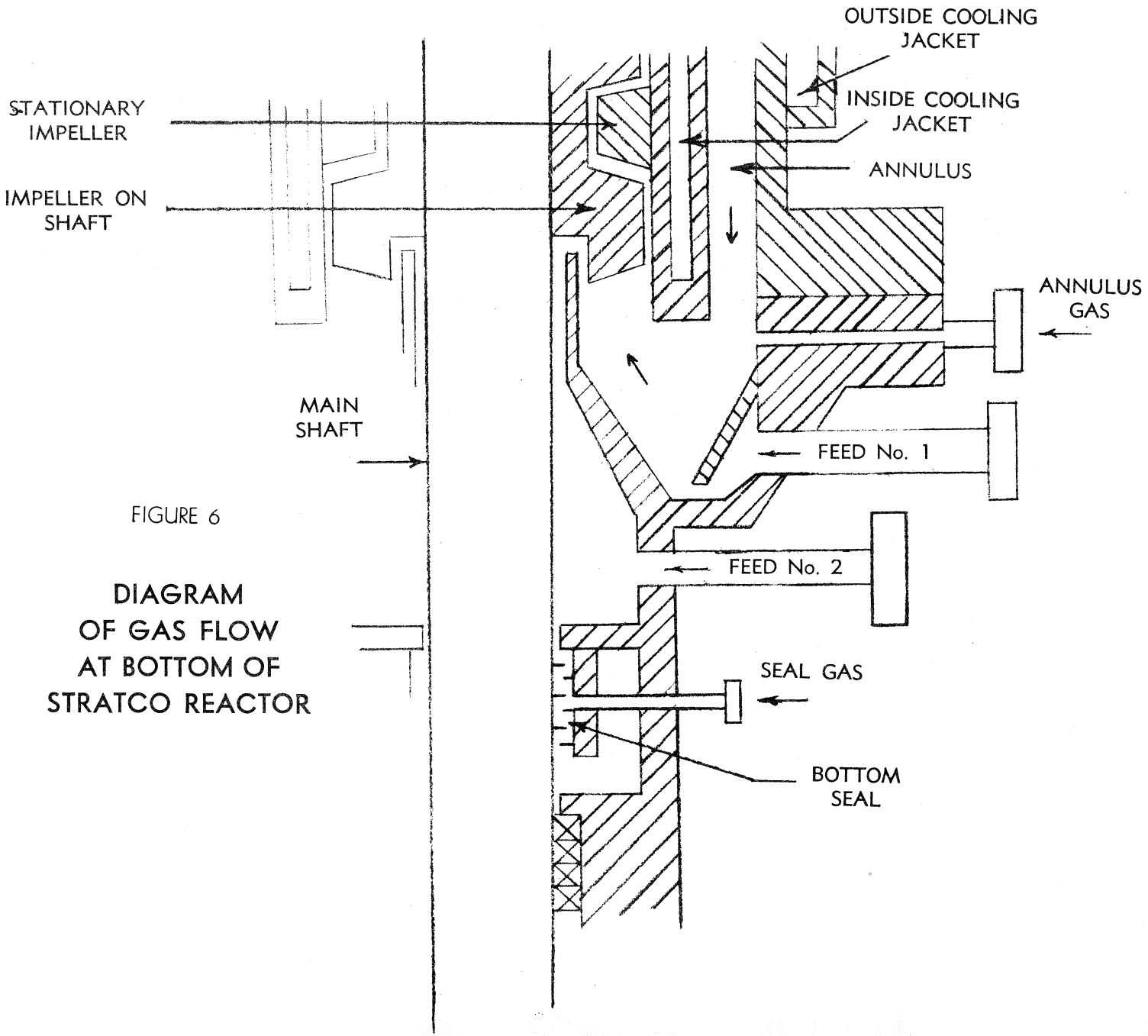
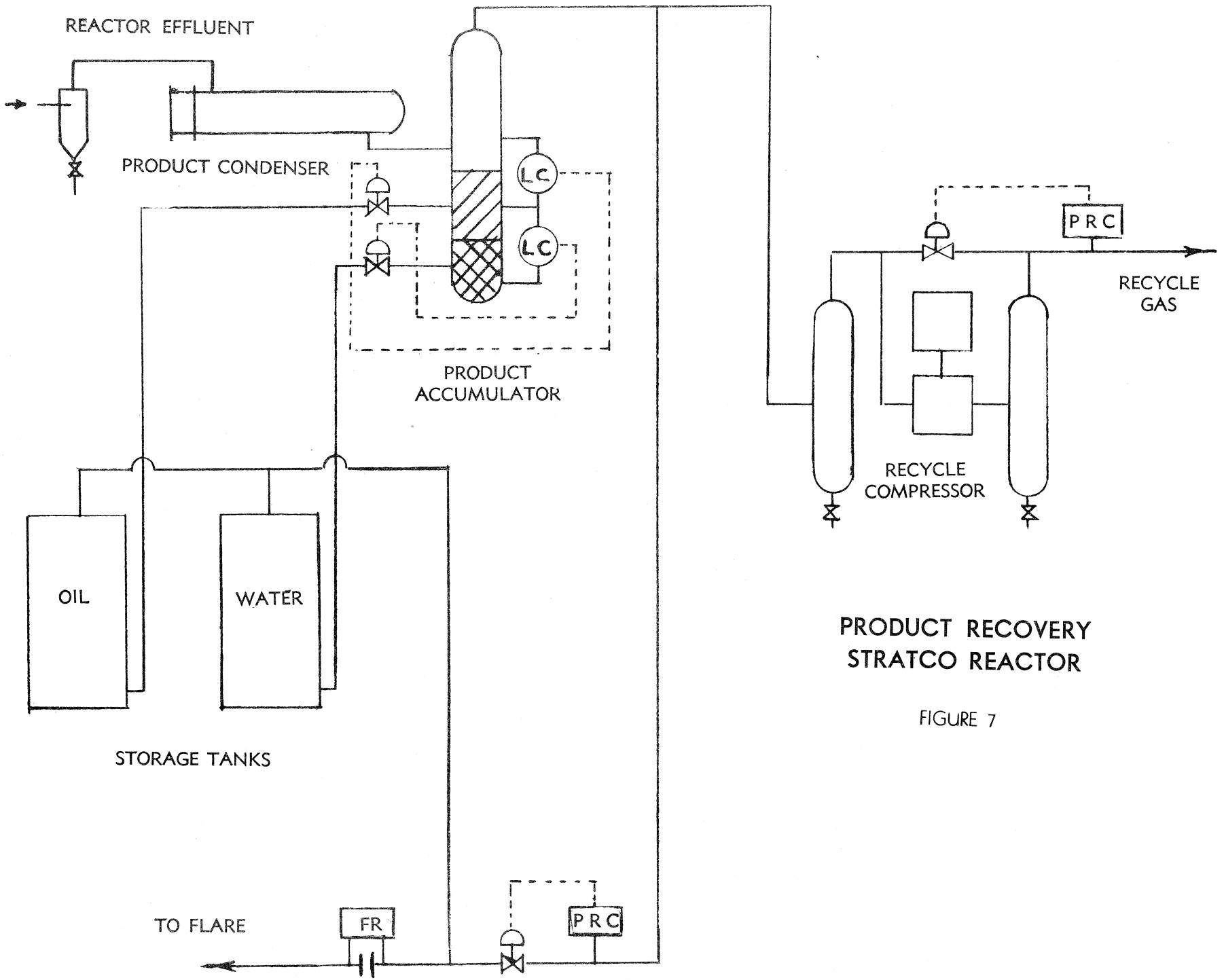


FIGURE 6

DIAGRAM OF GAS FLOW AT BOTTOM OF STRATCO REACTOR



PRODUCT RECOVERY
STRATCO REACTOR

FIGURE 7

the generator but these were only for control purposes.

The tests made on catalyst and product were by methods found in 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. It must be pointed out that this method was devised and calibrated using F.C.C.U. 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.

The specific gravity of the catalyst was determined by using carbon tetrachloride and a picnometer.

The alcohol content of the water was determined by salting out with potassium carbonate at 40°F. to 50°F.

c. Methods of Calculation

The yield data used in this report were obtained by forcing the weight balances on the assumption that any losses or gains were in wet gas flow measurements. The liquid hydrocarbon yields were calculated by the difference in carbon balances, and the water yields were calculated by difference on both hydrogen and oxygen balances.

B. EXPERIMENTAL RESULTS

Since the Stratco Reactor was by nature a complicated machine, the difficulties encountered in its operation were quite different from those experienced in previous reactors which did not use power to fluidize the bed. The reactor was the first one of its particular kind to be built and as originally constructed, was not designed to be operated at the 250 psi pressure level used in the runs. These factors necessitated an extended shakedown and

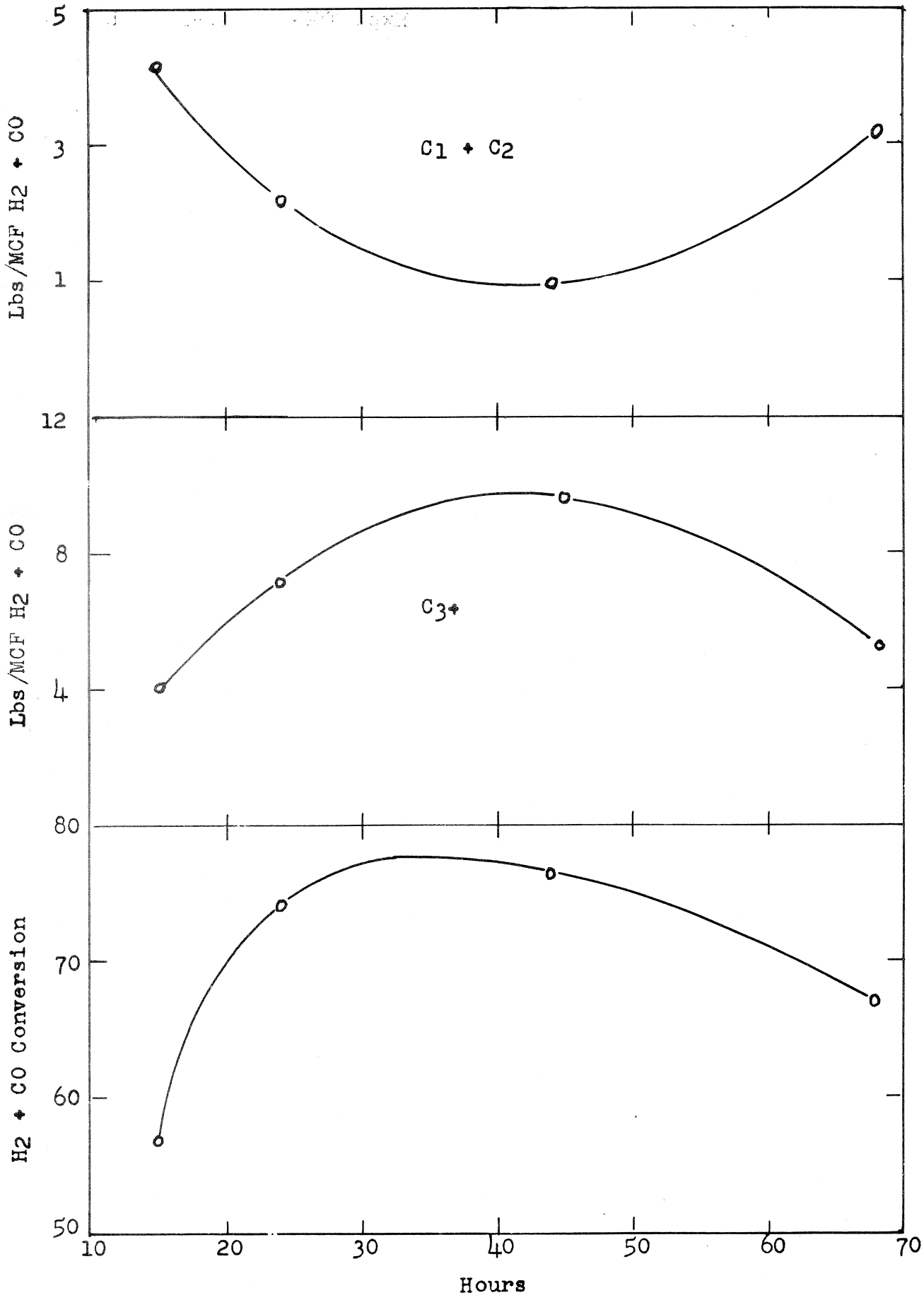


FIGURE 8
RUN 39

personnel training period during which many changes were made. Runs 39, 40, and 41 may be considered as part of this training and shakedown period and are discussed only briefly in the present report. Emphasis is placed on the data from Run 42 because this run was relatively long and unencumbered by mechanical difficulties, and the data were consistent from day to day.

1. Run 39

Run 39 was the first synthesis run made on the Stratco Reactor. A total of 743 pounds of reduced mill scale catalyst was used during the period. Considerable difficulty was experienced with maintaining the center shaft at a constant speed. The turbine stalled frequently, and finally the run was ended after 68 hours when it became impossible to turn the main shaft.

The yields of $C_1 + C_2$ and C_{3+} have been plotted chronologically as pounds yield per thousand cubic feet of $H_2 + CO$ fed. These data are given in Figure 8, opposite. In the same figure is shown the $H_2 + CO$ conversion variation with time.

The yields of $C_1 + C_2$ declined to a minimum of 1.13#/MCF of $H_2 + CO$ and then increased again to 3.22#/MCF during the last 24 hours of operation. The C_{3+} yields reached a maximum of 9.70#/MCF of $H_2 + CO$ after 44 hours of operation. The conversion of $H_2 + CO$ increased from a low of 57.1 per cent to about 78 per cent after 35 hours and then decreased to 66.9 per cent after 68 hours.

The yields were calculated during this run without forcing the wet gas to make 100 per cent weight balance. Since the overall weight balances on the reactor varied between 68 per cent (Run 39-C) and 113 per cent (Run 39-D), these data should be viewed with caution.

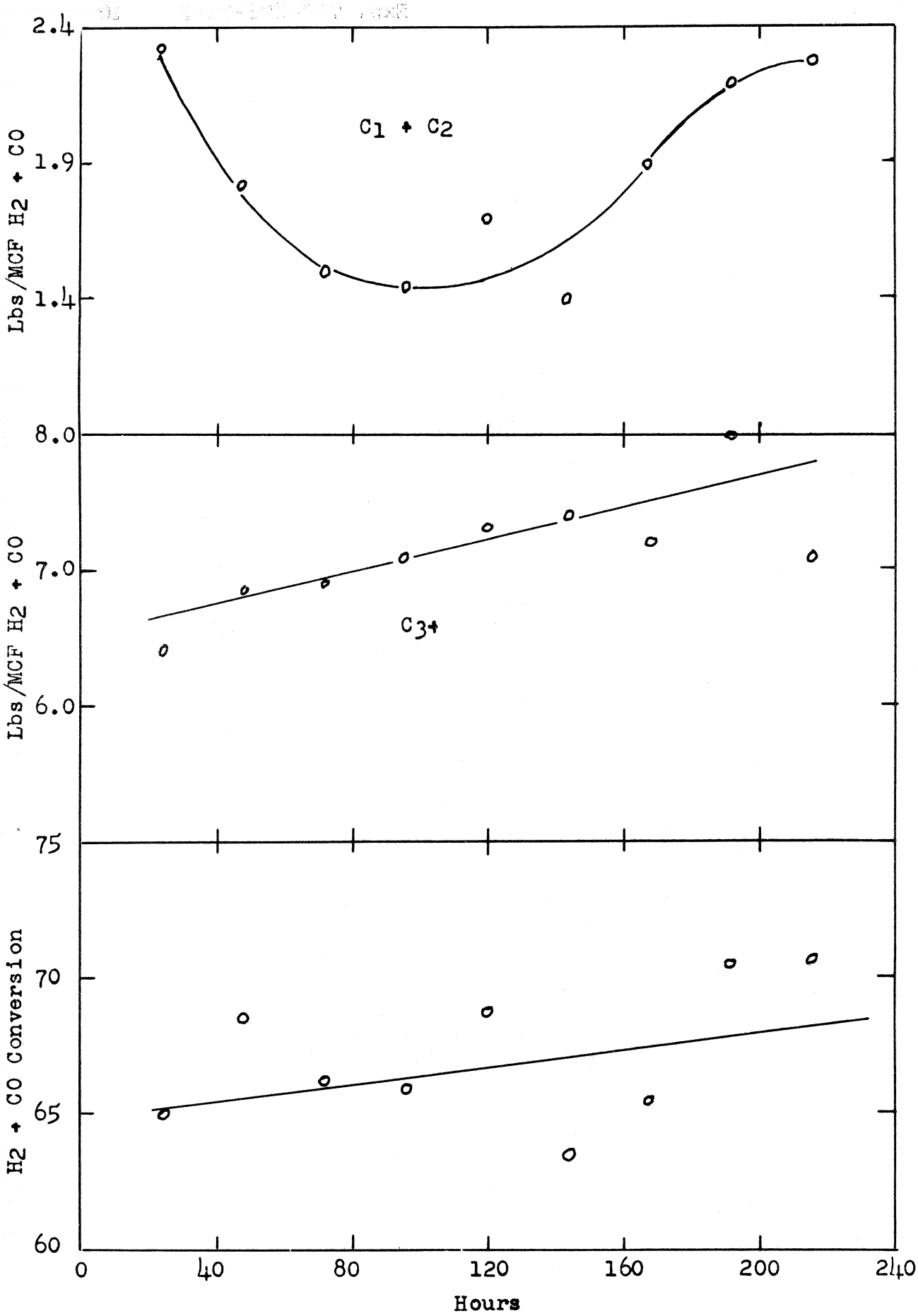


FIGURE 9
RUN 40

2. Run 40

Most of the catalyst was removed from the reactor in order to free the main shaft. Then Run 40 was started with 418 pounds of used catalyst from Run 39. Both fresh and used catalyst was charged during the run, making a total of 778 pounds used altogether.

The same shaft speed troubles were experienced in Run 40 as in Run 39. Various methods were tried to alleviate the trouble, such as varying the gas flows and temperatures; but it was decided finally that a larger turbine would be necessary, and the run was terminated after 216 hours.

Figure 9, opposite, shows the H_2 + CO conversion and yields of C_1 + C_2 and C_{3+} for Run 40. The yields from Run 40 were calculated the same as in Run 39. The weight balances were not as erratic, however, and usually were in the 85 to 90 per cent range.

The C_1 + C_2 yields declined steadily to about 1.4#/MCF H_2 + CO after 100 hours and then increased to 2.27#/MCF H_2 + CO after 216 hours. The C_{3+} yields and H_2 + CO conversion both increased steadily as the run progressed.

3. Run 41

A larger turbine was installed for Run 41, and although it solved the problem of controlling the speed of the main shaft and impellers, the circulation of the catalyst was so poor that the run was continued only 79 hours. There were 994 pounds of catalyst charged to the reactor for this run. Figure 10, following, shows the C_1 + C_2 and C_{3+} yields and the H_2 + CO conversion data for Run 41.

The yields of C_1 + C_2 declined to a minimum of 2.0#/MCF

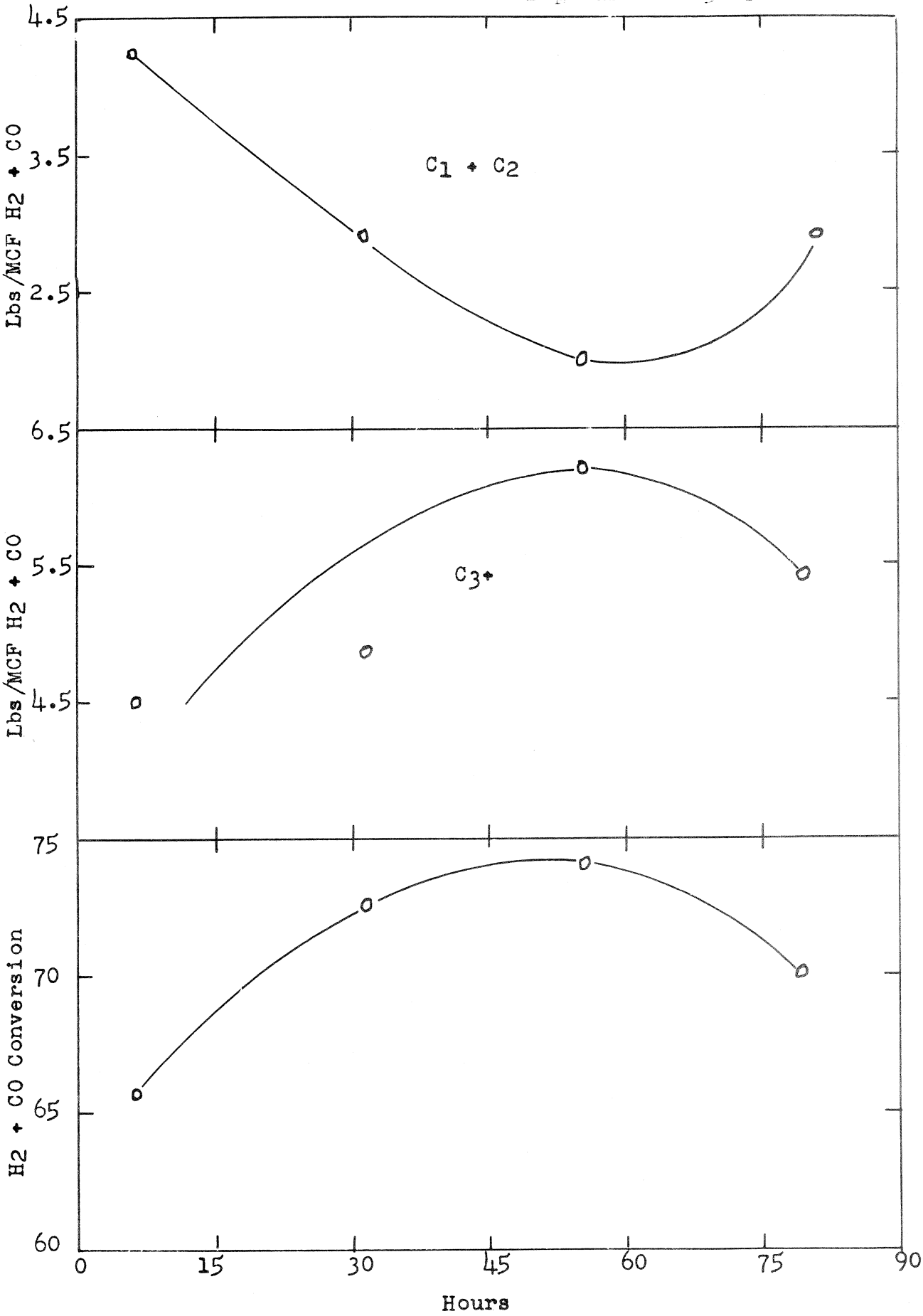


FIGURE 10
RUN 41

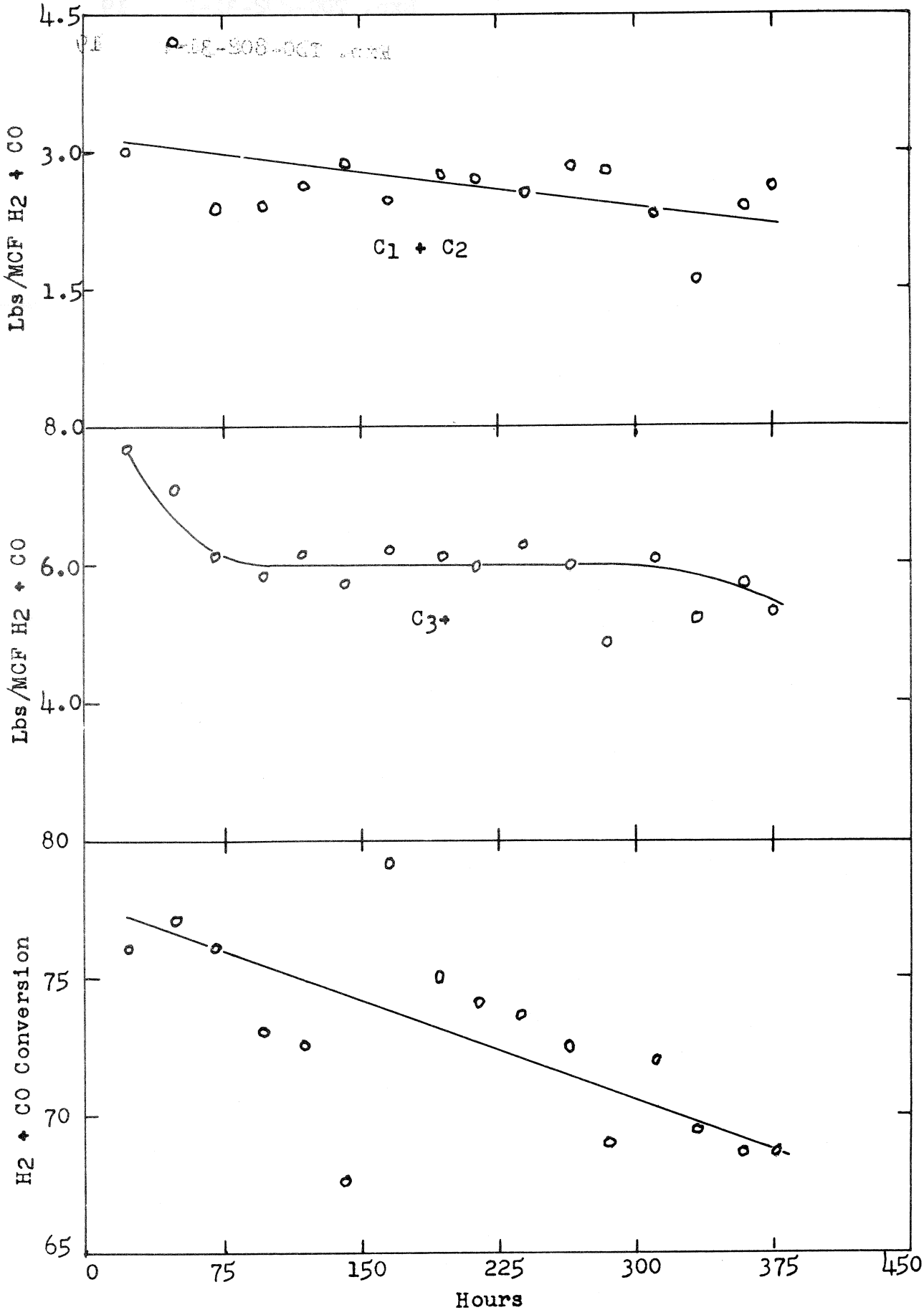


FIGURE 11
RUN 42

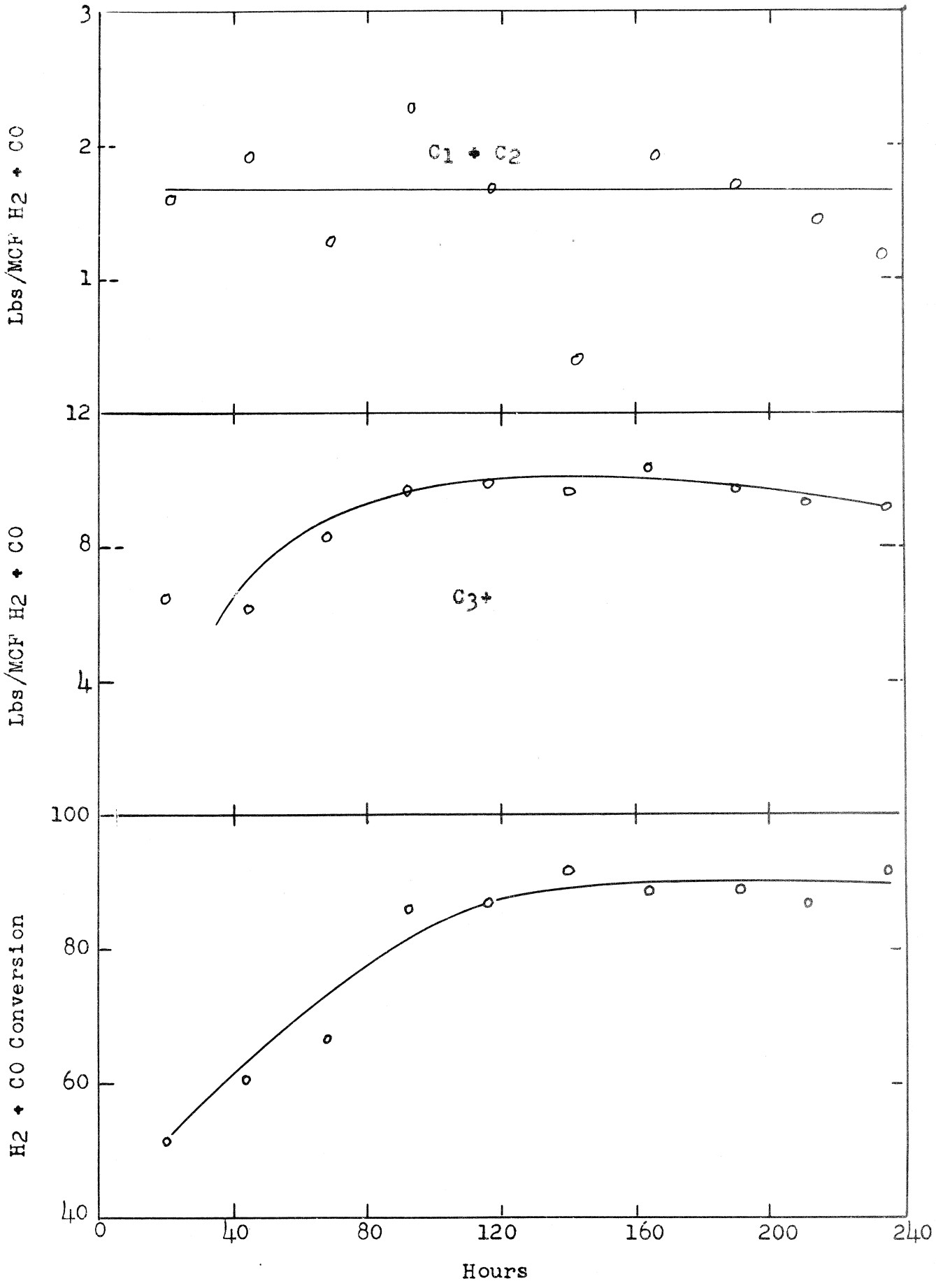


FIGURE 12
RUN 22

H_2 + CO and then increased again to 2.9#/MCF H_2 + CO. The minimum was reached after 55 hours. At the same time, the C_{3+} yields and H_2 + CO conversion had risen to maximums of 6.3#/MCF H_2 + CO and 74 per cent respectively.

4. Run 42

Run 42 continued for 378 hours and was the longest one made on the Stratco Reactor. A total of 899 pounds of catalyst was used. In general no mechanical difficulties were encountered until the run was terminated by an explosion in the generator system. The explosion, which split several pieces of pipe, was caused by a failure in the natural gas supply which created a large excess of oxygen in the fresh feed gas going to the reactor. An alarm, governed by the ratio of oxygen to gas flowing to the generator, was installed to prevent a recurrence of this incident.

Figure 11, page 19, shows the H_2 + CO conversion and yields of C_1 + C_2 and C_{3+} for Run 42. For comparison, the same type of data from Run 22 is shown in Figure 12, page 20. Run 22 was made with KF promoted pyrites ash catalyst on the original Montebello Vertical Tubular Reactor.(1) The yields of C_{3+} were considerably higher in Run 22, whereas the less desirable yields of C_1 + C_2 were lower. The 400 end-point fraction of the product oil was about 10 to 15 per cent higher in Run 42 than in Run 22 and reached a maximum of 82.6 per cent after 360 hours operation.

During a portion of Run 42, the methane content of the fresh feed varied between 1.6 per cent and 6.7 per cent while most other conditions remained constant. The fresh feed and wet gas were sampled every eight hours at identical times. This

(1) Partial Report No. 13, Experiment No. TDC-802

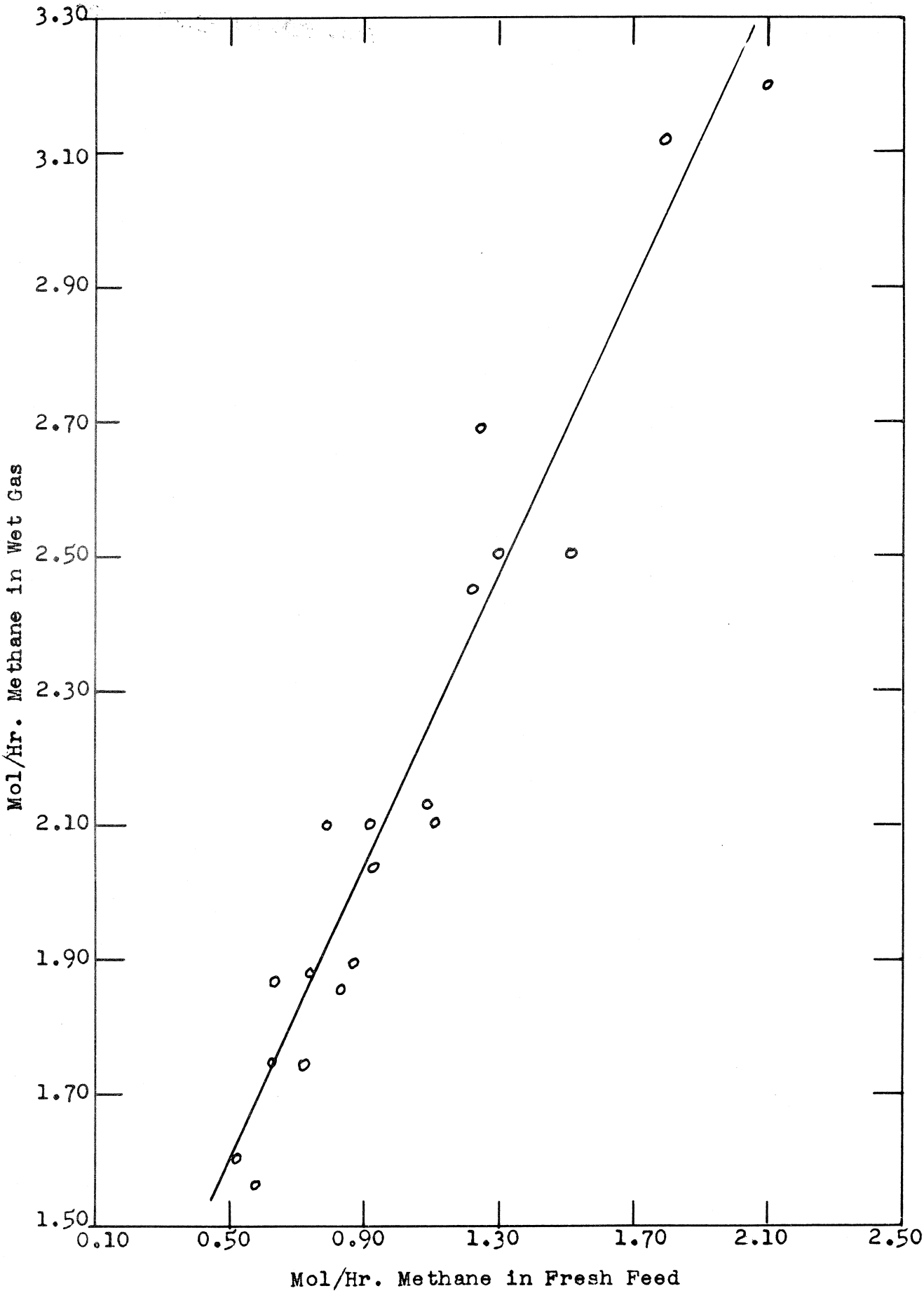


FIGURE 13
RUN 42

afforded an excellent opportunity to study what effect the methane content of the fresh feed had on the methane yield of the synthesis unit.

In Figure 13, opposite, the moles per hour of methane in the wet gas were plotted against moles per hour of methane in the fresh feed. This plot was a straight line and indicated that the methane yield of the reactor was almost constant during the test period, varying between 1.1 moles per hour and 1.2 moles per hour.

The catalyst particle size distribution for Run 42 is compared with that of Run 22 in Table I below. There was no make-up catalyst added to the reactor in Run 42 except for one charge of 120 pounds after 30 hours operation, but there were considerable amounts of catalyst added to the reactor at frequent intervals during Run 22.

TABLE I

Run No.	22	42	22	42	22	42	22	42	22	42
Hours	21	24	69	72	93	96	189	192	237	240
Microns										
420+	3.6	19.2	2.8	14.4	2.8	5.6	1.5	0.6	2.3	0.4
419-150	19.2	30.6	19.3	44.6	9.8	48.2	9.1	61.6	9.2	44.7
149-105	24.4	8.3	22.7	7.4	12.5	8.4	8.2	13.6	8.8	17.8
104-74	18.6	9.7	20.6	9.6	10.9	9.4	11.2	8.4	8.3	9.6
73-62	5.0	8.1	4.4	3.4	5.1	6.2	0.9	2.8	1.1	3.4
61-44	10.8	7.5	11.5	8.8	4.1	7.0	1.1	5.0	1.2	11.2
43-0	18.4	16.6	18.7	11.8	54.8	17.2	68.0	8.0	69.1	12.8

In order to give a picture of the size of the Stratco Reactor relative to throughput, some yield and dimensional data are given in Table II for Runs 42 and 45.(1) Run 45 was made on a conventional type Vertical Tubular Reactor using the same type of catalyst and approximately the same flow conditions as existed in Run 42.

The data indicate that yields of the same magnitude

(1)More complete data for Run 45 will be found in Partial Report 32 Experiment No. TDC-802.

were obtained with the Stratco Reactor as with the Vertical Tubular Reactor, using the same quantities of fresh feed, but at the expense of using a complicated vessel of twice the bulk size.

If it be assumed that most of the synthesis reaction takes place in the center tube (stirred section), then it appears that this section has very good reaction efficiency in view of the high space velocity in this section. This is more than offset, however, by the low efficiency in the annulus, making the overall efficiency lower than that of the Vertical Tubular Reactor.

TABLE II

	Run 42			Run 45	
	Gross	Net Open Space Used	Center Tube Open Space	Gross	Net Open Space Used
Height, Ft.	21	13	12	19	8
Cross Section, Sq. Ft.	1.4	0.6	0.275	0.79	0.66
Volume, Cu. Ft.	29	7.8	3.3	15	5.3
Feed Rate, SCFH	12,000	12,000	12,000	12,000	12,000
SCFH/Cu.Ft. Reactor	400	1,500	3,600	800	2,300
Yield, Gals. of C_{3+}/MCF H_2 + CO	1.2	1.2	1.2	1.2	1.2

5. Run 43

Run 43 was the last run of the present series made on the Stratco Reactor. The total number of hours on stream was 168 and the number of pounds of catalyst used was 1359. The system was shut down when a slug of water carried over from the generator system into the reactor, lowering the catalyst temperature and stopping the synthesis reaction.

The fresh feed rate during the last 48 hours on stream was about half of the rate which existed during the first 72 hours of the run, and the recycle to fresh-feed ratio was about doubled

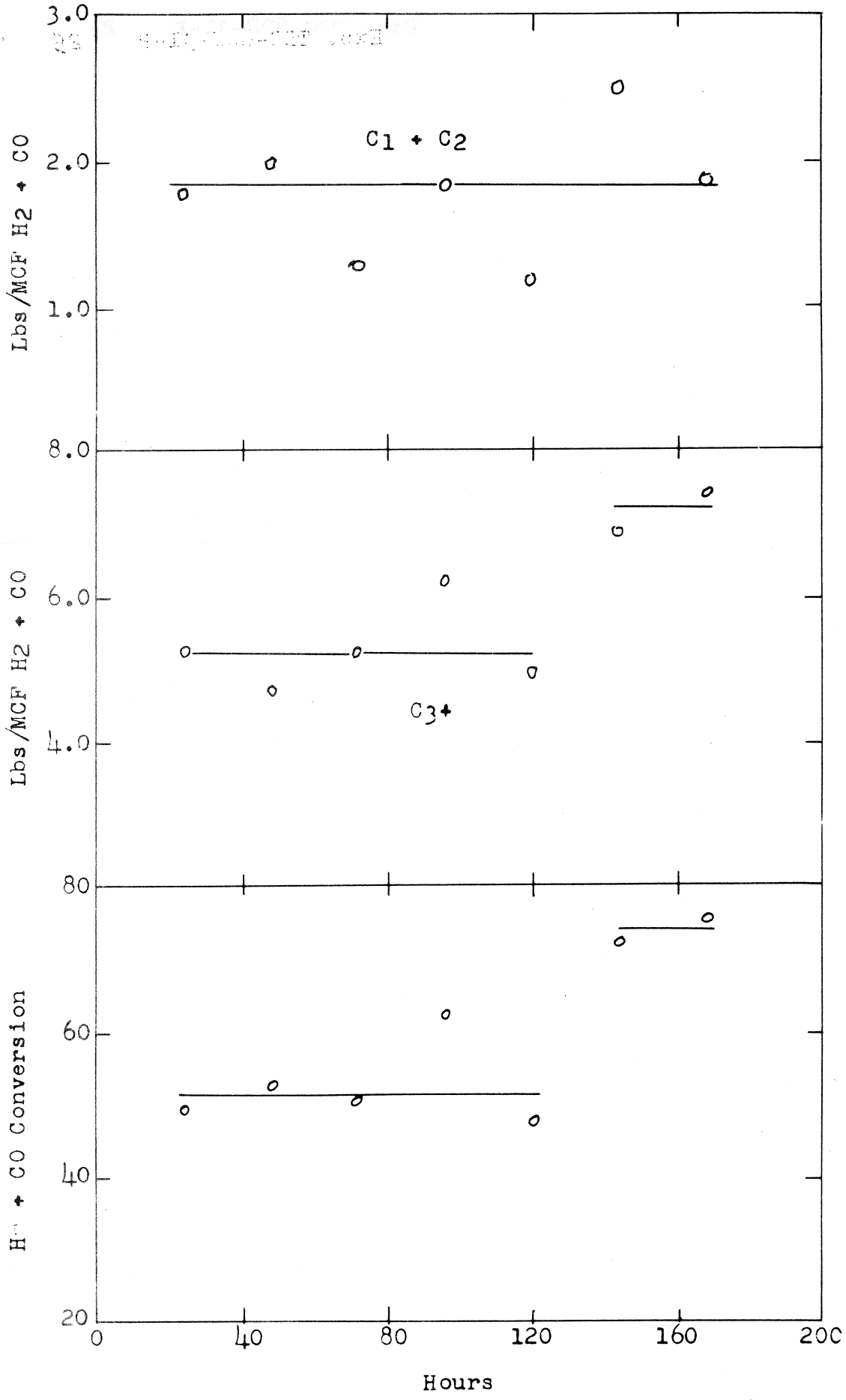


FIGURE 14
RUN 43

by lowering the feed rate. This change in feed rate was accompanied by an increase in yields of C_{3+} and an increase in $H_2 + CO$ conversion as shown in Figure 14, opposite.

6. Suggested Changes in the Stratco Reactor

It is thought that the operability of the Stratco Reactor for hydrocarbon synthesis could be improved by increasing the diameter-to-length ratio of the main shaft to reduce vibration and whipping. This could be accompanied by an increase in the volume of the reaction (stirred) zone in relation to the volume of the annulus. The outside cooling jacket possibly may be eliminated. In actual operation the outside jacket was used only as an air jacket in the runs discussed in this report. A change in design of the outside of the vessel to allow better insulation would be helpful because the heat loss from the Stratco Reactor was much higher than from the conventional type.