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 325 psig and at temperatures in the 2300°F. range. The natural gas 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 normally contained less than 4 per cent unconverted methane, 2 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]/

1/Partial Report Nos. 5, 10, and 13, Experiment No. TDC-802.
2/Data on the synthesis gas generations appear in the Appendix.

CYCLONE

TO FLARE

COOLER

PR

HYDROGEN CYLINDERS
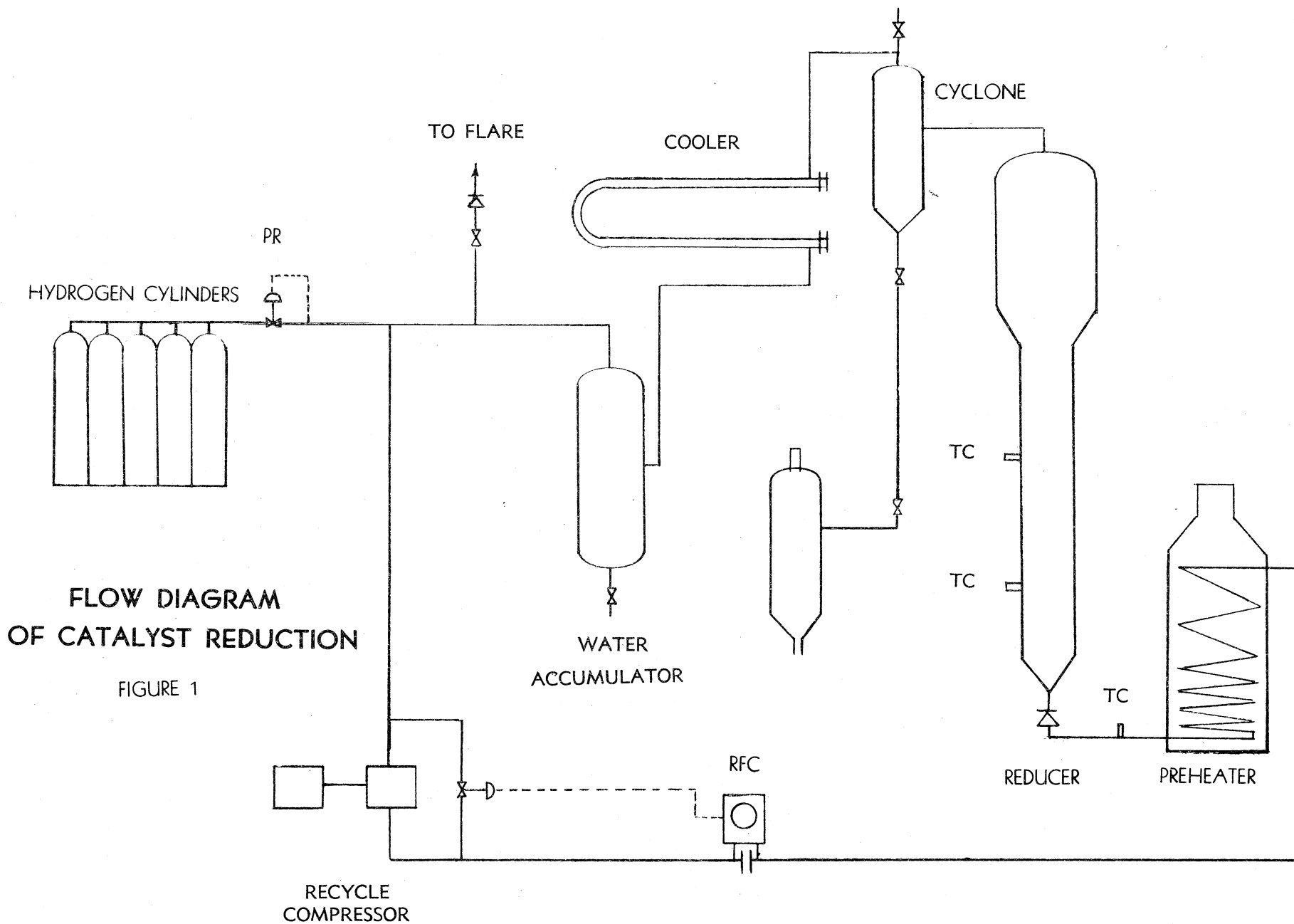
FLOW DIAGRAM
OF CATALYST REDUCTION

FIGURE 1

TC

TC

WATER
ACCUMULATOR

TC

RFC

REDUCER

PREHEATER

RECYCLE
COMPRESSOR

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, and sent to the Twining Laboratories of Fresno, California, for drying and grinding.

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

A.S.T.M. Sieve No.	Weight Per Cent
On 40	23.4
100	42.3
140	11.7
200	10.1
230	3.4
325	3.0
Through 325	6.1

The impregnation of the mill scale with potassium carbonate was conducted in a rectangular 3' x 7' x 1' 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.

CATALYST REDUCER

FIGURE 2
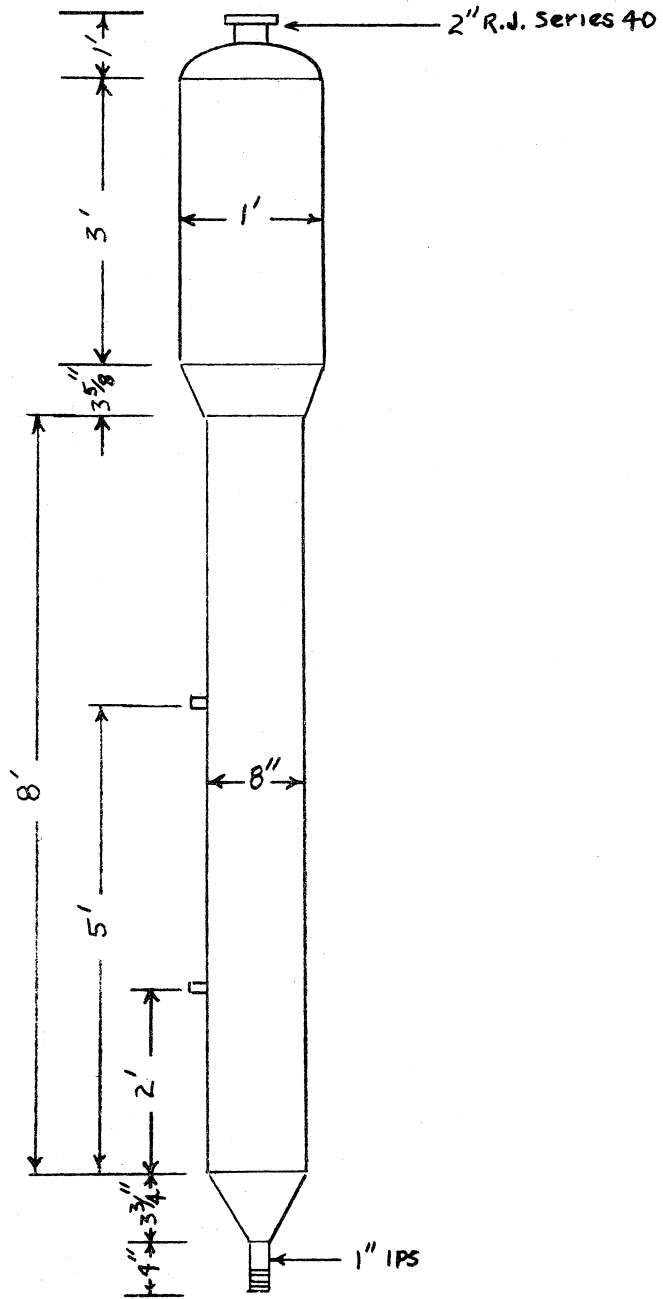
The catalyst was considered sufficiently reduced when water production decreased to approximately one-tenth pound per hour. After reduction and prior to use the catalyst was kept blanketed and handled in an atmosphere of carbon dioxide obtained by the evaporation of "dry ice" furnished by the Pure Carbonic Company of Los Angeles.

Hydrogen was used as a purging medium to remove air from the reactor system. The reduced catalyst was then charged to the reactor, and the bed temperatures were brought to the desired level by circulating hot hydrogen before introducing the synthesis gas.

3. Synthesis System

a. Description of Synthesis Reactor

The reactor consisted of a vertical, cylindrical vessel constructed from a 19-foot section of 12" seamless pipe having a 1/2" wall, and was fitted internally with three 2" schedule 80 steam tubes which extended the full length of the reactor. These tubes were connected with a steam drum at the top and a blow-down drum at the bottom, the boiler circuit being completed by an external 3" downcomer. This reactor had 2.82 square feet of cooling surface per cubic foot of free reactor space compared with 4.36 square feet in the original Montebello reactor.[1]/

The packing gland, to allow for expansion of the steam tubes, was placed at the top of the reactor instead of at the bottom as on the Reactor No. 1. There had been valves between the steam blow-down drum and the bottom of the steam tubes on the old reactor, but these were eliminated on the new one. The original reactor had been supported by a flared base which rested on the

1/The Brownsville Reactor was designed to have 3.71 sq. ft. of cooling surface per cubic foot of free space.

ground, but this base was also discarded and the new reactor was supported from the top by a framework of structural steel. These changes resulted in a more compact reactor system with much less heat loss, and made it possible to reach higher catalyst bed temperatures more quickly than before with less preheat on the feed gases. This was a distinct advantage when circulating hydrogen to raise the catalyst bed temperatures up to operating level prior to introduction of the synthesis gas. It also meant that the steam system could be put on stream before the fresh feed was cut in.

Synthesis gas and recycle gas were combined, preheated, and fed to the bottom of the reactor. The combined feed entered the reaction zone by passing through a 1/8" annulus around the bottom steam header. Two outlets were provided for the effluent gases from the reactor, one above and one below the top steam header. Since there was only a 1/8" annulus around the top steam header, it was deemed necessary to have an alternate outlet below the header in case the annulus became clogged with catalyst. The hot effluent gases passed through two external, cyclone separators to remove entrained catalyst, and then flowed to a condenser and to a separator where oil and water were removed from the gas. Product oil and water were discharged individually to storage while the gas was compressed and recycled, sufficient gas being released to the flare to maintain the desired reactor pressure.

The heat of reaction was removed by the steam system which worked on a thermal siphon principle. Water, which was almost boiling, entered the bottom of the steam tubes, picked up heat from the reaction zone, and bubbled up to the steam chest

LC - LEVEL CONTROLLER
TR - TEMPERATURE RECORDER
RPC - RECORDING PRESSURE CONTROLLER
RFC - RECORDING FLOW CONTROLLER
FR - FLOW RECORDER
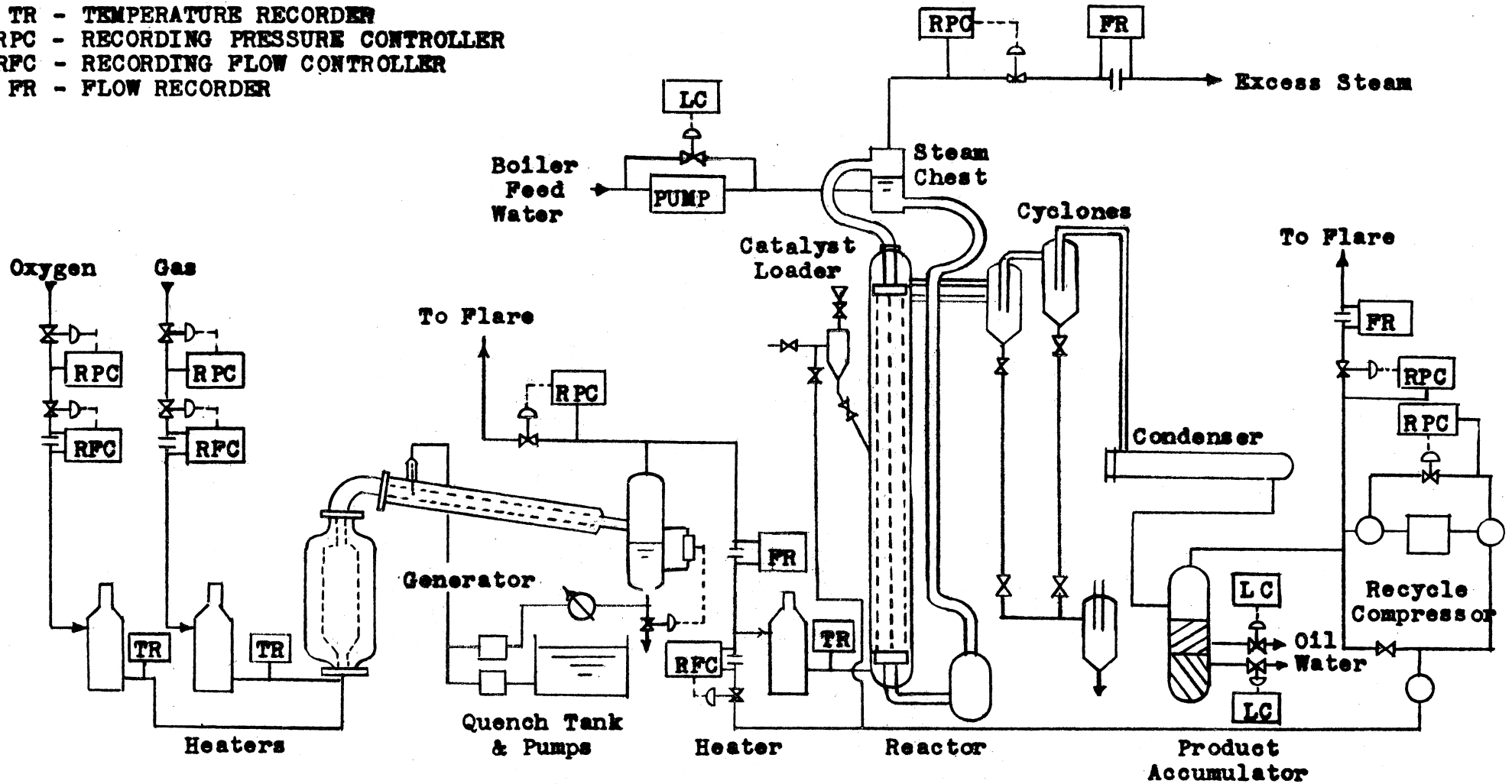
FLOW DIAGRAM OF GAS-FIRED GENERATOR
AND MONTEBELLO REACTOR

FIGURE 3

as a mixture of steam and water. Enough steam was released from
the steam chest to maintain the steam pressure at the desired level.
Slightly cooler water descended through the downcomer to complete
the boiler circuit. The water level in the system was maintained
by pumping in fresh boiler water at about 170°F. The entire steam
system was heavily insulated so that most of the heat removed from
the system was in the high pressure steam. Figure 3, facing, and
Figure 4, following, illustrate the reactor and steam systems.

The bed temperatures were controlled by varying both the
preheat temperature of the feed gas and the pressure in the steam
system. The higher the steam pressure, the less the temperature
differential between the steam tubes and the catalyst beds, and
the cooling effect of the steam diminished. The steam pressure
was normally above 650 psi. The feed gas preheat temperature was
usually in the range of 400 to 600°F.

The catalyst loader on the reactor consisted of a two-
foot section of 8-inch pipe swaged to a 2-inch cock on the bottom
and a 3-inch cock on top. The catalyst, blanketed with CO_2, was
poured through a funnel into the air-free loader while the bottom
cock was closed. After the top cock was closed, the loader was
pressured with recycle gas to about 75 psi more than the reactor
pressure. When the bottom cock was opened, the catalyst charge was
forced into the reactor. The loader remained full of recycle gas
when it was not in use.

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
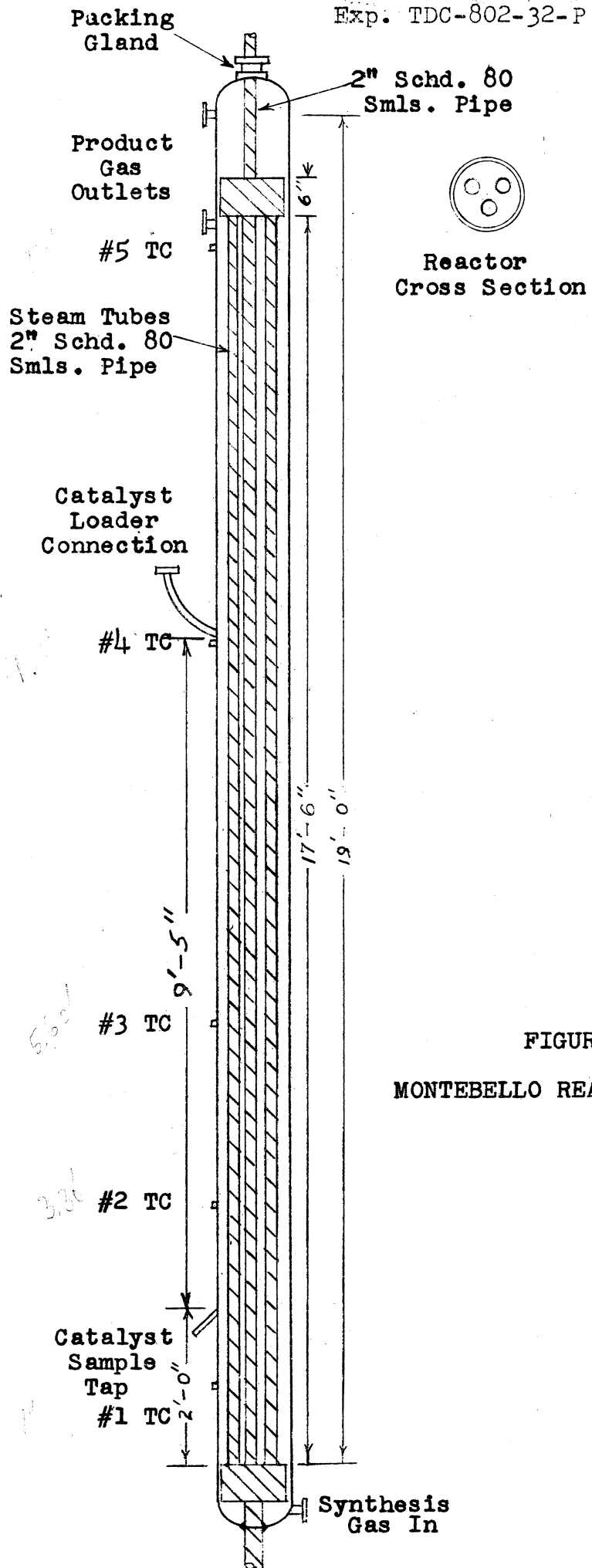24-hour average made of these three analyses.

Packing
Gland

2" Schd. 80
Smls. Pipe

Product
Gas
Outlets

#5 TC

Reactor
Cross Section

Steam Tubes
2" Schd. 80
Smls. Pipe

Catalyst
Loader
Connection

#4 TC

6"

17'-6"

19'-0"

9'-5"

#3 TC

FIGURE 4

MONTEBELLO REACTOR NO. 3

#2 TC

Catalyst
Sample
Tap

2'-0"

#1 TC

Synthesis
Gas In

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

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 the generator but these were only for control purposes.

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. 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 catalysts.

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

The water-soluble chemicals (alcohols) content of the water was determined by salting out with potassium carbonate at 40°F. to 50°F.[1] These chemicals were predominantly alcohols and did not include the light organic acids.

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[1] This 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 TDC-101-33.

c.   Methods of Calculation

The 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 yields of separated oil and water were based on actually measured quantities. The term "C_3+" has been used in this report to denote all hydrocarbons having three or more carbon atoms to the molecule, plus all of the water-soluble chemicals as determined by salting out with K_2CO_3.

B.   Experimental Results

Five hours after 610 pounds of reduced catalyst had been charged to the reactor under hydrogen pressure, the fresh feed was cut in to start Run 45. After 39 hours, a charge of 182 pounds of reduced catalyst was loaded. Again after 123 hours another 182-pound charge was loaded. Each time there was a temporary increase in yields of C_3+. Between periods 45-H and 45-I there was an interval of 55 hours when the generator was shut down. During this time, hot hydrogen was circulated through the catalyst to keep the bed temperatures about 650°F. This seemed to rejuvenate the catalyst because the yields of C_3+ were higher for the next 53 hours (150 to 203 hours). The oil yield decreased during period 45-M but was brought up by addition of 161 pounds of reduced catalyst after 229 hours and 170 pounds after 255 hours. The oil yield was declining again after 303 hours when 207 pounds of unreduced catalyst was loaded during period 45-P. The addition of unreduced catalyst was accompanied by difficulty in maintaining the proper bed temperatures, and the yield of C_3+ continued to decline. There was a three-hour shut-down during period 45-P, during which hydrogen was circulated in the reactor. The yield of
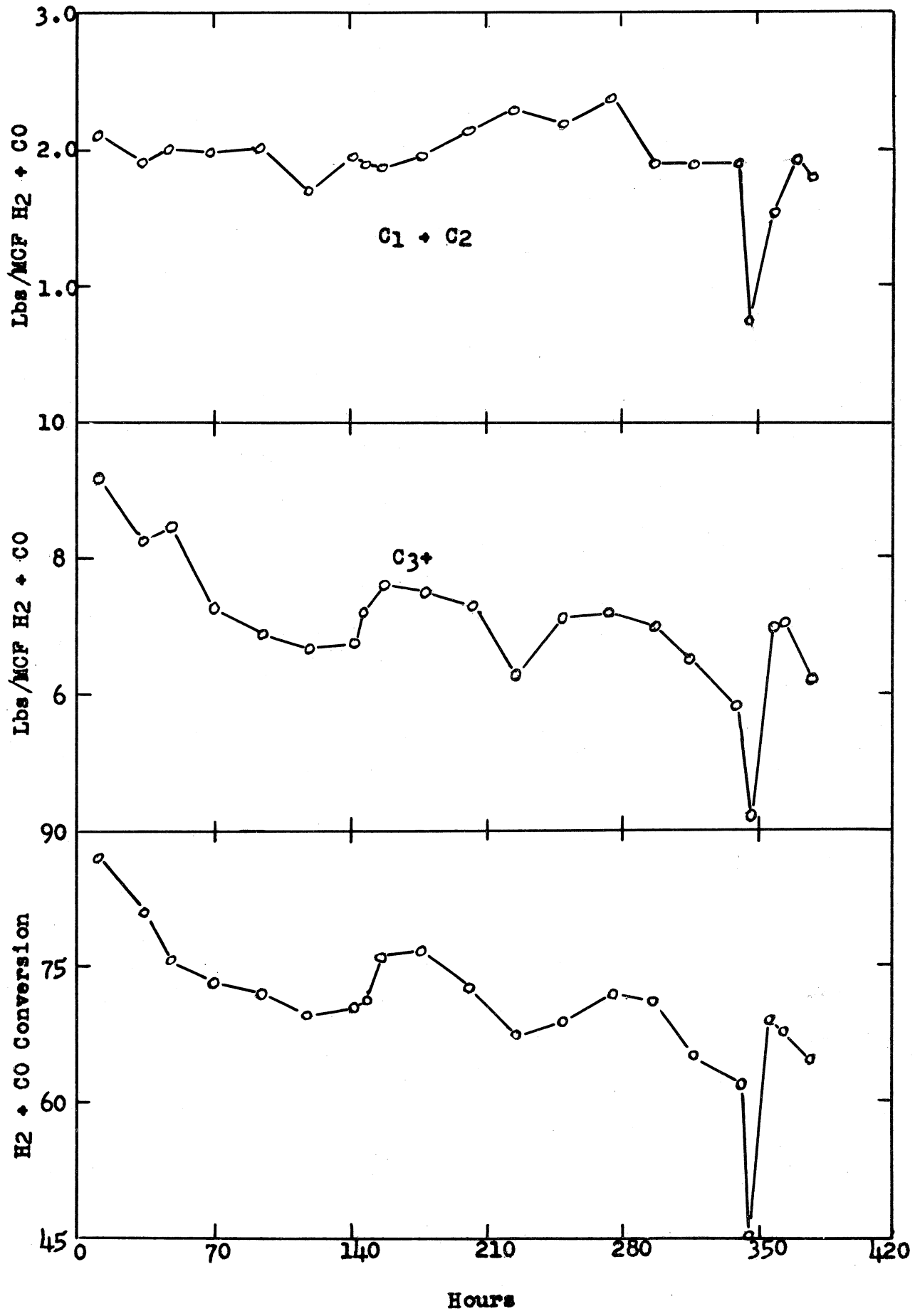
FIGURE 5
RUN 45

C_{3+} declined sharply during period 45-R-1 (343-348 hours) partly because of erratic bed temperatures. At times the temperature gradient of the catalyst bed was as much as 140°F., the bottom being 730°F., and the top being 590°F. During period 45-R-2, 188 pounds of reduced catalyst were loaded. This brought a sharp increase in C_{3+} yields. The bottom of the reactor became plugged, forcing a shut-down after 359 hours, but the run was continued again after a delay of 16 hours. The temperature gradient of the bed was about 600 F. when the feed was first cut in again, but within an hour it was down to about 50°F. Five hours later, a plug in the generator system caused a shut-down which lasted for 24-hours (end of period 45-S). After the unit was back on stream for 15 hours, a partial plug in the reactor terminated the run which had lasted for a total of 379 hours.

The reactor operated satisfactorily from a mechanical aspect. The better insulation and less cooling surface than in the preceding vertical-tube reactor made it possible to put the steam system on stream before cutting in fresh feed. The wild changes in bed temperatures at the beginning of previous runs were not encountered during the start-up of this run. The trouble with plugs in the reactor may have been caused by carbon from the generator or by the sudden addition of a large amount of unreduced catalyst, and could not be attributed to the reactor design.

The many variables such as shut-downs, different kinds of catalyst, circulation of hydrogen, and large bed-temperature gradients tended to prohibit examining the data for long-term trends.

In Figure 5, facing, the chronological yields of $C_1 + C_2$ and C_{3+} have been plotted as pounds per thousand cubic feet of
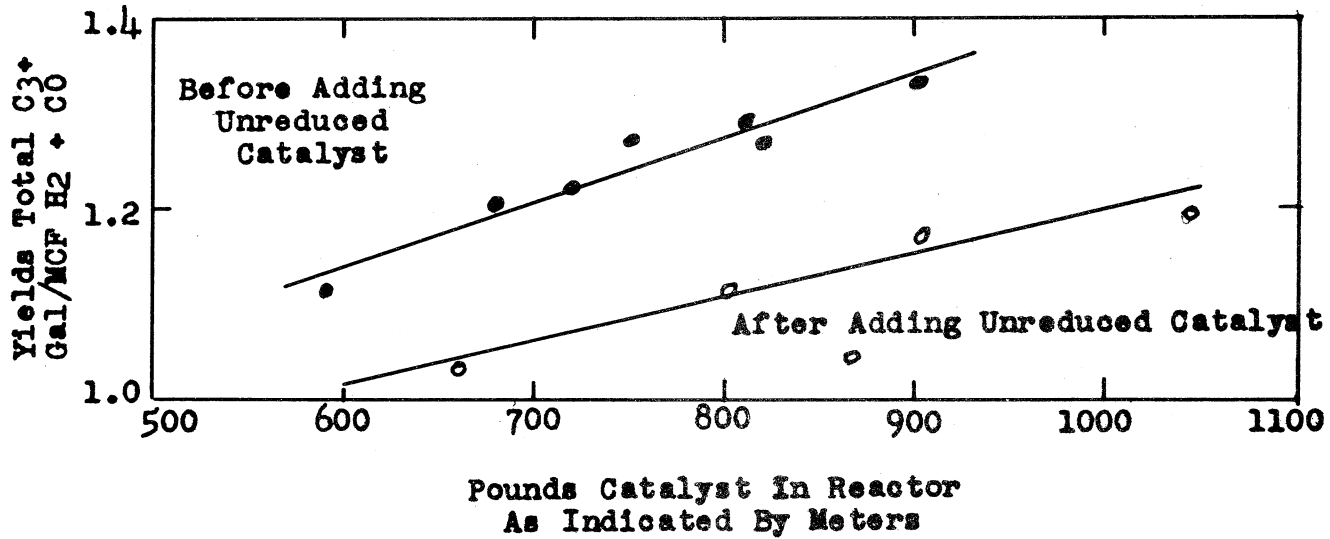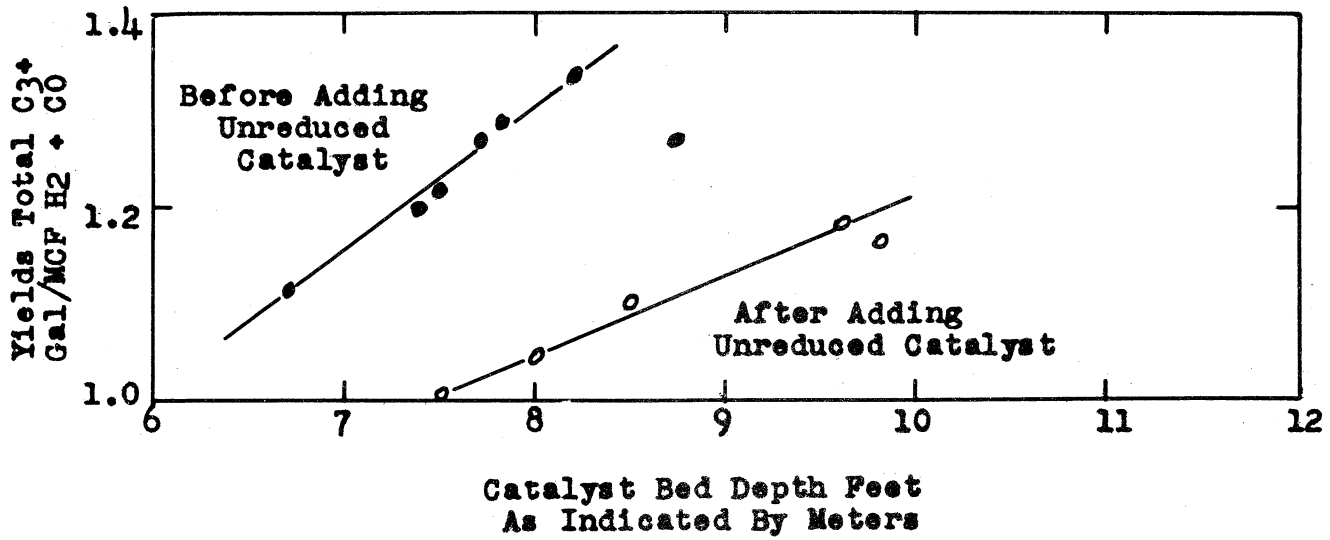
FIGURE 6

RUN 45

H2 + CO fed. The percentages of H2 + CO converted have also been plotted in the same figure. These plots show the previously-mentioned changes which reflect additions of catalyst and circulation of hydrogen through the reactor. It is difficult to say whether or not the addition of unreduced catalyst caused the drop in oil yield which occurred in Run 45-R-1 because it appears from the plots that the yields were probably already declining. The poor fluidization of the catalyst bed, as indicated by the large bed temperature gradients and frequent tendencies to plug, may have been caused by the sudden addition of a relatively large quantity of cold, low activity catalyst. Possibly if the unreduced catalyst had been loaded in smaller quantities over a longer period of time, the effects would have been more beneficial.

In Figure 6, facing, the yields of C3+ in gallons per thousand cubic feet of hydrogen plus carbon monoxide, have been correlated with catalyst-bed depth and with the weight of catalyst contained in the reactor. The catalyst data from periods 45-A through 45-H were not included because the catalyst meters were not working properly during this time. The data from the periods following the addition of unreduced catalyst gave different plots than the data from the periods before the addition of unreduced catalyst. If it be assumed that the unreduced catalyst acted only as a diluent, then altering the data by subtracting about 2.5 feet of bed depth and 275 pounds of catalyst inventory would make the plots practically coincide; but these figures correspond to a catalyst density of 167 pounds per cubic foot, which is slightly high. The plots diverged with increase in catalyst bed depth and inventory, when it appeared thay should have been parallel or
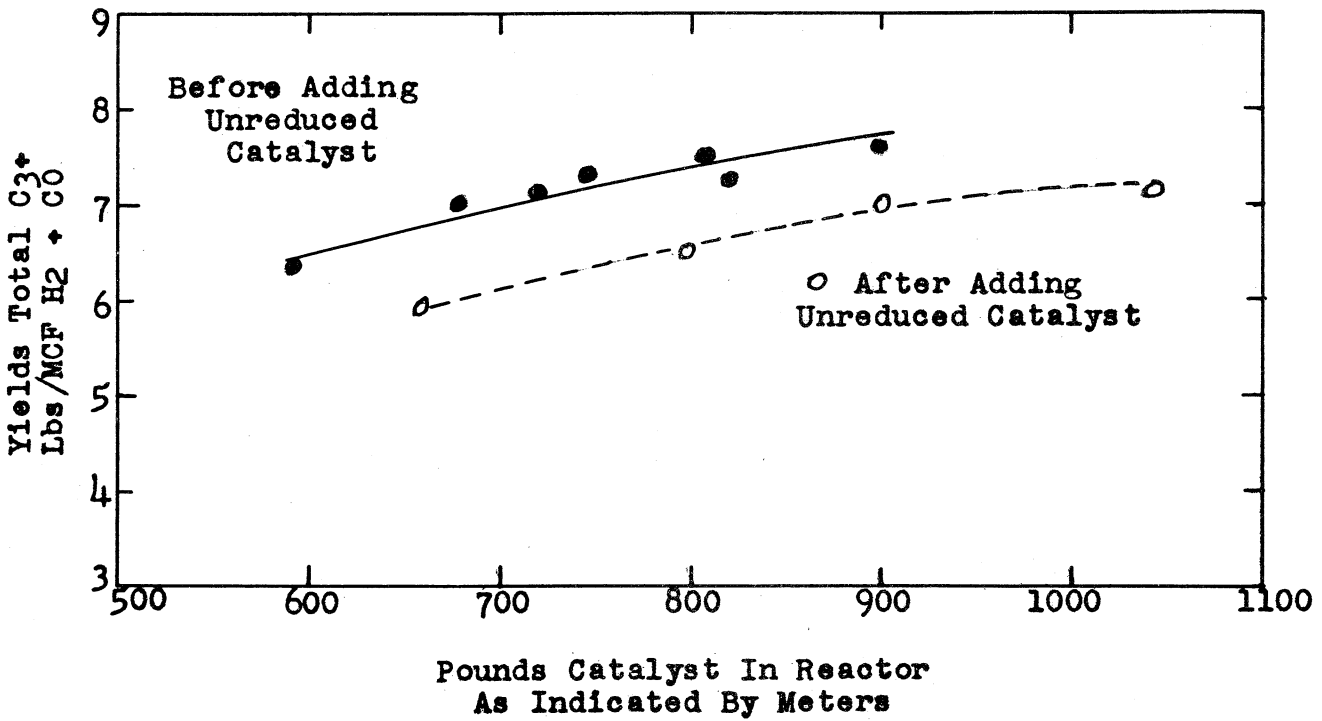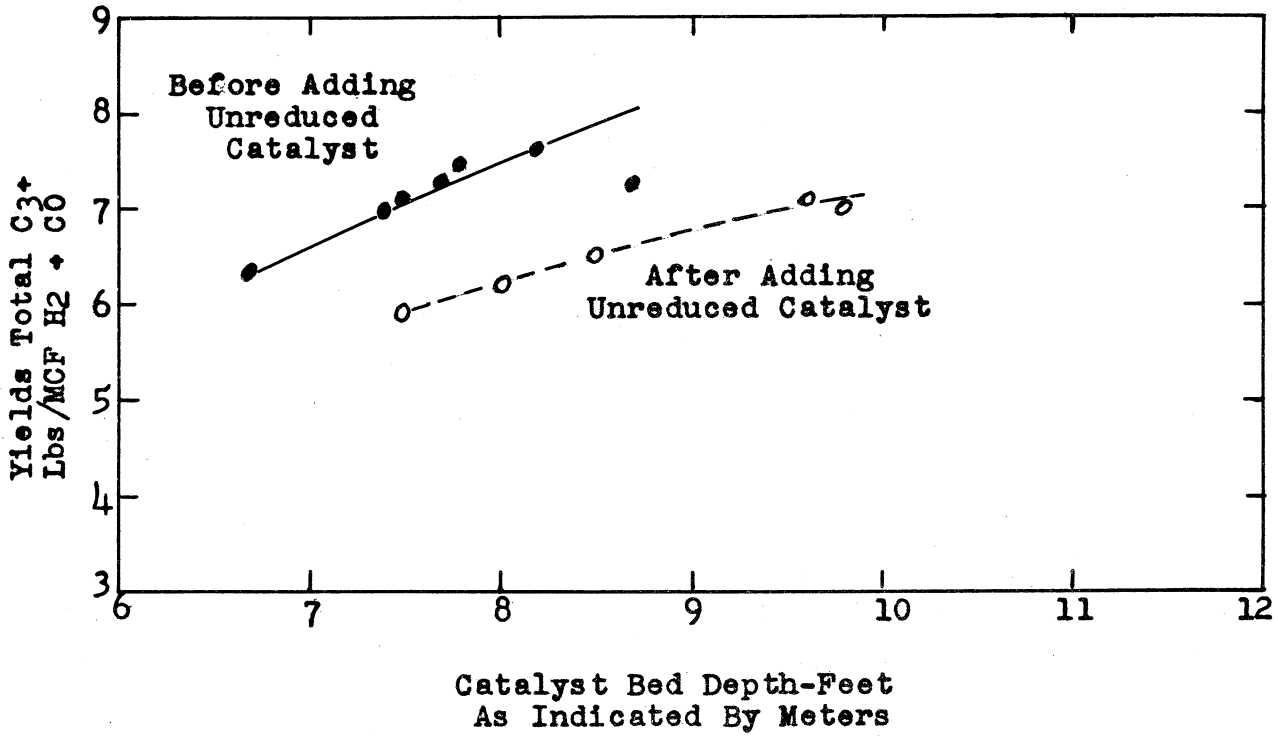
FIGURE 7

RUN 45

slightly convergent.

The same type of data have been plotted in Figure 7, facing, except that the yields have been expressed in pounds per thousand cubic feet of hydrogen plus carbon monoxide in the fresh feed. Two pairs of plots were obtained again, but the pair of lines plotted against catalyst bed height diverged only slightly and the pair plotted against pounds of catalyst in the reactor actually converged slightly. This indicated that the density of the C_3+ fraction might have been changing with variation of catalyst bed height.

The densities, expressed in pounds per gallon, of the C_3+ fractions have been plotted against the weight of catalyst in the reactor as shown in Figure 8, following. There seemed to be no indication of change in the density of the C_3+ fraction with change in catalyst inventory before the addition of unreduced catalyst; but after unreduced catalyst had been added, the density of the C_3+ fraction increased with catalyst inventory in the reactor, even though the changes in inventory were accomplished by adding reduced catalyst. The age of the catalyst, or any other time factor, cannot be used to explain this phenomenon because the catalyst inventory changes were not related to time, some of the later periods having higher or lower inventories than earlier periods.

In order to ascertain whether or not any particular component of the C_3+ fraction contributed heavily to these changes in density, the yields (in gallons per MCF $H_2 + CO$) of the C_3-C_6, 400°E.P., 400°-550°, 550°+, and the water-soluble chemicals fractions have been plotted against weight of catalyst in the
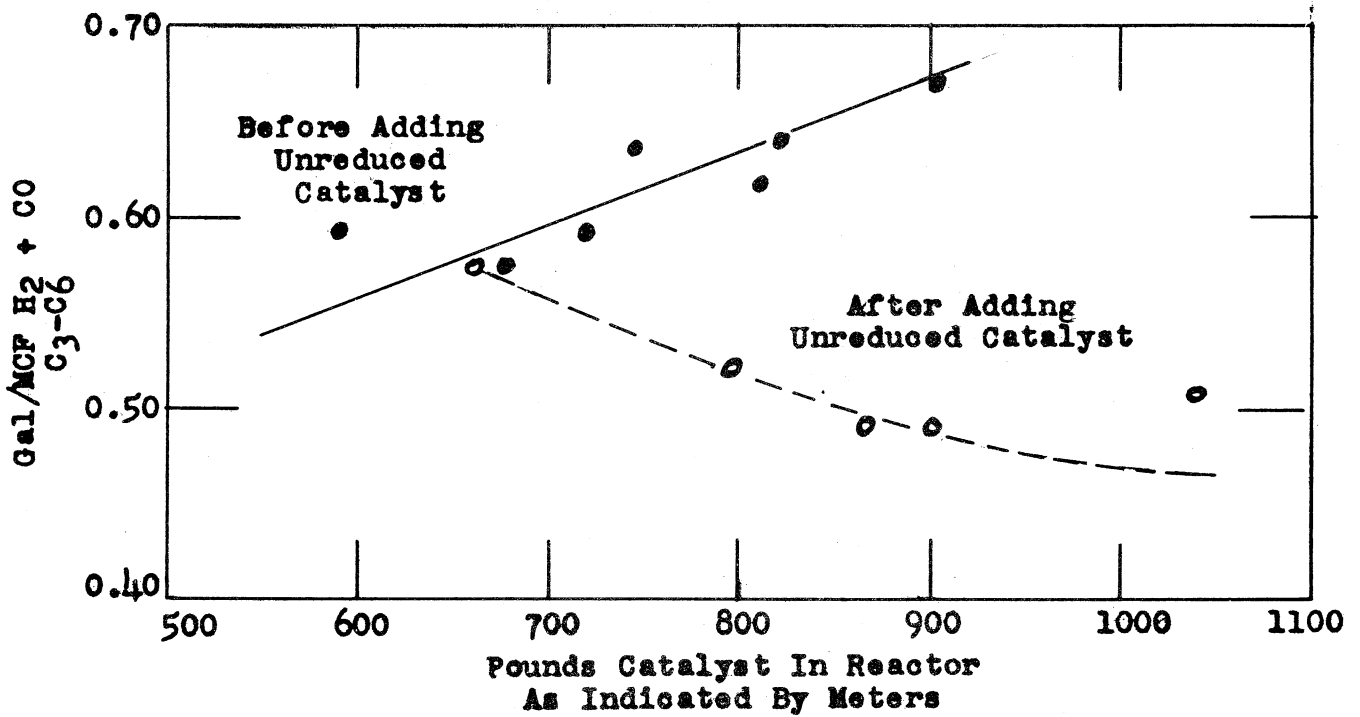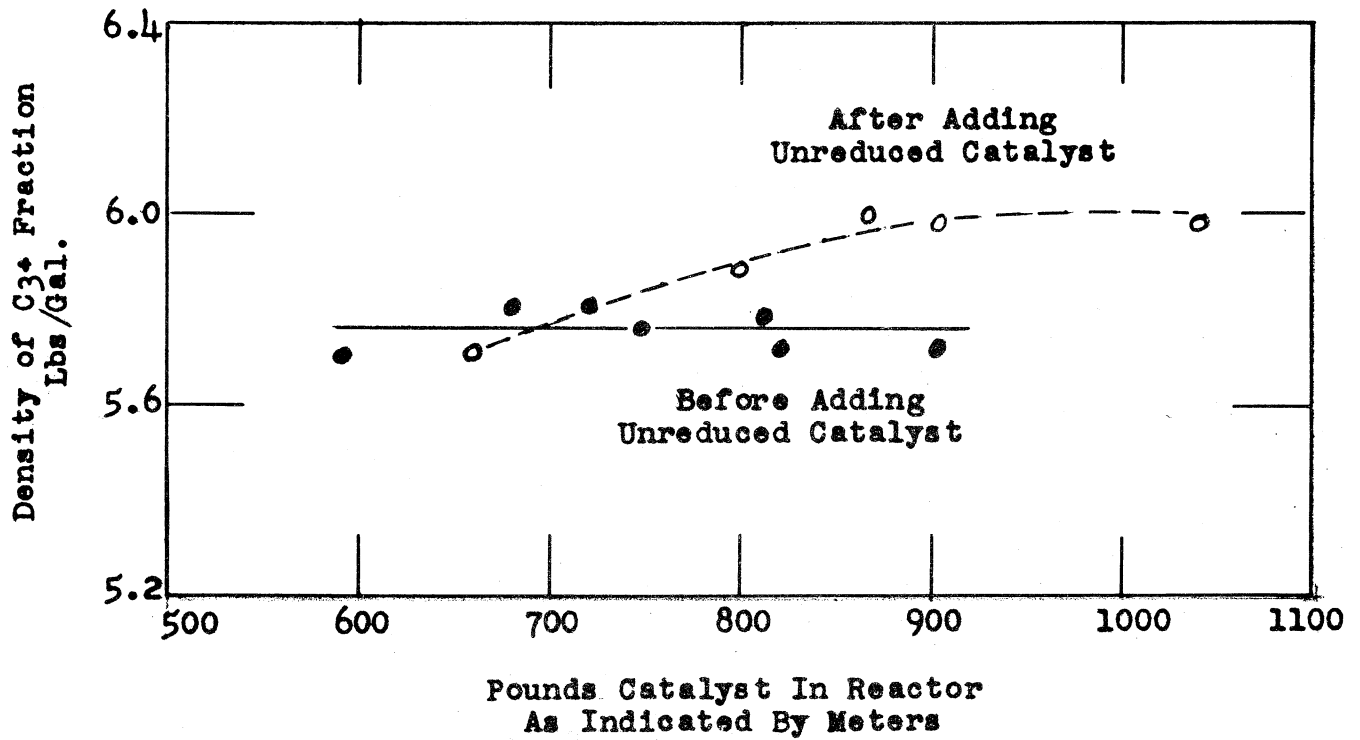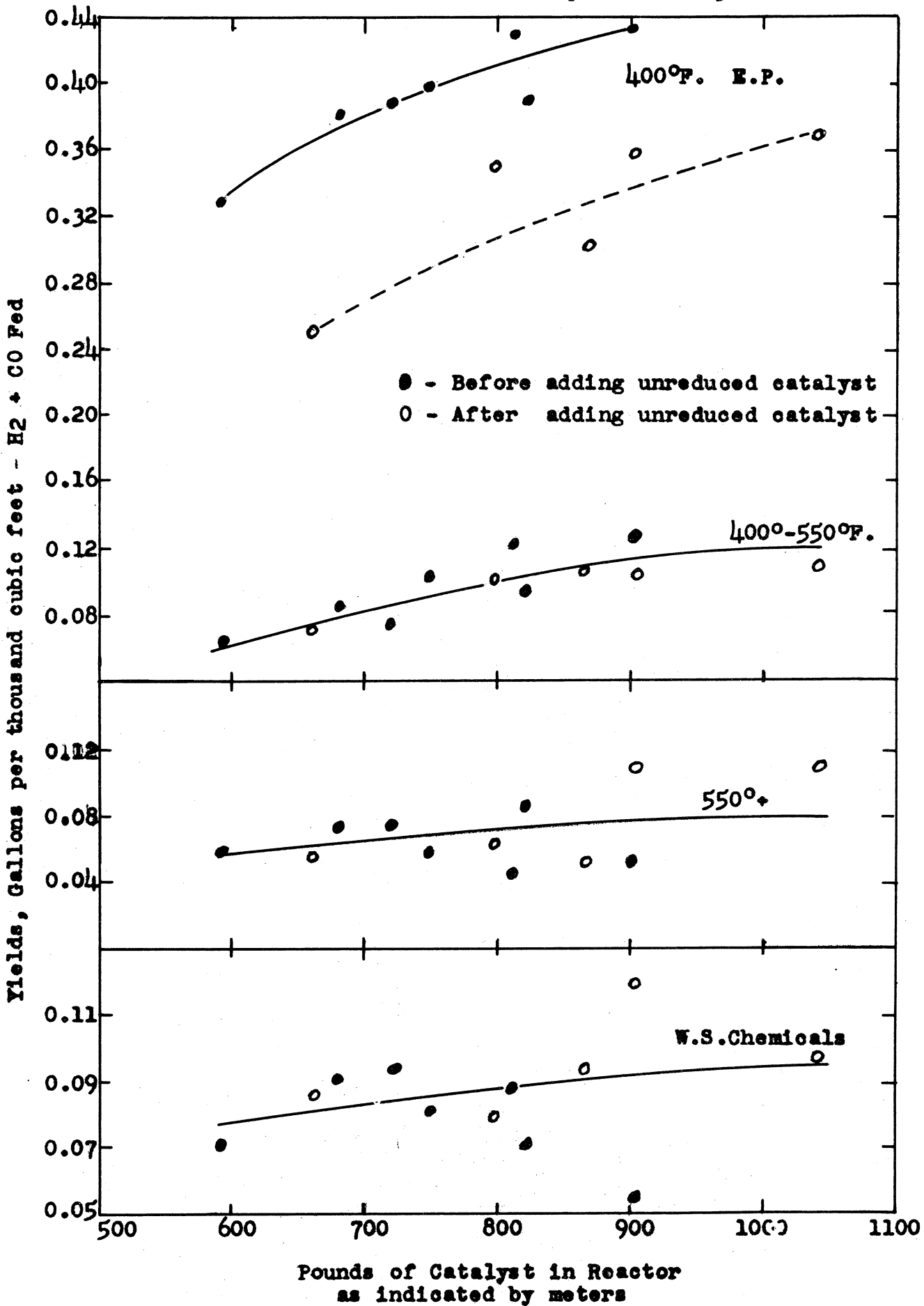
FIGURE 8

RUN 45

FIGURE 9

RUN 45

reactor and shown in Figure 8, page 19, and Figure 9, page 20.
The variation of the density of the C_{3+} fraction after addition of
unreduced catalyst seems to have been due primarily to the C_3-C_6
component. Before the addition of unreduced catalyst, the yields
of C_3-C_6 increased when the catalyst inventory increased, but once
unreduced catalyst had been put in the reactor the yields of
C_3-C_6 declined moderately with increasing catalyst inventory.