

ATTACHMENT

**AUTOCLAVE TESTING OF UCI CATALYSTS
IN SUPPORT OF THE
F-T TRIAL RUN IN A SBCR**

R. R. Frame and H. B. Gala

**UOP
DES PLAINES, ILLINOIS**

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The objective of this work was to provide support for the trial Fischer-Tropsch (F-T) run that was carried out in the slurry bubble-column reactor (SBCR) at the LaPorte Alternative Fuels Development Unit. UOP support consisted of: autoclave (continuous stirred-tank reactor) testing for catalyst evaluation and correlation of autoclave data with SBCR data. A total of seven different runs with six different catalysts were carried out. Information collected during this support activity is discussed in two parts in this report. Part I of this report describes the seven runs carried out and Part II compares the performance of the catalyst in autoclave with that observed in the SBCR.

PART I.

SUMMARY OF AUTOCLAVE RUNS

Five catalysts prepared by United Catalysts Inc. (UCI) were evaluated in a slurry autoclave plant at UOP. These catalysts were prepared as potential catalysts for use in the SBCR demonstration run at LaPorte, Texas. The initial catalyst (UCI "O") was prepared to have the same composition as a commercially available Ruhrchemie catalyst which was also evaluated as part of this work. The fifth catalyst ("Composite" catalyst) was the one actually used in the LaPorte run.

The UCI "O" catalyst composition and performance differed from the Ruhrchemie catalyst necessitating preparation of additional catalysts. Specifically, the UCI "O" catalyst was less selective for light ends than the Ruhrchemie catalyst. The objective in preparing the subsequent catalysts was low wax production (high light ends production). The reason was that catalyst/wax separation was expected to be a key problem in SBCR operation. It was presumed that low wax-producing catalysts will not put as much stress on the separation process (filtration).

All catalysts evaluated were four component catalysts, that is they all contained iron, copper, silicon and potassium in their oxide form. Catalyst compositions are summarized in Table 1.

For the tests carried out with the Ruhrchemie (Run 31), UCI "O" (Runs 44 and 48), UCI "A" (Run 50), UCI "B" (Run 51), and UCI "Start-up" (Run 53) catalysts, UOP's standard procedure for activation and testing was used. The slurry autoclave reactor used for these runs is operated in a hot box which is maintained at 130°C. A schematic of the plant as it was operated in Runs 31 and 44 is shown in Figure 1. For Run 48 and onwards a second trap was added to the hot box so that overhead condensate from the product gas and wax from the periodic wax withdrawals could be trapped separately. A schematic of this modified configuration is shown in Figure 2. The hot box traps are maintained at a pressure 5 psi less than the autoclave. Feed is added continuously below the level of liquid in the reactor. Overhead gas is removed continuously from the reactor, the part of it that does not condense in the hot box trap is taken first into a trap which is maintained at 0°C and 50 psig followed by a -78°C trap (atmospheric pressure). Slip streams of the gas leaving the 130°C hot box and the 0°C trap are analyzed with on-line GC analyzers by, respectively, boiling point and gas type analyses.

The liquid level in the autoclave is maintained at a constant level by periodic withdrawals of wax. This wax is taken into the train of traps described above.

The autoclave was loaded with 72.7 g of the as received catalyst and 290 g of Ethylflo™ 164 (a C₃₀ oil obtained from the Ethyl Corporation). The catalyst was activated by heating it to 280°C under a nitrogen atmosphere. After pressure testing the plant, the feed syngas blend which is made up of hydrogen, carbon monoxide and argon in the molar ratio 0.7:1.0:0.1 is introduced. Argon is used as an internal standard. The catalyst is then reduced for a period of 12 hr. The syngas feed rate, and reactor temperature and pressure were maintained at 2 Ni/hr/gFe, 280°C and 153 psig, respectively during this 12-hr period. During the remainder of the run the feed rate, temperature, and pressure were controlled at 2.4 Ni/hr/gFe, 265°C and

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290 psig, respectively. In Run 53, as will be discussed below, condition changes were made during the run. These conditions are noted at the top of the figures which summarize the performance of each individual catalyst (See Appendix A).

Run 31

This run was performed with a commercially available Ruhrchemie catalyst. The performance of this catalyst at line-out conditions (time-on-stream: 240 hr) is summarized in the material balance data presented in Table 2. Detailed run summary data are illustrated in Appendix A, Figures A-1 through A-7. These run summary plots show that after pretreatment this catalyst still required 200 hours to reach a stabilized conversion. During this 200 hours the conversion gradually increased. UOP catalysts tested previously under DOE contracts have reached a stable conversion quicker than the Ruhrchemie catalyst and during the time before line out have lost, not gained, activity. However, the UOP catalysts have a different composition than the Ruhrchemie catalyst. It is possible that the pretreatment conditions used were not adequate to fully activate (reduce) the Ruhrchemie catalyst.

In Run 31, the methane and ethane selectivities (Figures A-4 and A-5) increased throughout the 200 hr line-out period. The sum of the methane and ethane selectivities at line-out was 7.6 mole %. This is a fairly high number compared to the UCI catalysts discussed below. However, it is not extraordinary compared to historic Fischer-Tropsch catalysts.

The $H_2:CO$ usage ratio decreased from 0.73 to 0.68 during the 200 hour line-out period. Plots of $H_2:CO$ usage ratio versus $CO + H_2$ conversion are available. For instance, the curve in Figure 3 resulted from Run 43; a run performed as part of UOP's DOE contract but with a UOP-prepared catalyst. During this run, after line out was achieved, feed rate changes were made to vary the conversion. The small change in the usage ratio in Run 31 resulted not after but during the line-out period. The $CO + H_2$ conversion changed from 67% to 70%. The change in usage ratio might not be solely due to the different conversions during line-out period and it is possible that the change in product composition during this period is also contributing to the observed change in the usage ratio. A lower usage ratio will result if the olefinicity of the products is increasing or if the slope of the Schulz-Flory plots for the heavier products is flattening out. Data for Run 31 show that during the line-out period, methane selectivity is increasing and the olefin to paraffin ratio for C_2 to C_4 (Figures A-5 to A-7) is decreasing. This is indicative of a higher, not lower, $H_2:CO$ usage ratio. So the observed decrease in lower $H_2:CO$ usage ratio may be due to the change in the selectivity of the heavier products.

Run 44

This run used a catalyst prepared by UCI (catalyst "O") which was targeted to have the same composition as that of the Ruhrchemie catalyst. The compositions of the two catalysts were

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similar but not the same; the UCI "O" catalyst had more potassium (4.1 versus 1.4 wt%, Table 1) than the Ruhrchemie catalyst.

The Ruhrchemie and UCI "O" catalysts were evaluated under identical conditions. The performance of the UCI "O" catalyst is summarized in Figures A-8 to A-14 and a summary material balance for line-out conditions at 475 hrs-on-stream (HOS) is presented in Table 3. There were performance differences between these two catalysts tested in Run 31 and Run 44. The UCI "O" catalyst began at a very high conversion (80% CO conversion, Figure A-8) but lost activity as the run progressed, whereas the Ruhrchemie catalyst started at a lower conversion and gained activity. Run 31 was shorter than Run 44 but in both runs the catalysts' activities appeared to be lining out at run's end. The activities of these two catalysts were similar at line-out with the Ruhrchemie catalyst perhaps being slightly more active.

Part way through Run 44 a new lot of feed (Feed B) was received. When it was introduced at 225 HOS there appeared to be a step loss in activity. A small amount of the original feed (Feed A) was left and when it was re-introduced there appeared to be an increase in activity. Although it would appear that there was something in the feed which caused a reversible deactivation, attempts to determine what it was through feed analysis were unsuccessful (Table 4).

Both the Ruhrchemie and UCI "O" catalyst became increasingly selective for methane (Figure A-4 and A-11) as the runs progressed. The UCI "O" catalyst was about 1% less selective for methane than the Ruhrchemie catalyst at any time on stream. The ethane selectivities for Runs 31 and 44 had not lined-out by runs' end. Again, the UCI "O" catalyst was less selective to ethane. The sum of the methane and ethane selectivity was 5.2% at the end of Run 44.

The $H_2:CO$ usage ratio was 0.58 for the majority of the run whereas for Run 31 it decreased from 0.73 to 0.68 as the run progressed. Although less light weight material (for instance, methane) was produced in Run 44 than in Run 31, this was compensated for by the higher olefinicity (higher olefin:paraffin ratio) of the light products formed during Run 44. The UCI catalyst was likely less able to hydrogenate olefins than the Ruhr catalyst.

Run 48

This run used a fresh sample of the UCI "O" catalyst that was also used in Run 44. The performance of the catalyst during this run is summarized in Figures A-15 to A-22 and material balance data for the two different periods are shown in Tables 5 and 6. The conditions at the outset were the same as Run 44, however, the initial conversions were different for reasons which are not yet clear. It is possible that this was caused by slight, undetectable, differences in the activation procedure during the two runs. However, the conversions were about the same by 75 HOS, since during Run 44 there was a continual loss in activity, whereas, during Run 48 the conversion was relatively constant. There was a temperature spike at 75 hours, although it

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registers at 317°C (Figure A-16), it is possible that even higher temperatures were attained before the operator recorded this high temperature. It appears that the temperature spike was sufficiently high to cause some irreversible loss of activity. The CO conversion was 70% before the spike and 60% after.

The effect of an increase in temperature on catalyst performance was determined near the end of the run. Clearly a conversion increase can be obtained through temperature increase. Furthermore, the catalyst ran stable at this higher temperature, perhaps because the increase in temperature was not as great as the earlier temperature spike which might have taken the edge off the catalyst.

The conversions/selectivities for Runs 44 and 48 are compared in Table 7. The reproducibility was not as good as expected based on previous work with UOP catalysts in the slurry autoclave. The CO conversion at 70 hours, which was just before the temperature spike, was 70%, at this time the run 44 CO conversion was 78%. There were also differences in the selectivities, for instance the methane selectivity for Run 44 was 3.6% versus 5.4% for Run 48. The reasons for these differences are not known. Earlier studies of plant reproducibility indicated better reproducibility than this. It is unfortunate that the temperature spike occurred, because it appeared that the Run 48 CO conversion was holding at 70% whereas the Run 44 CO conversion dropped from a high initial conversion of 80% to a lined out CO conversion of 60% at 500 hours. Perhaps the differences between the two runs would not have been as great if it was possible to compare them when they were lined out.

Table 7 also shows a slight difference between the H₂:CO ratios for the two runs, this usage ratio was 0.62 for Run 48 versus 0.58 for Run 44. This difference is slight and assigning an explanation to it might be tenuous.

A Schulz-Flory plot is attached as Figure 4. Figure 5 is a plot of the Schulz-Flory data up to carbon number 16 and a curve fitted to the data using a non-linear regression model. The calculated α_1 and α_2 were, respectively 0.52 and 0.92. Figure 6 illustrates product distribution obtained during 144 to 163 HOS in Run 48.

The H₂:CO usage ratio was 0.62 before the temperature spike and 0.63 after it. The usage ratio dropped back to 0.62 after the temperature increase from 265°C to 285°C. These usage numbers were close to those observed for Run 44. The small differences in the case of these two runs could have been due to the slightly different conversions.

Run 50

This run used the UCI "A" catalyst (Table 1). Summary material balance data at the end of the run are shown in Table 8 and the conversion and selectivity data are shown in Figures A-23 to A-29. There was a continuous loss in activity over the 280 hour run. The final CO conversion

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was 47%. The methane selectivity was low throughout the run and did not vary much as the run progressed (Figure A-26), this selectivity was about 2.8%. The ethane selectivity was also low and did not vary much as the run progressed (Figure A-27), this selectivity was 0.7%. The sum of the methane and ethane selectivities was 3.5% which is very low.

The $H_2:CO$ usage ratio varied from 0.57 to 0.60 from the beginning to the end of the run (Figure A-24). This usage ratio is closer to that observed in Runs 44 and 48 than in Run 31. Although of different composition catalysts UCI "O" and UCI "A" were less prone to hydrogenate olefins than the Ruhrchemie catalyst, thus the lower $H_2:CO$ usage ratio and the higher olefin to paraffin ratios with the UCI catalysts. Also both UCI catalysts produced less methane which is hydrogen rich compared to all other products.

The UCI "A" catalyst did not have the hoped for properties, namely high selectivity for gaseous products. In fact, this catalyst was among the lowest yet tested at UOP for light gas production. That coupled with the apparent instability of this catalyst forced the preparation of additional catalysts by UCI.

Run 51

This run used UCI "B" catalyst, its performance is outlined in Figures A-30 to A-35 and material balance at line-out conditions is summarized in Table 9. Unlike catalyst UCI "A", this catalyst was quite stable. The CO conversion was 60% which is the same as the line-out conversion for UCI "A" catalyst in Run 50. The ultimate selectivities for light products were high, characteristic of a low wax-producing catalyst; however, it took ten days to achieve high light end selectivity.

The $H_2:CO$ usage ratio was about 0.65, which is the highest of the three UCI catalysts. This catalyst produced a higher level of) than the previous two and also had a lower olefin to paraffin ratio for the C_2 to C_4 olefins (Figures A-33 to A-35).

Even though the selectivities to light products increased markedly during this run (5.9% methane conversion at line-out, Figure A-33), the $H_2:CO$ usage ratio was consistently at 0.61 to 0.62. Although the catalyst selectivity performance was obviously changing during this period the CO + H_2 conversion was nearly constant. The effects of the selectivity changes (more methane, more olefins) may have counterbalanced resulting in a stable usage ratio.

After comparing the first three UCI catalysts ("O", "A", and "B") it was decided that the commercial-scale preparation for the LaPorte SBCR test should follow the recipe of the first catalyst (UCI "O" tested in Runs 44 and 48). UCI "A" catalyst (Run 50) produced more wax (less methane) than UCI "O" (Run 44 and 48). Although the ultimate performance of UCI "B"

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catalyst (Run 51) was superior to UCI "O" and "A" (for the objectives of the run of testing a low wax-producing catalyst), it took ten days in Run 51 to achieve this performance. Since the LaPorte test was going to last about twenty days, a ten day line-out period was considered too long.

Run 53

This run used UCI "Start-up" catalyst. It is a sample from an aliquot that UCI withdrew from the initial several hundred pound portion of their commercial-scale production run of catalyst for the August, 1992 slurry bubble-column reactor run at LaPorte, Texas. The composition of this catalyst was not the same as the catalyst from the main part of the run, UCI "Composite" catalyst. The "Composite" catalyst was loaded into the SBCR at LaPorte and was tested at UOP in Run 54.

The performance of the "Start-up" catalyst is summarized in Figures A-36 to A-41 and material balance for three different conditions is summarized in Tables 10 to 12. Run 53 started at the conditions (265°C, 290 psig, and 2.4 NI/hr/gFe) which had been used for the runs with the Ruhrchemie and UCI "O", "A", and "B" catalysts. However, after the plant had been on stream for 120 hours a series of condition changes were made to determine catalyst performance under conditions that were planned to be used at LaPorte. During the final part of the run the plant was returned to the initial conditions to find out if the performance had degraded during the run.

At the time of the first condition change at 120 hours the catalyst appeared to have reached line out at 63% CO conversion and 3.3 mole % methane selectivity. Decreasing the pressure from 290 to 200 psig resulted in a decrease in conversion to 50% and about a 0.5% increase in the methane selectivity (Table 10). Increasing the feed rate from 2.4 to 5.0 NI/hr/gFe caused 50% loss in conversion and an increase in the methane selectivity of close to 1%. Next the plant pressure was increased to 400 psig at the same high feed rate. This resulted in an increase in CO conversion to 48%, but little change in the methane selectivity (Table 11). Finally, the plant was brought back to the initial conditions in two steps, first a decrease in the feed rate from 5 to 2.4 NI/hr/gFe and then a decrease in plant pressure (from 400 to 200 psig), the combined effect of which was an increase in conversion to 55% and a decrease in methane selectivity to 2.1%. The final step was an increase in plant pressure to 290 psig which brought the conversion back to where it was at 120 hours, however, the methane selectivity was 3.0% versus the earlier 3.5% (Table 12). The selectivity to the other light hydrocarbons (C₂ to C₄) also decreased between 120 hours and the end of the run. Apparently the aging process did not change the conversion but did shift the selectivity toward heavier products.

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Run 54

This run used the UCI "Composite" catalyst which is an aliquot of the 800 lb batch of catalyst that was loaded in the LaPorte SBCR. This catalyst was of finer mesh size than other catalysts used in this study. The "Composite" catalyst is believed to have at least some particles < 10 microns.

The activation procedure used for Run 54 was similar to that used for the LaPorte SBCR run; however, it was different from that used in Runs 31, 44, 48, 50, 51, and 53. Initially the catalyst was heated in nitrogen to 200°C and then a gas mixture containing 25% nitrogen and 75% syngas was used to raise the reactor temperature to 280°C. The reactor pressure was maintained at 150 psig. After 12 hours at 280°C, the pressure, temperature, gas composition, and gas flow rate were changed to bring the reactor to the baseline operating conditions. UOP followed the run plan for the LaPorte run and tested the UCI "Composite" catalyst at four different conditions:

1. baseline (200 psig, 265°C temperature, gas flow rate of 2.5 nL/h/g-Fe),
2. high gas flow rate (200 psig, 265°C temperature, gas flow rate of 5.5 nL/h/g-Fe),
3. high pressure (400 psig, 265°C temperature, gas flow rate of 5.95 nL/h/g-Fe),
and
4. baseline-revisited (200 psig, 265°C temperature, gas flow rate of 2.97 nL/h/g-Fe).

The feed to the autoclave reactor consists of 6 mole% argon as internal standard so the syngas flow is lower than the total gas flow rate. Also, as will be discussed below, during the run some catalyst was inadvertently lost, and as a result the space velocities are higher than intended.

There were operational problems during this run which were in part due to the small particle size of the catalyst. At approximately 180 HOS, the 0.5 micron filter on the gas outlet line plugged. At the same time the operators were experiencing difficulties with the thermocouple which is used to monitor the temperature change across the gas/liquid interface within the autoclave. Because of this the position of the liquid level was not known, and as a result the liquid level reached the top of the autoclave and might, in fact, have caused the plugging of the gas outlet filter. The normal way of opening a plug, namely back purging with feed failed. This necessitated bypassing the filter, i.e. removing whatever was present in the top of the autoclave without filtering. When the liquid level reached the top of the autoclave it began to exit through the unfiltered gas outlet line. This resulted in wax and catalyst entering the 130°C trap which normally only accumulates small amount of condensate (liquid) present in the product gas. Figure 7 contains a plot of the amount of material in this trap as a function of time. The overflow apparently began about 200 hrs when higher than expected weights were recovered from this trap. Confirming this was the observation that the trap material was not a liquid but a solid wax similar in texture to the wax in the other hot box trap which collects material from

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the periodic liquid (wax) withdrawals. The amount of catalyst lost from the reactor was determined by calcining the recovered wax. The catalyst weights so determined are also plotted in Figure 7. Of the original 72.7 grams of catalyst, 11.4 grams were lost during the time wax overflowed into the hot box trap. By 300 HOS the plant operators were once again able to determine the position of the wax and had re-established the target wax level.

The filters on the wax outlet line functioned during the entire run. This is not too surprising because there are two wax filter assemblies each with two filters, whereas there is only one gas filter assembly and it only has one filter (Figure 1). During the LaPorte run the wax outlet filters plugged during the first two hours of use and could not be reopened. However, the flux through the LaPorte wax outlet filters was higher than through the UOP slurry autoclave wax outlet filters.

During the time the plant overflowed condition changes were also being made. The timing of the condition changes and the conversions and product selectivities are in Figures A-42 to A-48. Material balance information for each condition change is also shown in Tables 13 to 16. A problem with the on-line gas analysis resulted in loss of about 225 hr of selectivity data. The initial conversions were high, as high as conversions with the best previous catalysts evaluated at UOP and also higher than resulted from any of the previous UCI or Ruhrchemie catalysts tested at UOP. The catalyst used in this run contained some very fine mesh catalyst (<10 microns). The UOP catalysts were always sieved before use (through 40, on 400 mesh) to give granular catalyst pieces of about 40 to 150 micron in size. It is possible that the very small particle sizes present in the UCI "Composite" catalyst caused high conversion.

The objective in making this UCI catalyst was to make a high- α catalyst, namely one which makes high levels of light products, including methane, and low levels of wax. The initial selectivities illustrate that just the opposite happened and the catalyst produced a very low level of methane. The methane selectivities during this run are compared to methane selectivities in some previous runs on this autoclave plant in Figure 8. The comparison catalysts were all prepared at UOP as part of the current contract as low methane-producing catalysts. It is obvious that the UCI catalyst compares favorably to these previous catalysts as a low methane-producing catalyst.

Because the operational problems came at 200 hours, comparisons between Runs 53 and 54 should be made at times before 200 hours. The final plan for the LaPorte run was to operate at 200 psig plant pressure, therefore, Run 54 began at this pressure rather than 290 psig. Thus to make a direct comparison between Runs 53 and 54 requires use of Run 53 data after the pressure was decreased to 200 psig at 130 hours. At this time during Run 53 the CO conversion was 53% and the methane selectivity was 4.0 mole %, compared to 80% CO conversion and probable about 3.2 mole % during Run 54. Because of the on-line analyzer problems 130 hour selectivity data for Run 54 must be obtained by extrapolating 100 hour selectivity data.

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The two samples of catalyst from the UCI production run differed both in elemental analysis and performance. The "Composite" sample was more active than the "Start-up" catalyst. The "Composite" also appeared to be the finest mesh of all the UCI catalysts; this might have contributed to its high activity. The fine size probably also contributed to the plugging of the gas filter.

Table 7 shows a comparison of the initial (70 HOS) conversions and selectivities obtained for all the catalysts tested at UOP in support of the LaPorte SBCR run. Among all the catalysts, the "Composite" catalyst had the highest conversion (at a lower pressure) and the second lowest $C_1 + C_2$ selectivity.

PART II

COMPARISON OF SLURRY AUTOCLAVE DATA WITH SLURRY BUBBLE COLUMN DATA

As discussed earlier, UOP slurry autoclave Run 54 was carried out with UCI "Composite" catalyst that was tested in the SBCR at LaPorte.

Calculations of Kinetic Parameters

With the assumptions that: (a) the reaction rate is first order with hydrogen concentration and (b) there is no mass transfer resistance in the slurry autoclave, the kinetic parameters were calculated from the data collected in the slurry autoclave pilot plant. Results of these calculations for the four operating conditions of Run 54 are shown in Tables 17 to 20. As discussed before, during Run 54 some catalyst was inadvertently lost. Corrections were made to account for the catalyst that was lost from the reactor but was recovered in the product.

Comparison with Slurry Bubble-Column Data

Two models were used to calculate the performance of the "Composite" catalyst in the LaPorte SBCR:

- a. Model 1 - both the gas and the liquid are assumed to be in plug flow, and
- b. Model 2 - the gas phase is assumed to be in plug flow and the liquid phase assumed to be perfectly mixed.

Bukur's correlation was used to calculate the gas hold-up and Akita-Yoshida correlations were used to calculate the mass transfer coefficients. The liquid phase mixing and volume contraction (α) factor was set at -0.5.

Kinetic information obtained from Run 54 for baseline conditions (Table 17) were used to predict the performance of LaPorte SBCR Run AF-R6.1-A to Run AF-R6.1-H. The solid concentration in the model calculations was adjusted to match the model column space velocity with the experimental value. A trial and error method was used to calculate hydrogen conversion in the reactor. Once the hydrogen conversion was set, other conversions and productivity numbers were calculated.

Similar procedure was followed to predict the LaPorte SBCR performance in Runs AF-R6.2, AF-R6.3, and AF-R6.4 from the data obtained in Run 54 for high gas flow rate (Table 18), high pressure (Table 19), and baseline-revisited (Table 20) conditions, respectively. A summary of calculations for each run conditions are shown in Tables 21 to 34. The results predicted by the models are compared with the observed SBCR performance in Figures 9 to 11.

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Observations and Conclusions

1. In Run AF-R6.1, the loss in CO conversion (Figure 9) with increasing HOS (at the same inlet gas velocity) is due to the continuous loss of catalyst from the reactor.
2. When the gas velocity is doubled from 0.13 fps in Run AF-R6.1 to 0.27 fps in Run AF-R6.2, the conversion drops by almost one-half (Figures 9 and 10). The effect of doubling the reactor pressure from 200 to 400 psig in Run AF-R6.3 is not as pronounced because the conversion from Run AF-R6.2 to Run AF-R6.3 increases by only about 66%. Previous studies in Fischer-Tropsch synthesis have also made similar observation on the effect of pressure.
3. Run AF-R6.1 and AF-R6.4 are carried out under similar pressure, temperature, and gas velocity. However, significant quantities of the catalyst is lost during the run resulting in an increase in the space velocity. The observed performance of catalyst in Run AF-R6.1 and AF-R6.4 almost falls on a straight line which is consistent with the increase in the space velocity. Also, the CO conversion rate obtained at the end of Run AF-R6.1 and Run AF-R6.4 is same. These data would suggest that there was no catalyst deactivation in the SBCR; however, it is hard to say so conclusively. In the LaPorte SBCR, the catalyst was allowed to settle in the wax outside the reactor and then the concentrated catalyst/wax slurry was recirculated back to the reactor. This recirculation will bring "fresh" (less deactivated?) catalyst to the reactor and maintain (or increase) the activity of the catalyst in the reactor.
4. At lower space velocities (less than $4 \text{ Nm}^3/\text{hr}/\text{kg-Fe}$), Model 1 predicts higher conversions than Model 2. At higher space velocities, as might be expected, both models converge. Predicted conversions and CO conversion rates (Figures 9 to 11) are higher than that observed at LaPorte in Runs AF-R6.1 and AF-R6.2, and lower than that observed at LaPorte in Run AF-R6.4. For Run AF-R6.3, the predicted CO conversion rate is higher, while predicted conversions match with those observed.

FIGURE 1
SCHEMATIC DIAGRAM OF UOP SLURRY AUTOCLAVE PLANT

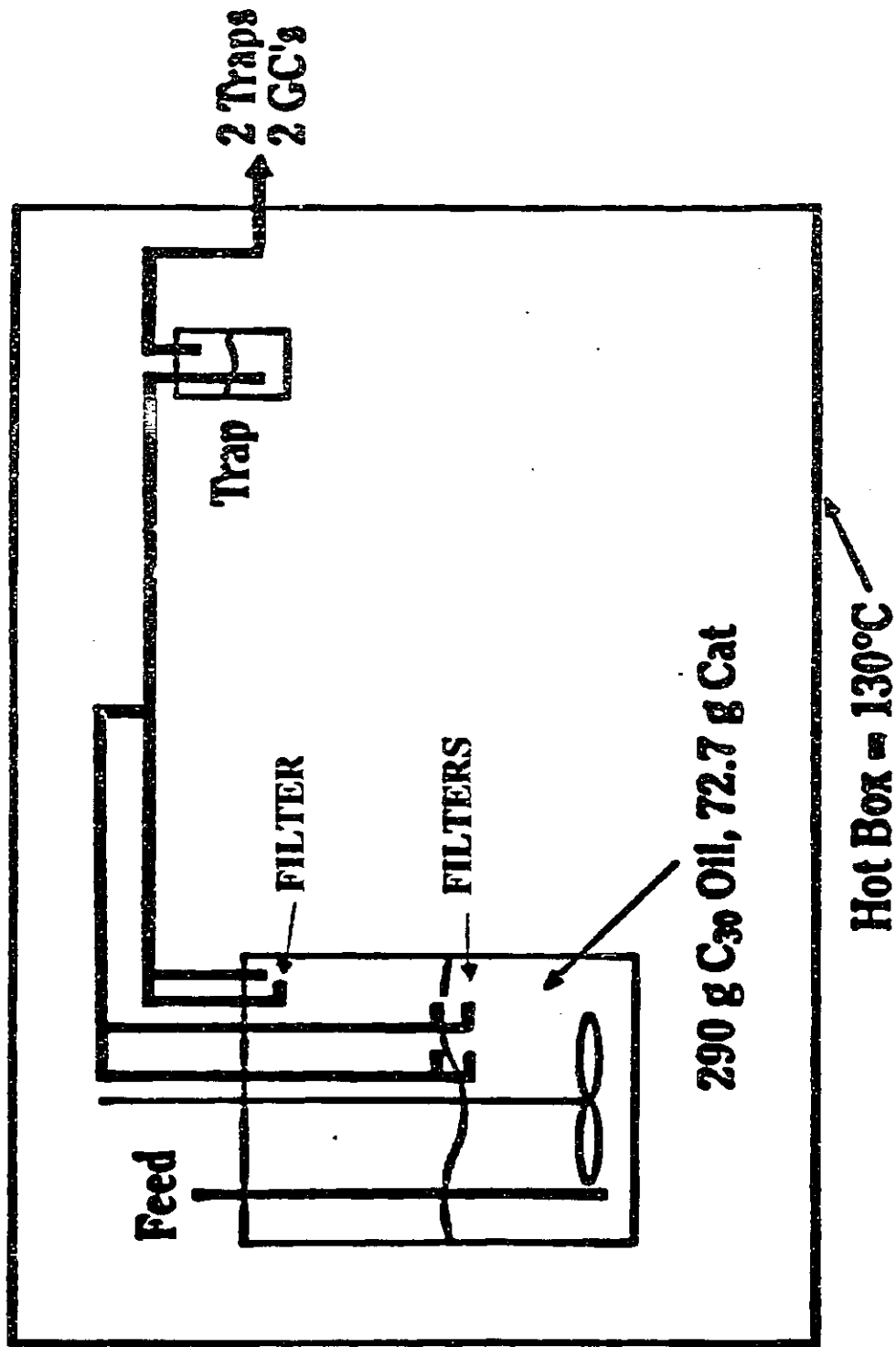


FIGURE 2
SCHEMATIC DIAGRAM OF UOP MODIFIED SLURRY AUTOCLAVE PLANT

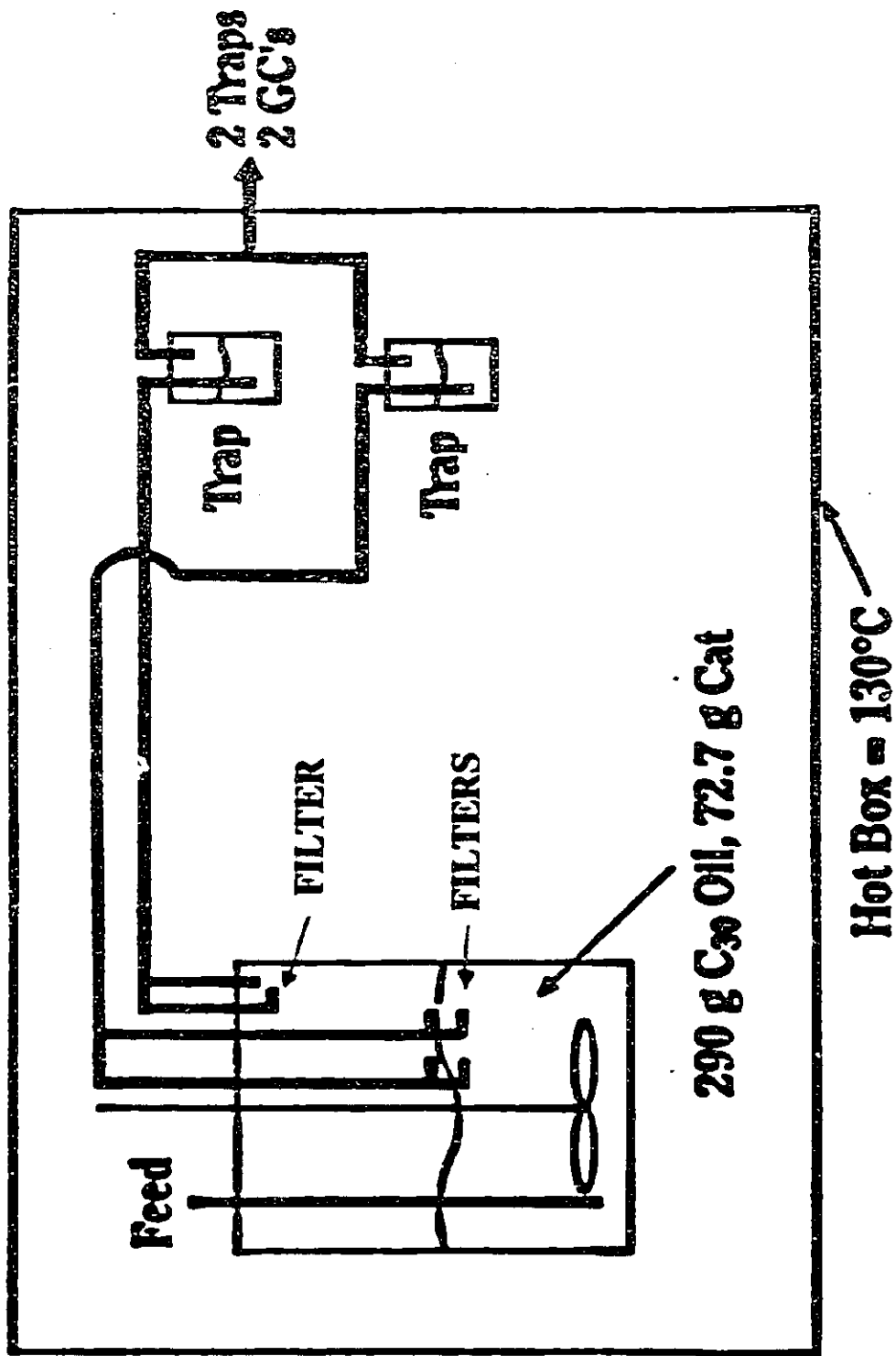
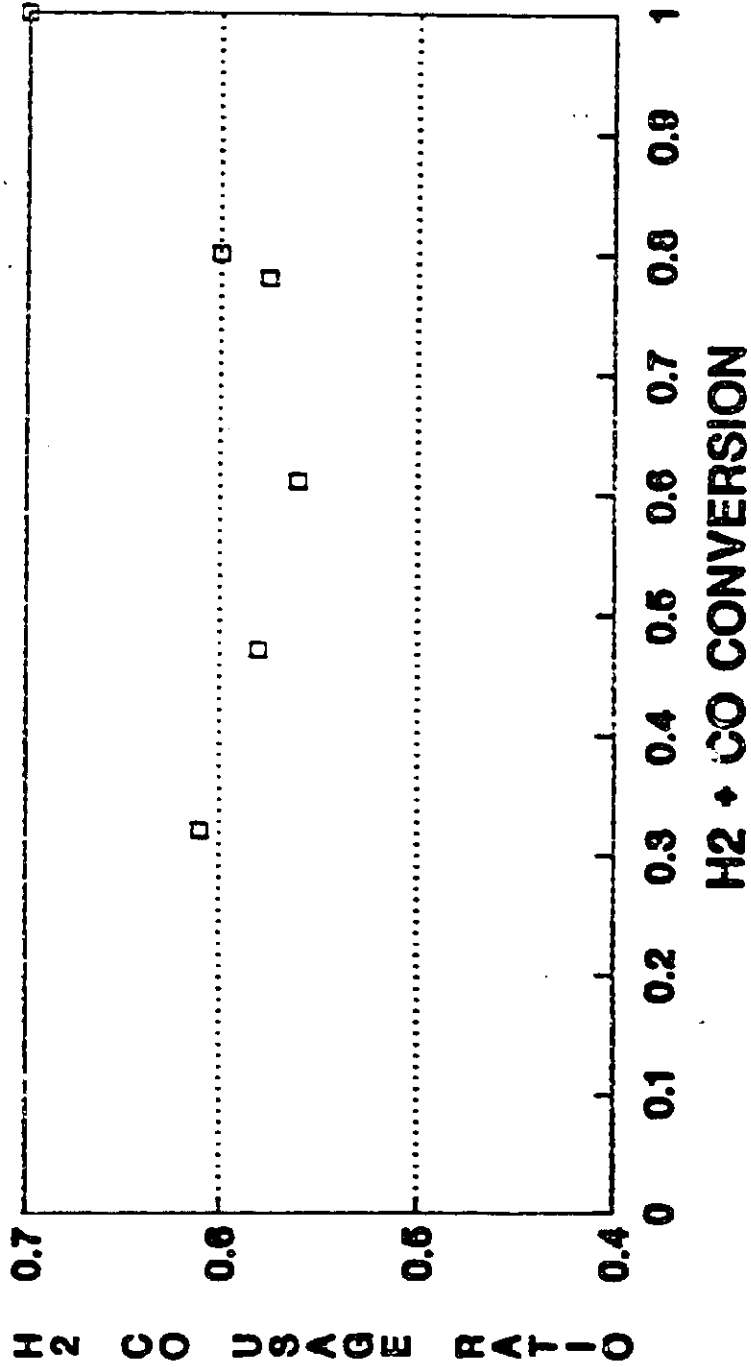


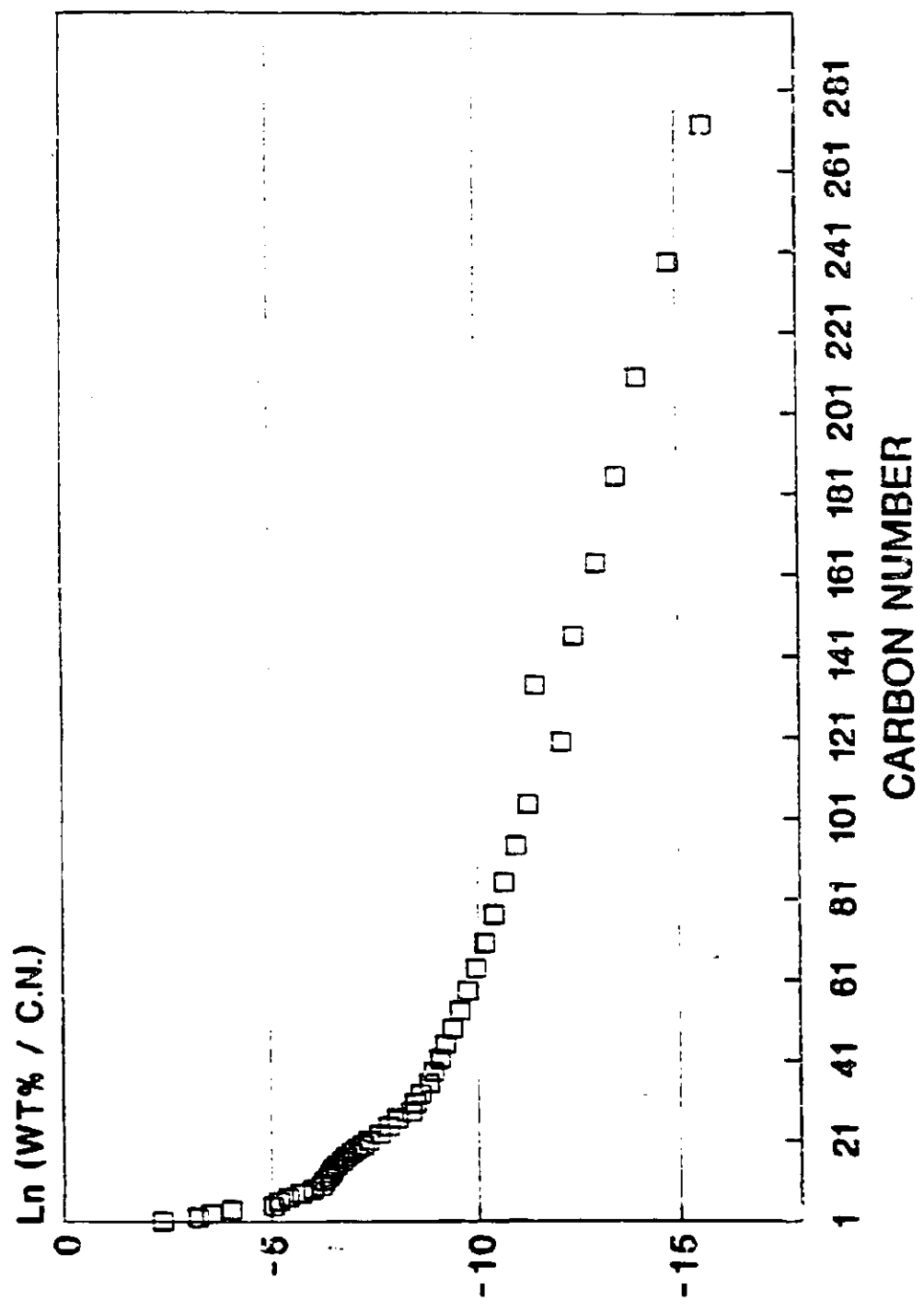
FIGURE 3
EFFECT OF CO+H₂ CONVERSION ON H₂:CO USAGE RATIO



286 DEG C

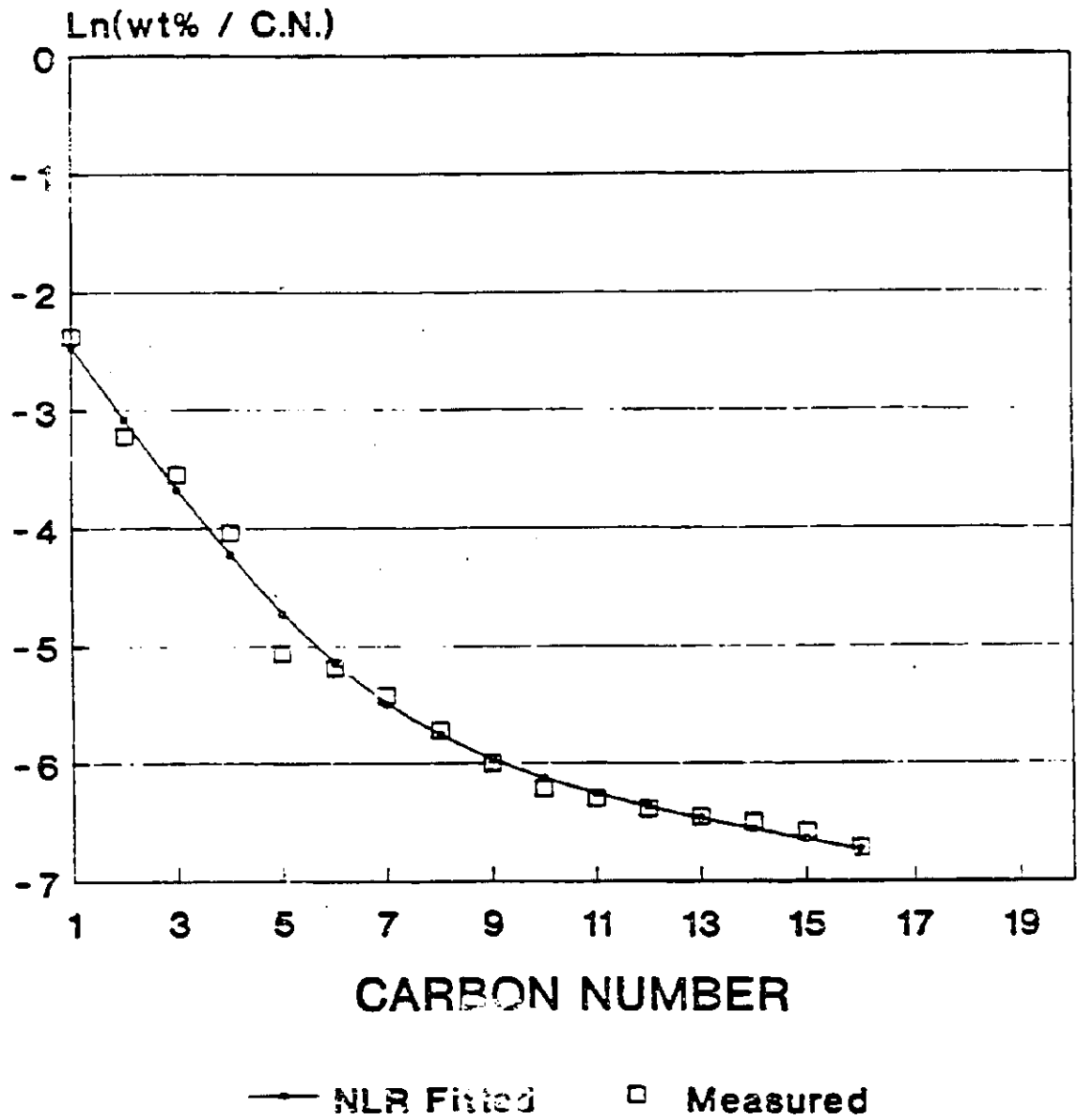
□ RUN 43

FIGURE 4
SCHULZ-FLORY PRODUCT DISTRIBUTION FOR RUN 48 (144-163 HOS)



LIQS BY OFFLINE; GAS BY ONLINE ANALYSIS

FIGURE 3
NON-LINEAR REGRESSION OF S-F PRODUCT DISTRIBUTION
RUN 48 (144-163 HOS)



ALPHA 1=0.52; ALPHA 2=0.92; XI=8.2;
PHI=0.222

FIGURE 6
PRODUCT BREAK-DOWN FOR RUN 48 (144-163 HOS)

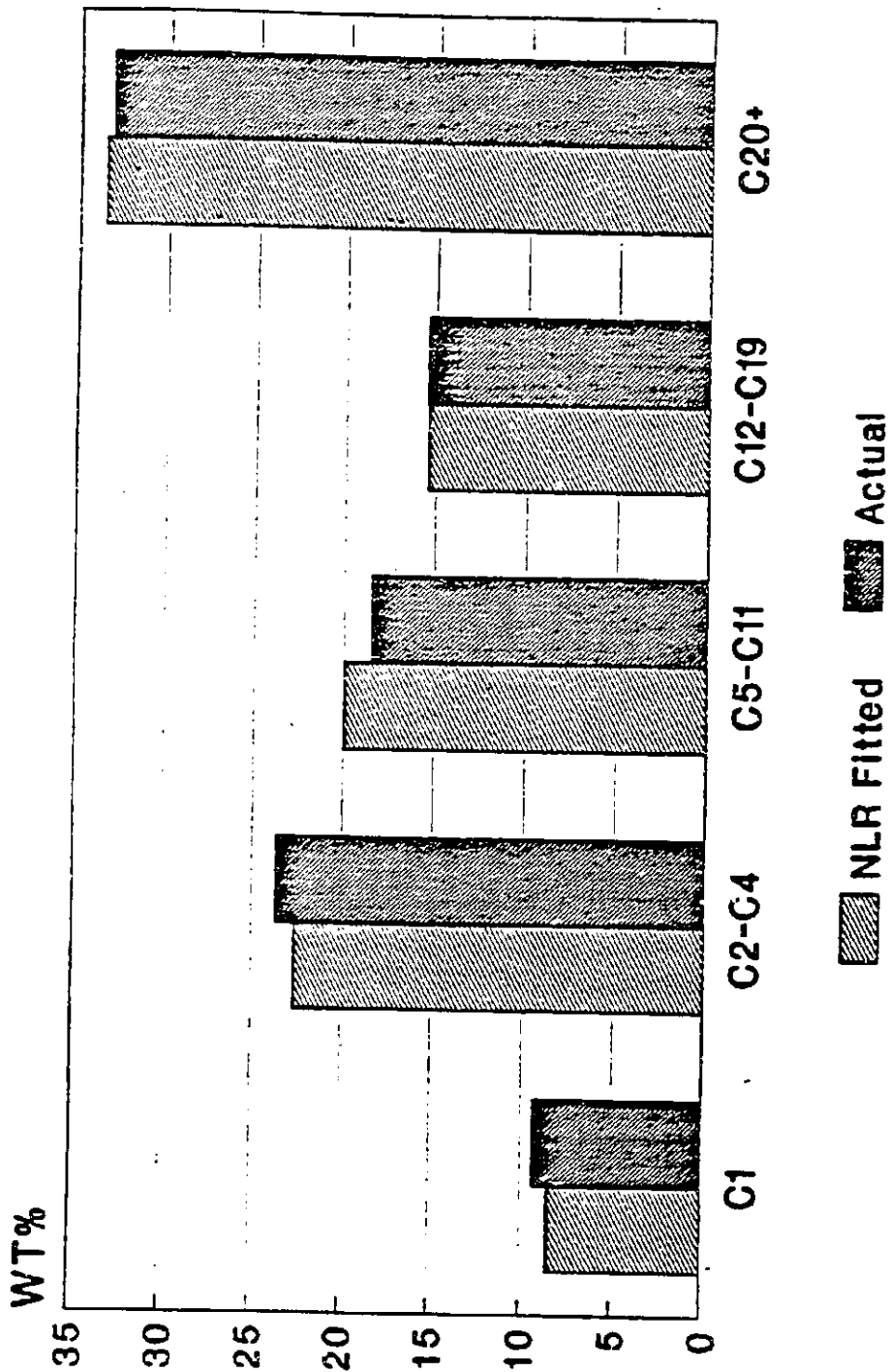
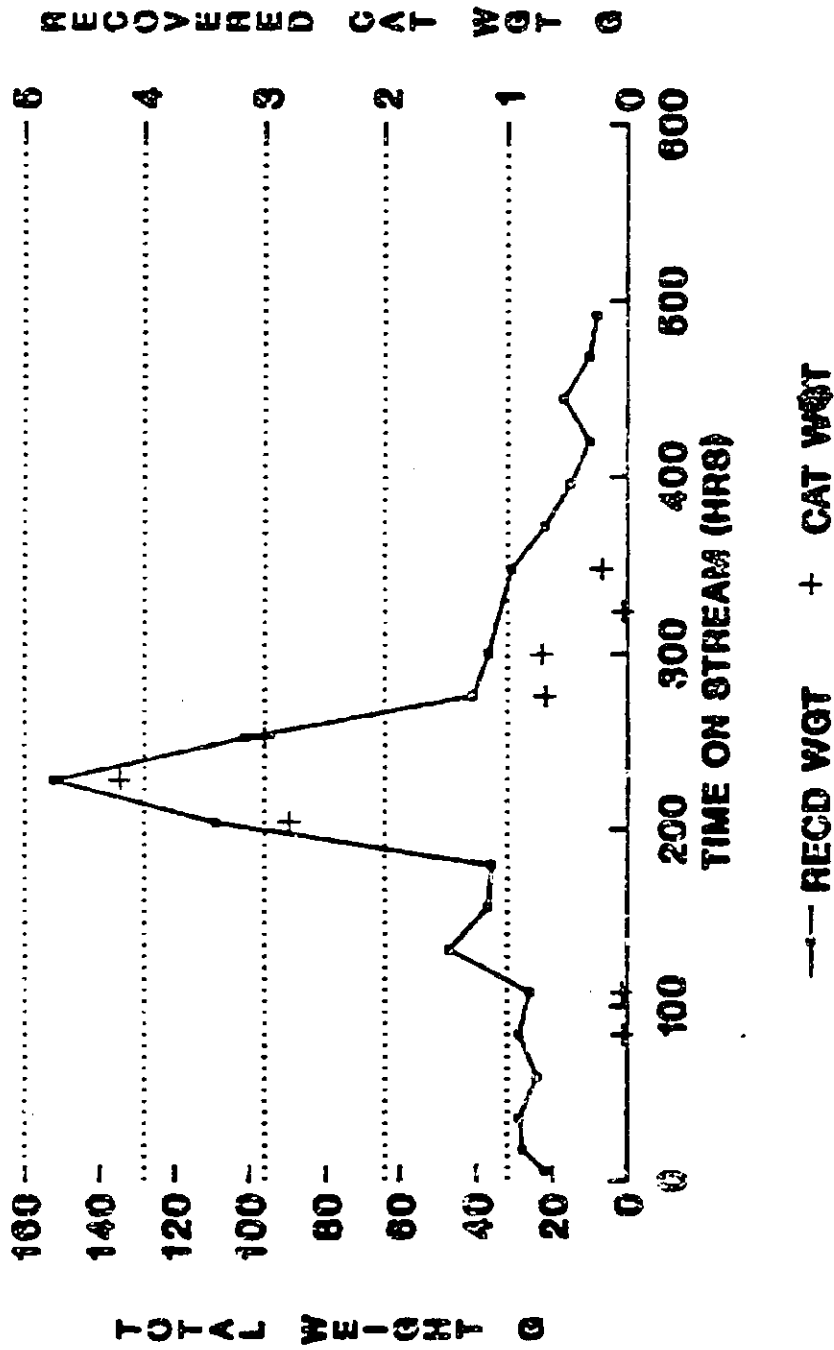
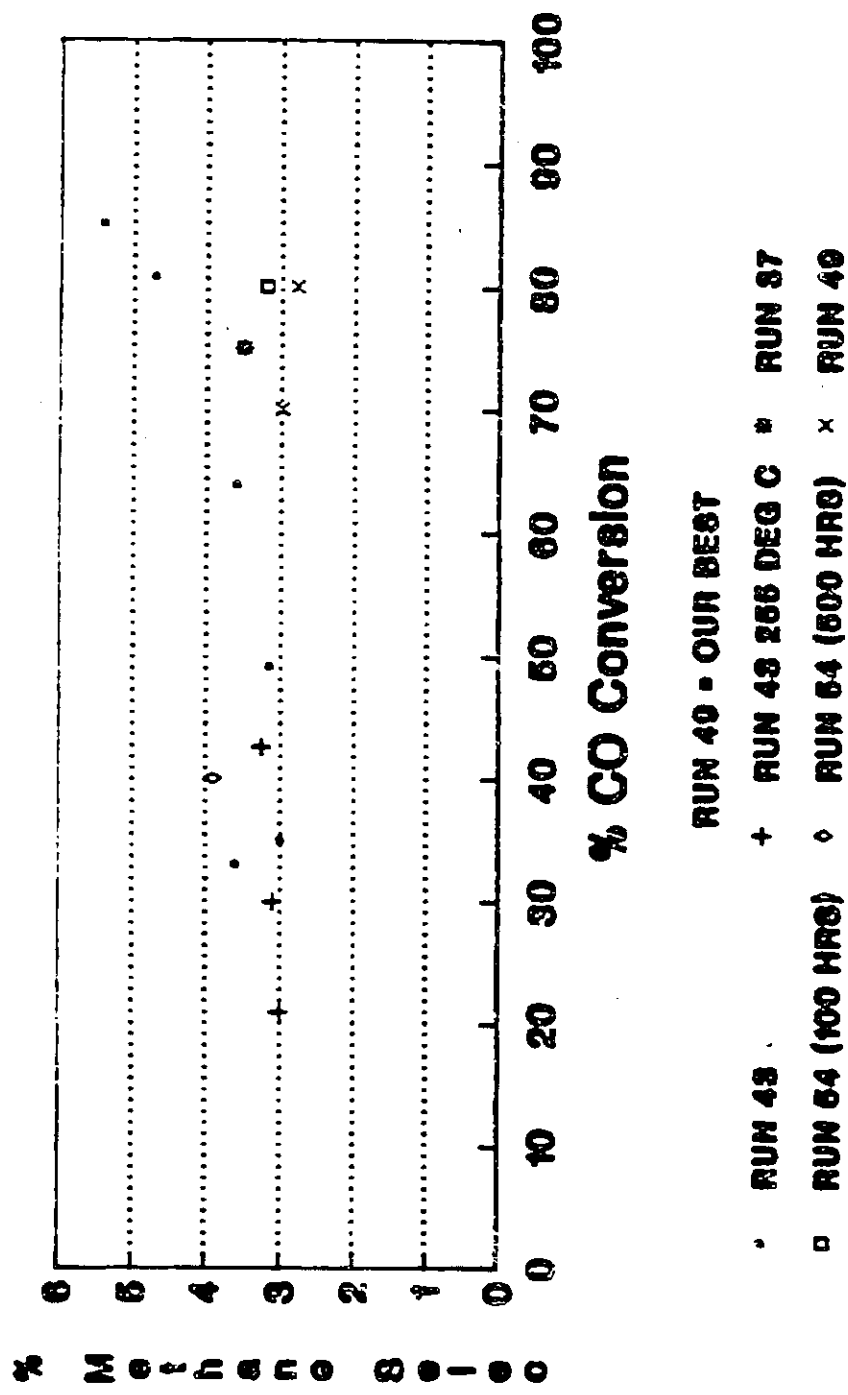


FIGURE 7
WEIGHT OF WAX AND CATALYST RECOVERED IN RUN 54



**CATALYST CALCINED DURING RECOVERY THERE-
 FORE WGT CAN BE COMPARED TO CAT LOADED
 WHICH WAS 72.7 G**

FIGURE 8
METHANE SELECTIVITY OF VARIOUS F-T IRON CATALYSTS



H₂:CO = 0.7. PRESSURE = 200 PSIG
TEMP = 265 DEG C UNLESS OTHERWISE NOTED

FIGURE 9
OBSERVED AND PREDICTED CO CONVERSION DATA

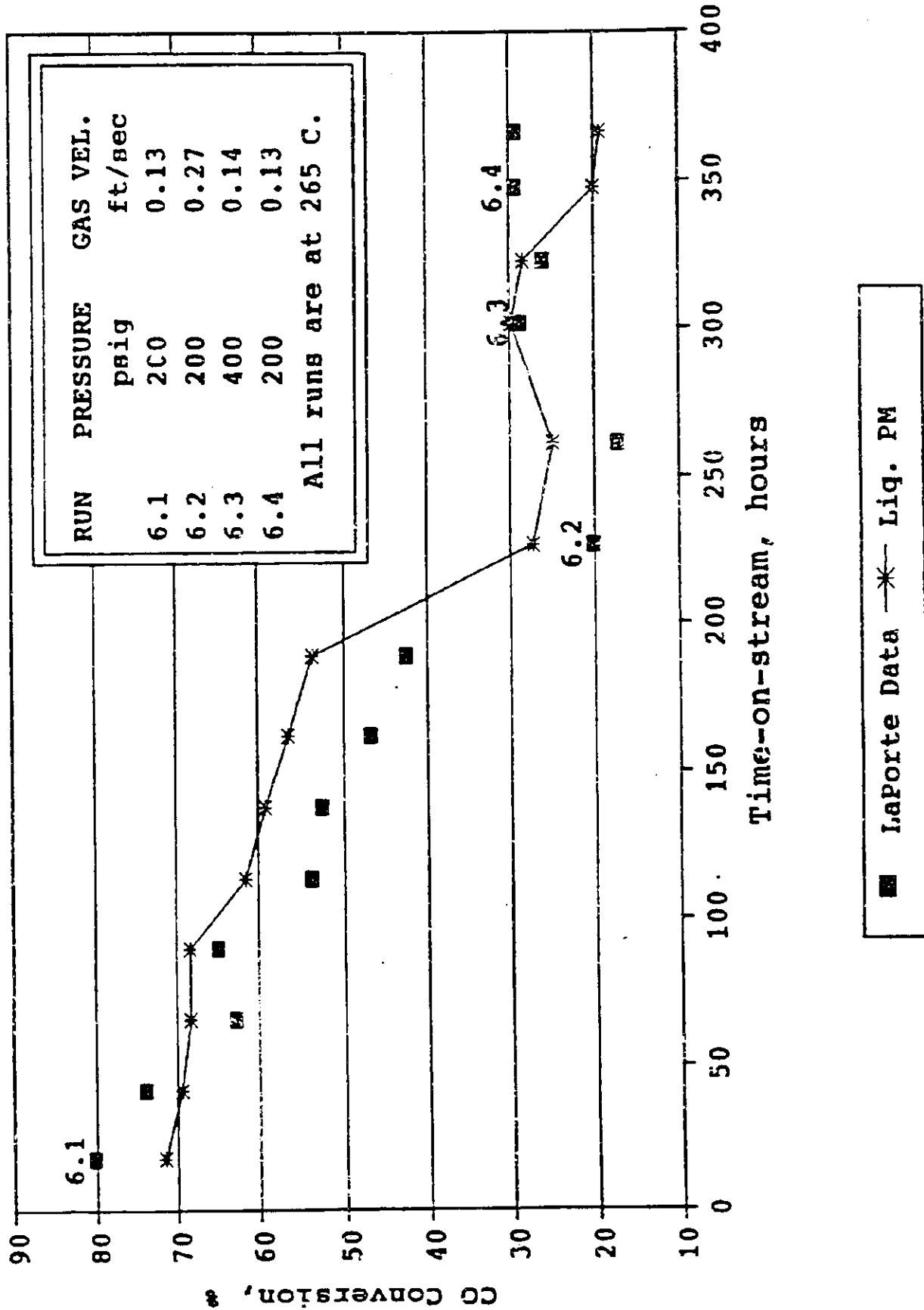


FIGURE 10
OBSERVED AND PREDICTED CO+H₂ CONVERSION DATA

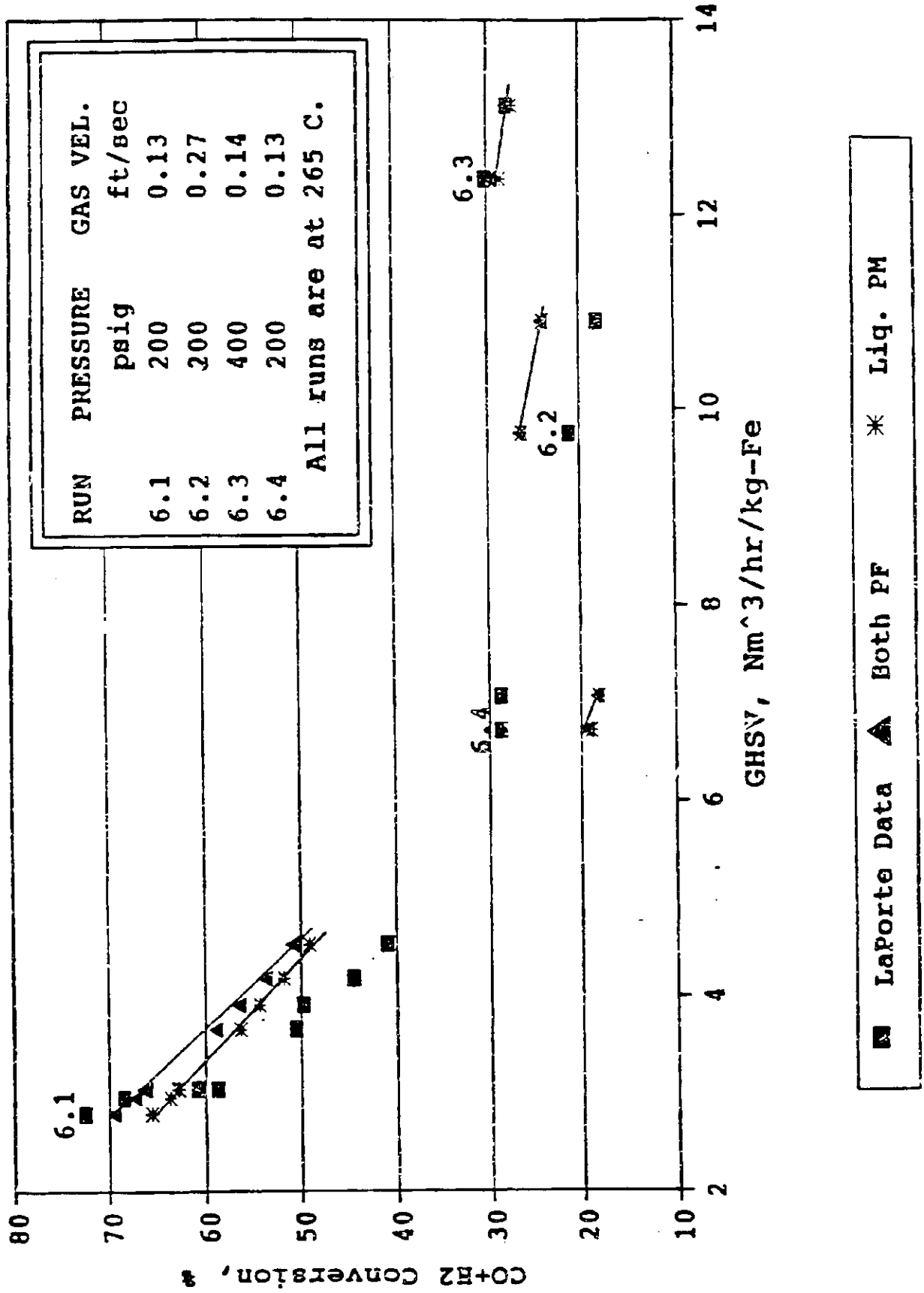


FIGURE 11
OBSERVED AND PREDICTED CO CONVERSION RATE DATA

