

SLURRY PHASE FISCHER TROPSCH CATALYSIS

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ABSTRACT

A major advantage of the slurry reactor system is the ability to handle low H₂/CO ratio feed gases without a preliminary, energy consuming water-gas-shift step. Recent experiments have used a precipitated iron copper catalyst impregnated with potassium and pretreated with carbon monoxide. Synthesis gas compositions from 50 to 59% by volume of CO were investigated. Activity attained peak values at 48 to 72 hours on stream independent of syn gas ratio. H₂ + CO conversion levels of 80 - 85% were observed. Syn gas ratio was found to strongly influence catalyst activity maintenance. Catalyst deactivation was moderate when the feed H₂/CO \geq 0.86 but was noticeably more rapid for feed H₂/CO \leq 0.8. The activity declined approximately 50% over an additional 170 hours when the feed H₂/CO \leq 0.8. In contrast, for the catalyst exposed to a feed H₂/CO \geq 0.86, the activity decreased to a level of 85% of its maximum value. Also, the hydrocarbon product became heavier with time on stream for the catalysts exposed to feed H₂/CO \geq 0.86. Methane levels were in all cases 3-4% of the hydrocarbon product at the time of termination of the experiment.

INTRODUCTION

Fischer-Tropsch (F-T) synthesis in the slurry phase has attracted attention in recent years because of its numerous advantages (see discussions in References 1-3). Among these advantages are: the ability of the liquid phase to handle the large heats of reaction and thereby control reaction temperature; the ability to handle low H₂/CO ratio synthesis gas without needing a preliminary water-gas-shift step (4); and the relatively low capital and operating costs for slurry systems (3). Slurry phase work at PETC has focused on understanding the effects of catalyst preparation and pretreatment, of reaction conditions (T, P, H₂/CO), and of operating conditions (space velocity, methods of wax removal) on the catalyst's synthesis behavior (activity, selectivity, and maintenance of activity and selectivity). Better understanding of the effects of these factors on FT synthesis leads to improvements in process technology.

The ability to handle low H₂/CO ratios of gas allows the slurry reactor to accommodate the improvements in coal gasifier design. The newer generation of coal gasifiers, e.g. Texaco, Shell/Koppers, obtain higher thermal efficiencies, but at the expense of lower H₂/CO ratios than are typical for older model gasifiers (5,6). These lower H₂/CO ratios, typically between 0.5/1 and 1/1, cannot be used by the older FT catalysts or reactors, which require inlet H₂/CO ratios on the order of 2/1 or greater. A preliminary water-gas-shift step could be used to increase the H₂/CO ratio, but this step consumes energy and thereby negates the advantage of using the more thermally efficient gasifier. The slurry FT reactor solves this problem by accepting low H₂/CO feeds. In a slurry system, the water-gas-shift step occurs in the

reactor, not before syngas reaches the reactor. An indirect liquefaction process coupling a thermally efficient gasifier with a slurry FT reactor increases yields of liquid fuels by 30-70 % when compared with SASOL technology.(1)

Previous work at PETC has focused on the effects of catalyst pretreatment on synthesis behavior (7) and the effects of catalyst preparation (8). This paper describes an investigation of the influence of synthesis gas composition, specifically H₂/CO ratio, on a precipitated iron based catalyst.

EXPERIMENTAL PROCEDURE

The first step in preparation of the catalyst was preparation of a catalyst precursor in a continuous precipitation unit described elsewhere(9). In this unit, a flowing aqueous solution of Fe(NO₃)₃ and Cu(NO₃)₂ was mixed with another flowing solution of NH₄OH. The pH of precipitation was measured with a pH meter and was controlled at pH = 7.0 by adjusting the flow rate of the NH₄OH solution. The precipitate obtained was then filtered, washed, and dried in an oven at 383 K for 48 h in N₂, then for 24 h in vacuum. Each preparation yielded about 50 g of catalyst precursor. Each batch was analyzed for percentages of Fe, Cu, and O, and for BET surface area and pore volume. Batches of similar composition and surface area were combined and thoroughly mixed to make a 300 g master batch. The master batch had an Fe/Cu of 100/5.

Samples from the master batch were impregnated with a K₂CO₃ solution. For each 50 g sample of the master batch to be impregnated, 20 ml of solution was added and mixed with the precursor. Each impregnated sample was then oven dried at 383 K for 24 h. The concentration of K₂CO₃ solution was adjusted to yield precursor batches containing 0.29% K. The final composition of the catalyst was Fe/Cu/K of 100/5/0.5. Before use, each impregnated batch was also calcined in an air oven; the temperature was raised stepwise to a final temperature of 623 K.

Figure 1 is a simplified schematic of the reactor system described in more detail elsewhere(10). Table 1 summarizes the conditions of the reaction experiments described here. In each experiment, 13 g of calcined catalyst precursor was charged to a stirred autoclave containing 320 g of purified n-octacosane wax. The catalyst in each instance was "CO pretreated". The catalysts were exposed to a flow of CO at 553 K, at atmospheric pressure, for 24 h before synthesis. During synthesis operations several parameters were held constant. The reactor pressure was 200 psig. The impeller speed on the autoclave was maintained at 1000 rpm. GHSV (gas hourly space velocity, volume of gas per hour/volume of slurry) was 70 h⁻¹. The carbon monoxide content of the feed stream was adjusted to range from 50 to 59 % of the inlet volume. The resulting H₂/CO ratios explored were: 1.0, 0.9, 0.86, 0.8, and 0.7.

Table 1. Conditions for Reaction Experiments

.13 g calcined Fe/Cu/K suspended in n-octacosane

	PRETREATMENT	SYNTHESIS
Gas	CO	H ₂ /CO
Concentration of CO (%)	100	50 to 59
Resulting H ₂ /CO ratios	---	0.7 to 1.0
Temperature (C)	280	260
Pressure (psig)	Atmospheric	200
GHSV (h ⁻¹)	67	70
Impeller Speed (rpm)	1000	1000
Duration (h)	24	24/pd

RESULTS

USEAGE RATIO

Figure 2 shows the usage ratios of the calcined catalysts for various syngas compositions. It is noticeable that with rising inlet ratio, the H₂/CO usage ratio increases only slightly, being 0.58 at the feed ratio of 0.7, and at a feed ratio of 1.0 the usage ratio is 0.7. The H₂/CO usage ratios for this particular catalyst converge to a value of approximately 0.6 with time on stream. This result, the usage ratio being less than the inlet ratios, indicates that the catalyst employed in this study has a high activity for the water-gas-shift reaction at all the feed ratios explored. Since the usage ratio is less than the inlet ratio, the H₂/CO exit ratio is larger than the inlet ratio (Figure 9). Hence, the hydrogen concentration will be large enough in the slurry reactor to suppress carbon formation due of the Boudouard reaction.

ACTIVITY

The activity of the catalyst at the different syngas compositions as measured by H₂ + CO conversion is shown in Figure 3. As can be observed, the catalyst activity levels reached the highest levels within 72 hours of exposure to synthesis gas regardless of the feed gas ratio. These levels were 80-85% conversion, approaching the maximum achievable when the CO conversion is 100%. However, after approximately 100 h TOS (time on stream) there is a significant loss of catalyst activity when the synthesis gas feed ratio was ≤ 0.8 . The activity level continuously declined to only 50% of its high value after a total on stream time of 240 h. Examining the activity levels when the feed ratios were ≥ 0.86 , it can be seen that the loss of activity is not as significant as with feed ratios of ≤ 0.8 . Activity levels with the higher ratio feeds were still 85% of their high value at 240 h TOS.

PRODUCT SELECTIVITY

Figures 4, 5, 6, and 7 show the overall selectivities of this catalyst at the various synthesis gas compositions. Figure 4 shows the hydrocarbon distribution at 72 hours exposure to the various feed compositions. Generally, the lower the synthesis gas ratio the heavier the hydrocarbon product. The C1-C4 fraction composing approximately 20% of the product at a ratio of 0.7, and this fraction increasing to about 30% at the ratio of 0.86. Selectivities at ratios of 0.86 and greater are nearly identical. Methane accounts for about 6% of the product. The C2-C4 fraction making up 24%, C5 + material being 47% and wax accounting for the remainder.

Figure 5 represents the hydrocarbon distribution at 168 h TOS. Again, it is observed that the lower ratio feed gases exhibit the heavier product distribution. C1-C4 material at this exposure time are approximately 17% of the hydrocarbon product at feed ratios of ≤ 0.8 . At H₂/CO ratios of ≥ 0.86 this fraction accounts for 22% of the product. Comparison of the product slates at the different TOS indicates that the hydrocarbon product selectivity is changing with TOS. The selectivity towards light products decreases over time. This can be observed more clearly in Figure 6 showing methane levels. The methane concentration increases with increasing synthesis gas ratio up to a ratio of 0.86; being less than 5% with a feed ratio of 0.7 and nearly 8.0% at ratios of ≥ 0.86 at 48 h TOS. Evident from the figure is that the methane levels at all feed ratios decrease with TOS. The methane levels upon termination of the experiments were 3.0% at the lower ratios and 4.0% at the three higher feed ratios.

Figure 7 shows the wax fraction yield as a function of TOS for the various feed gas ratios. The wax fraction during synthesis operation using any feed ratio of 0.8 or greater showed an increase with TOS. This fraction of the hydrocarbon product increasing to as much as 3 times the level exhibited during the early periods of synthesis. This increase in wax make is especially evident with the higher ratio feed gases. The exception to this trend is for exposure of the catalyst to a feed gas ratio of 0.7. The wax fraction with this feed composition was initially $>50\%$ of the hydrocarbon product, but had gradually dropped to 40% at the termination of the experiment. It is likely that the more severe deactivation in 0.7 gases, combined with the H₂/CO ratio actually in the reactor, reduced the selectivity to wax.

OLEFIN SELECTIVITY

Selectivity differences attributable to secondary reactions of primary FT products were not major. Figure 8 shows the selectivity differences attributable to the secondary hydrogenation of the olefins in the C2-C4 fraction. The percentage of olefins in this fraction increased with TOS independent of the synthesis gas ratio. Initial values with ratios of ≤ 0.8 were 70-75% and continuously increased to values of 80-85%. Whereas when ratios were ≥ 0.86 the initial percentage of olefins in this fraction was 60-65% and increased to approximately 75%. This shift in selectivity can be attributable to the H₂/CO ratio of gas actually in the reactor (Figure 9). H₂/CO ratios in the reactor were very high, as high as 6/1, for the higher feed ratios. This ratio decreased with TOS corresponding to the increased olefin content of the C2-C4 fraction.

SUMMARY AND CONCLUSION

The Fischer-Tropsch synthesis reaction on a precipitated iron based catalyst was studied in a stirred tank reactor. The investigation was to evaluate the effect of H₂/CO feed ratio on the activity and selectivity of this catalyst. At comparable operating conditions, the highest activity levels are very similar, nearly reaching maximum achievable, within a short time period following exposure to synthesis gas independent of the feed gas ratio. Maintenance of activity is much better with the higher (>0.86) ratio gases. A synthesis gas ratio exist for this particular catalyst, somewhere between ratios of 0.8 and 0.86, where deactivation suddenly becomes quite severe after about 100 h TOS.

The synthesis gas feed ratio did have an effect on selectivity. It was shown that the lower the feed ratio, the heavier the resulting hydrocarbon distribution. Similar product distributions were noted for feed gas ratios of 0.86 or greater at comparable TOS. The hydrocarbon product generally became heavier with TOS regardless of the feed gas composition. The secondary reaction, hydrogenation of the primary olefin, is more significant with the higher feed ratios, but decreases with TOS.

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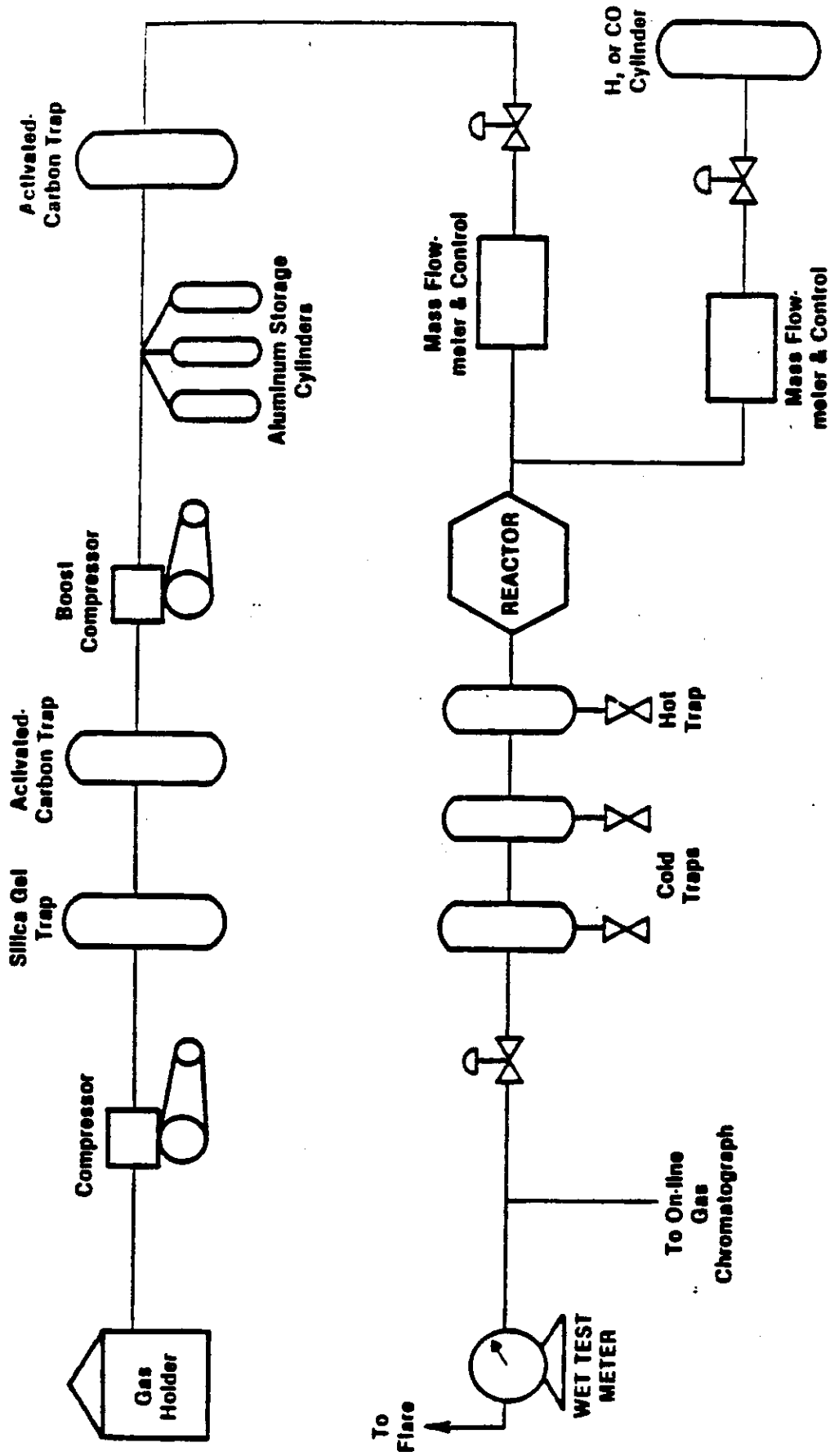
DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding, and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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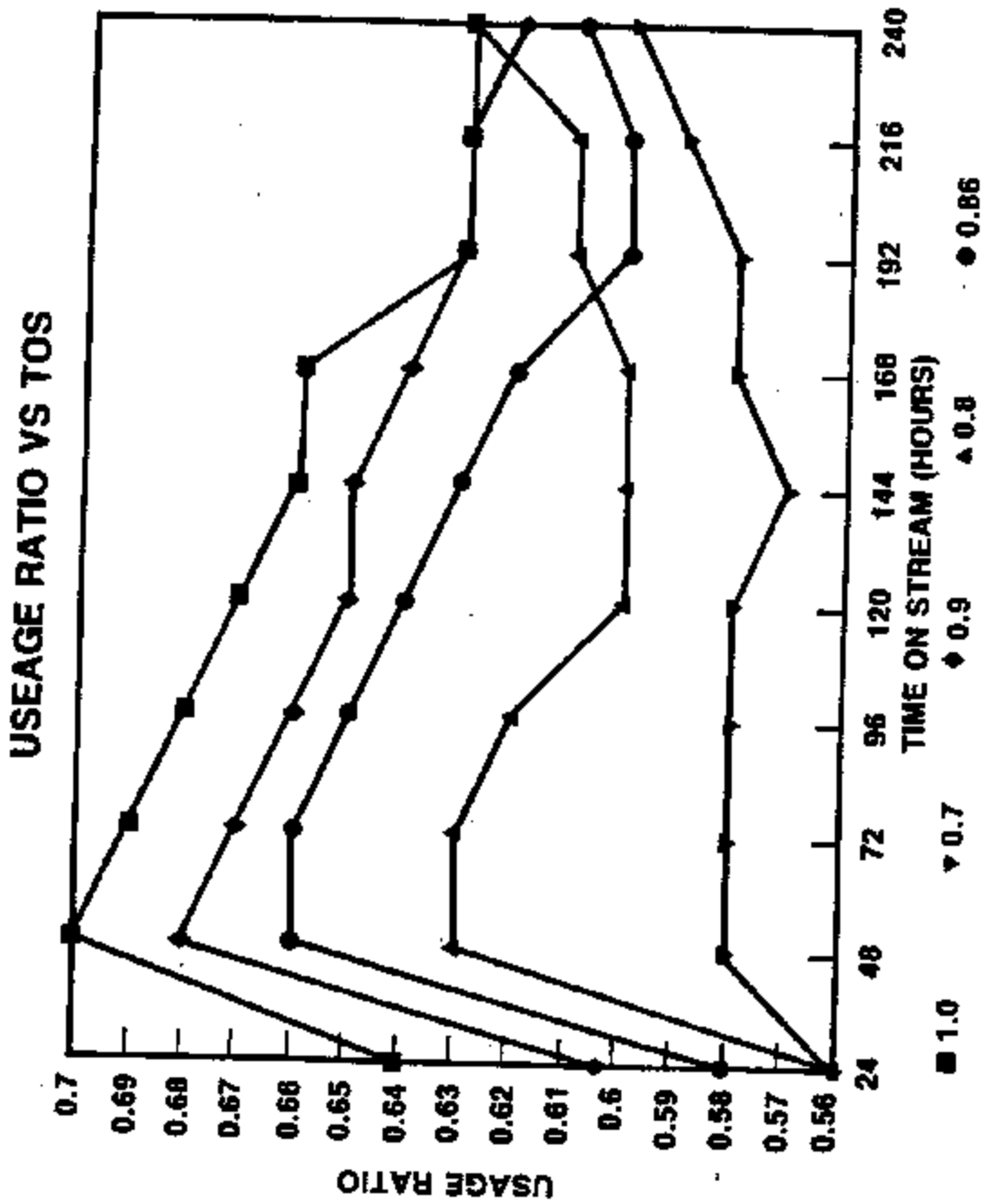
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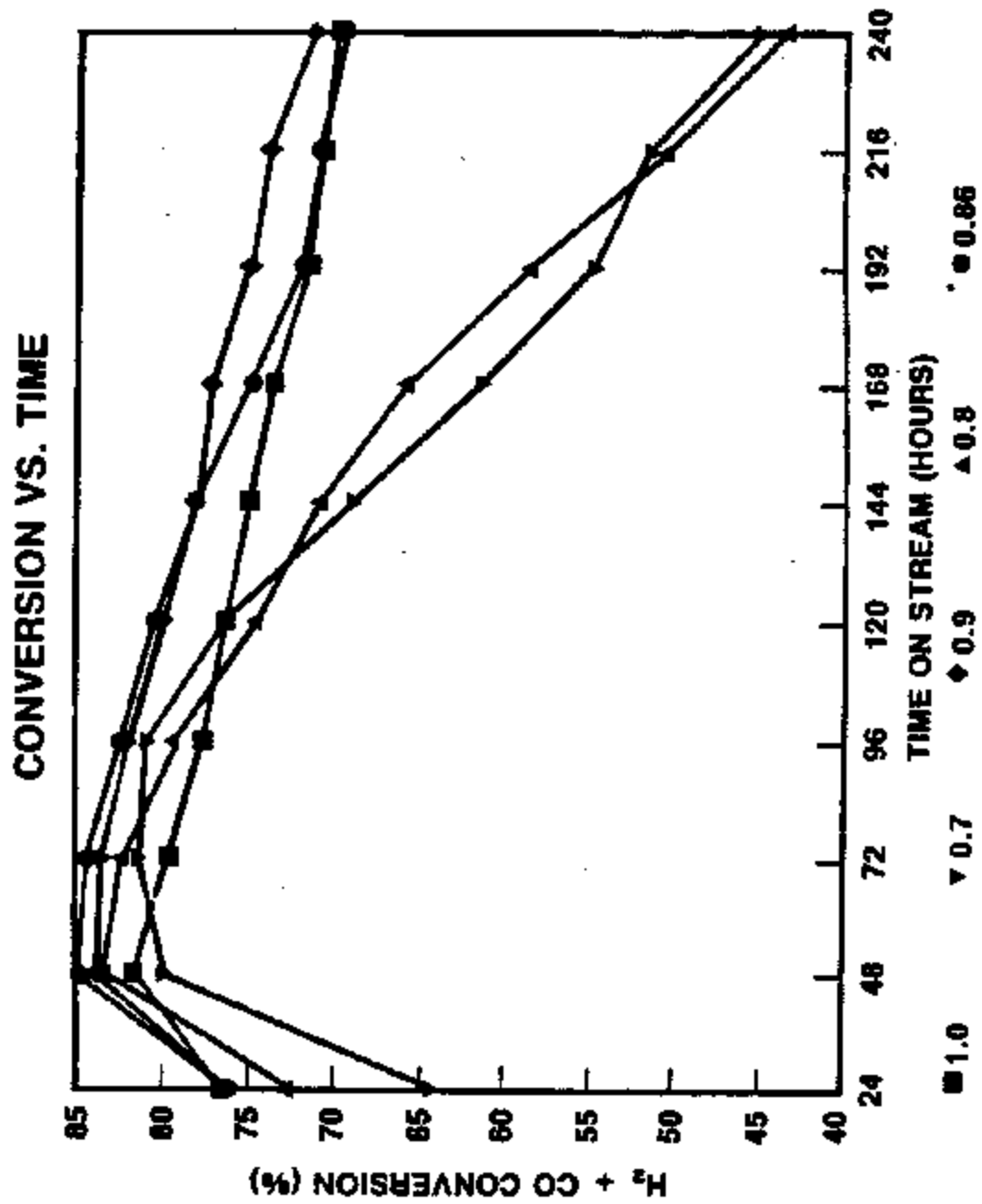
SCHEMATIC OF REACTOR SYSTEM.

FIGURE 1



H₂/CO USAGE RATIO

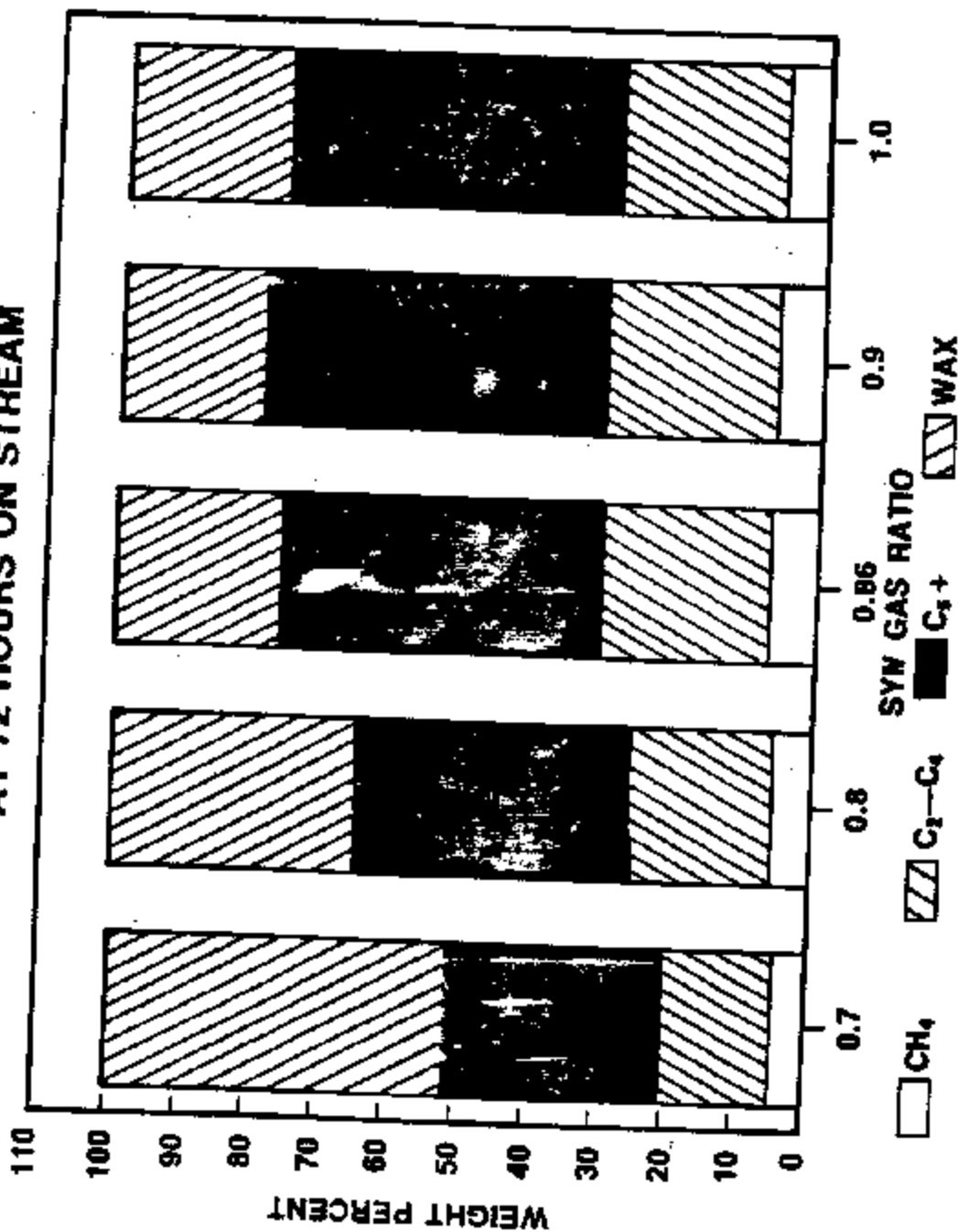
FIGURE 2



H₂ + CO CONVERSION

FIGURE 3

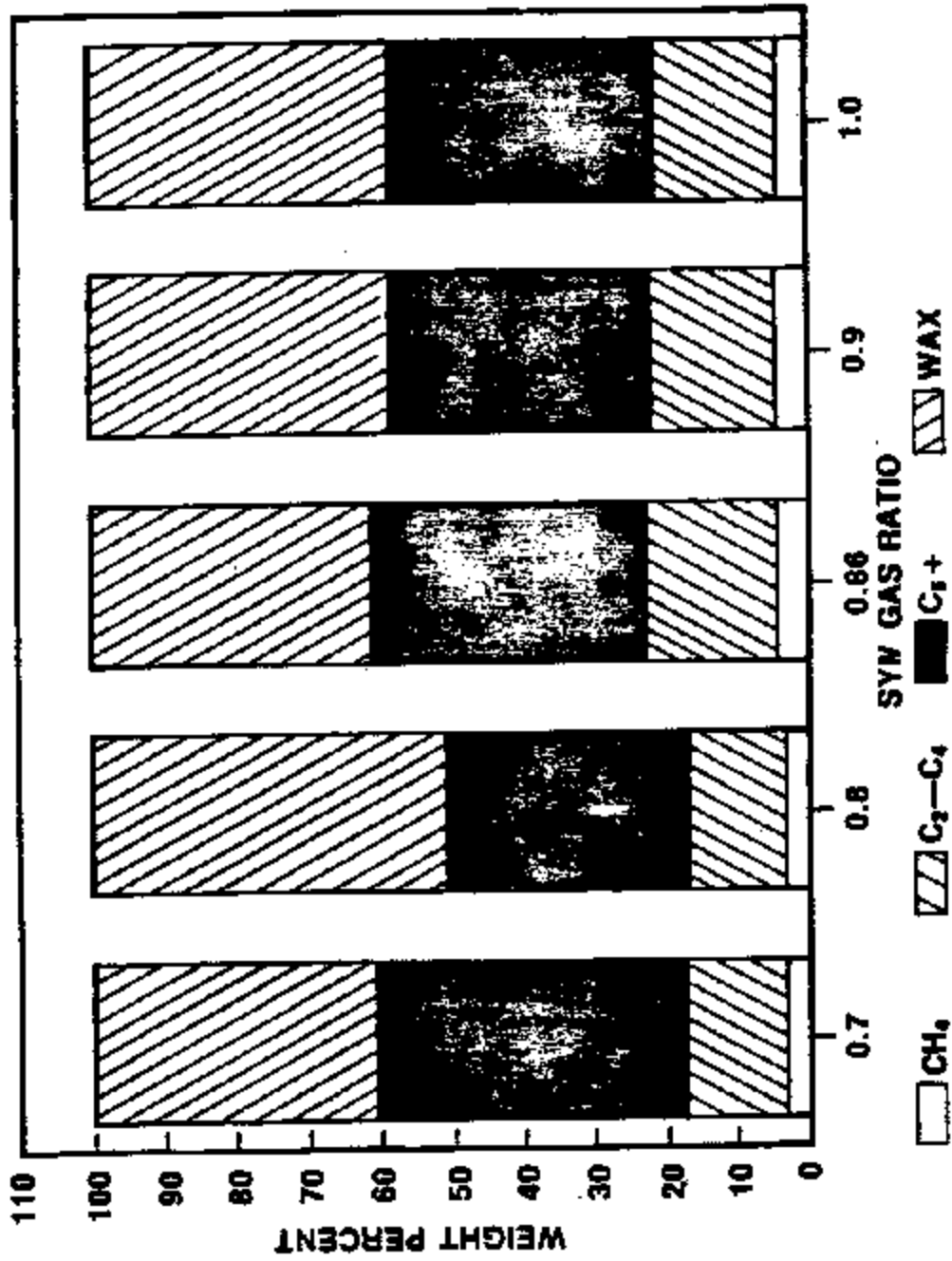
**HYDROCARBON DISTRIBUTION
AT 72 HOURS ON STREAM**



HYDROCARBON DISTRIBUTION AT 72 HOURS

FIGURE 4

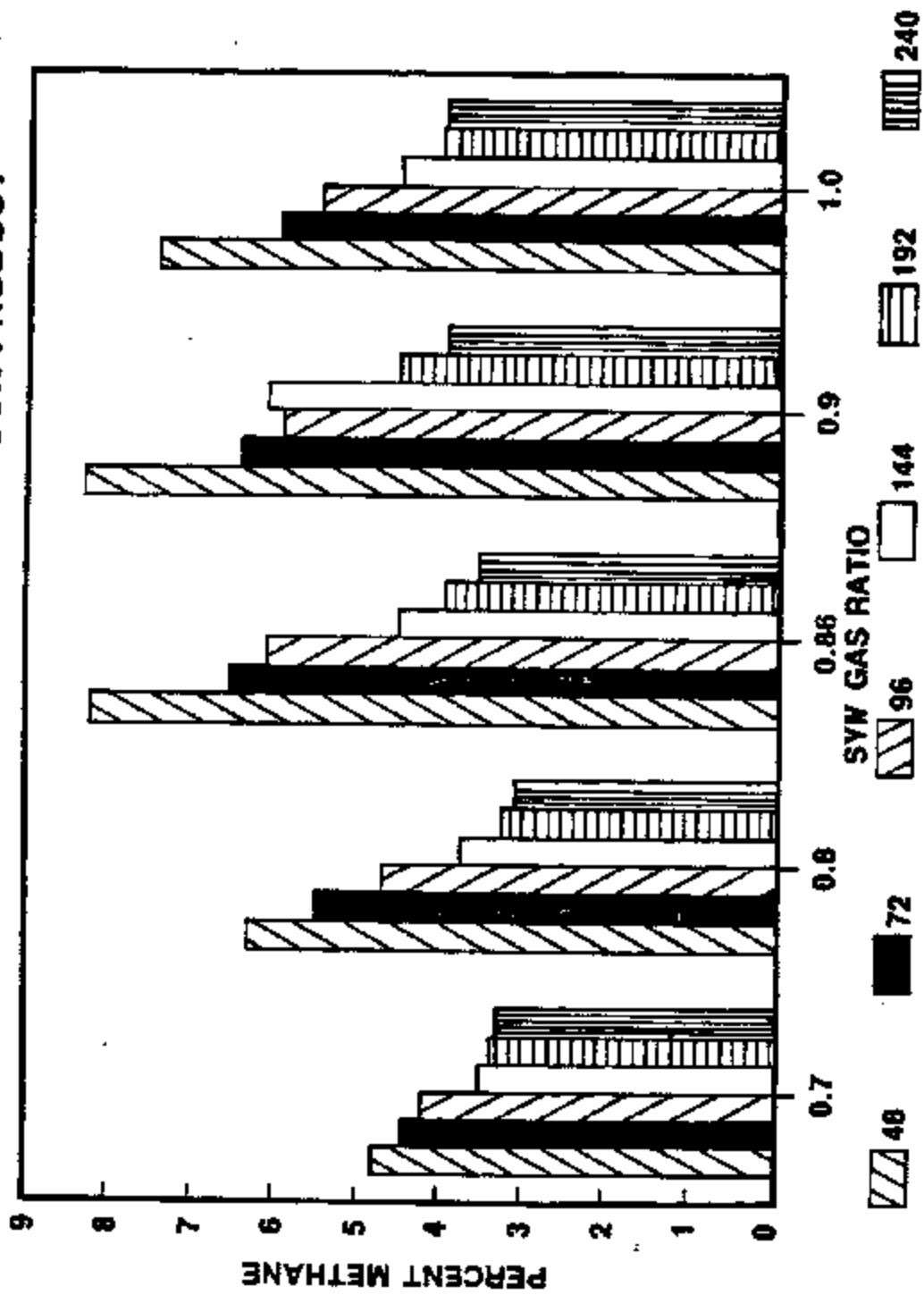
**HYDROCARBON DISTRIBUTION
AT 168 HOURS ON STREAM**



HYDROCARBON DISTRIBUTION AT 168 HOURS

FIGURE 5

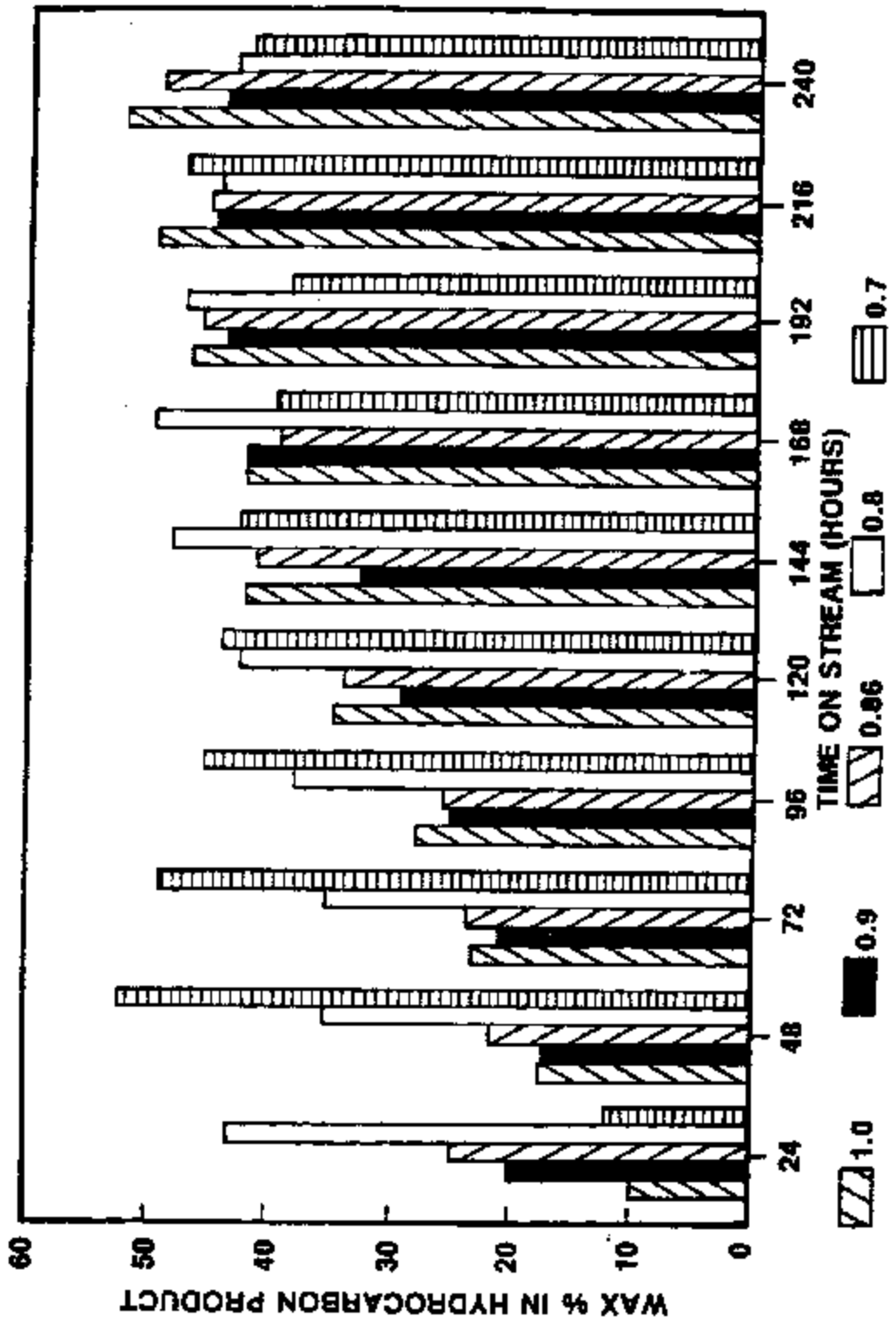
METHANE CONTENT IN HYDROCARBON PRODUCT



METHANE CONTENT OF HYDROCARBON PRODUCT

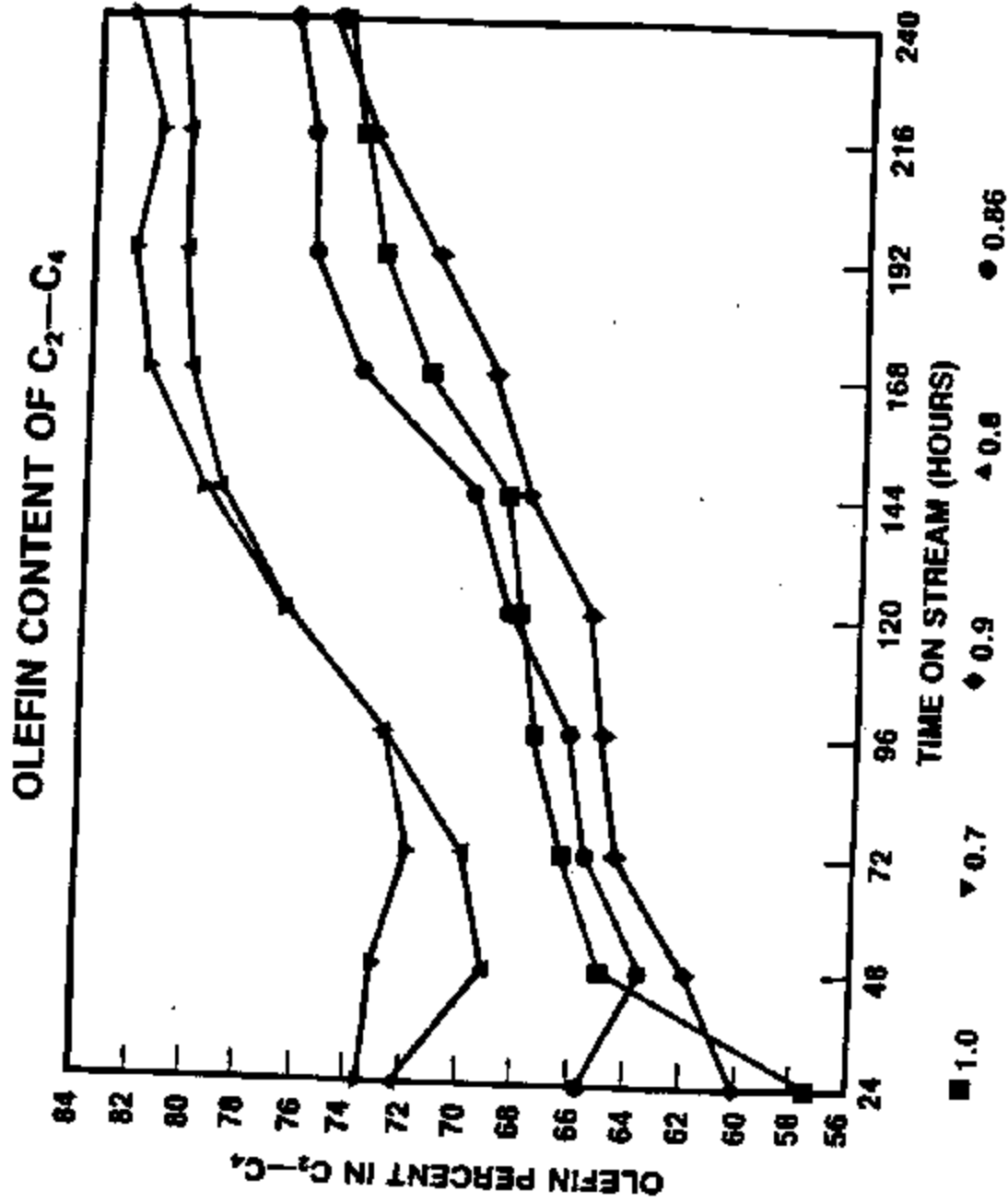
FIGURE 6

WAX LEVEL VS TIME



MAX LEVEL IN HYDROCARBON PRODUCT

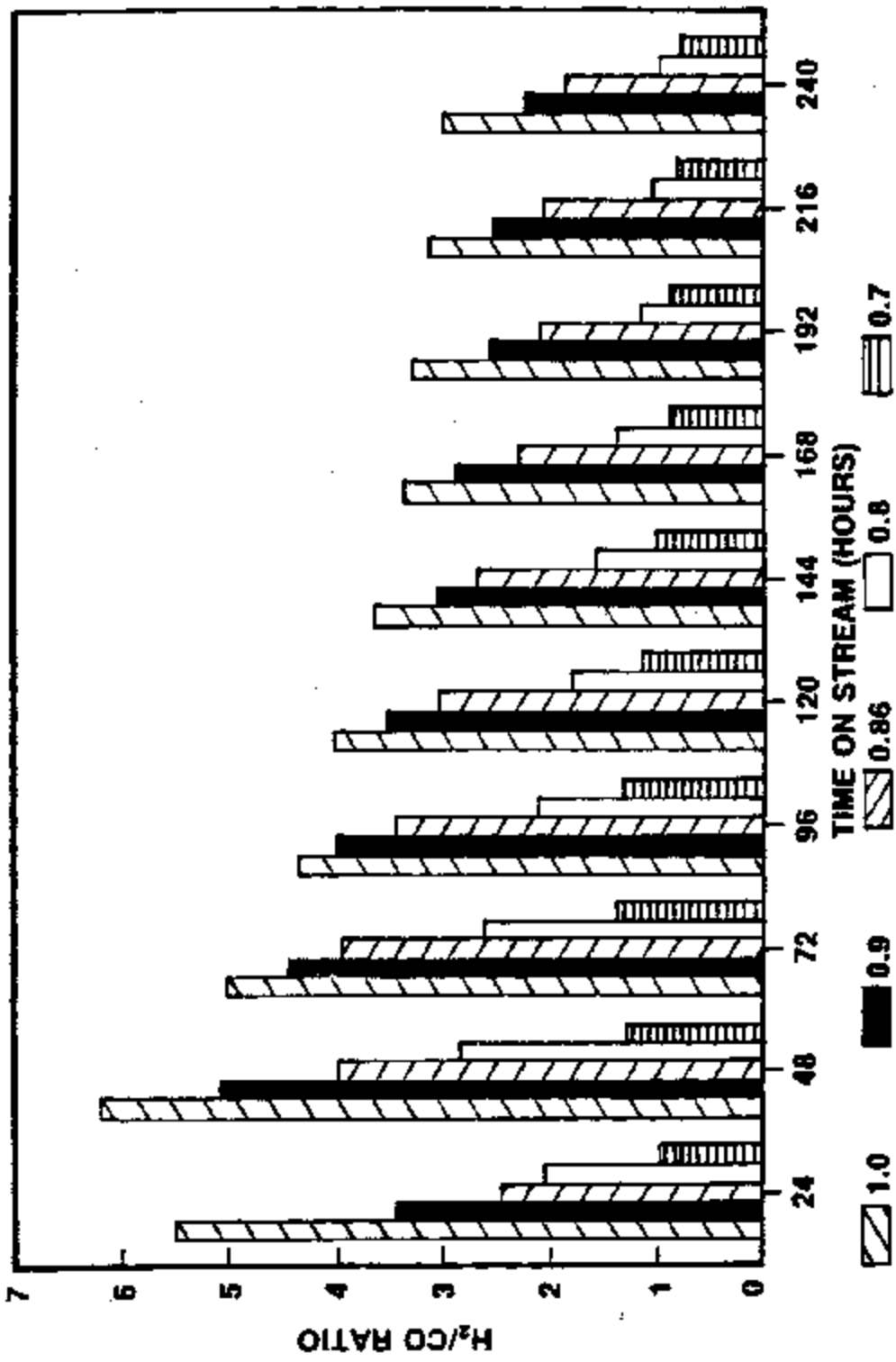
FIGURE 7



OLEFIN SELECTIVITY

FIGURE 8

H₂/CO RATIO IN TAIL GAS



H₂/CO RATIO IN TAIL GAS
FIGURE 9