Title: INFLUENCE OF LIQUID MEDIUM ON THE ACTIVITY OF A LOW-ALPHA FISCHER-TROPSCH CATALYST

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OBJECTIVE

The purpose of this research was to measure activity, selectivity, and the maintenance of these properties in slurry autoclave experiments with a Fischer-Tropsch (FT) catalyst that was used in the "FT II" bubble-column test, conducted at the Alternative Fuels Development Unit (AFDU) at LaPorte, Texas during May 1994. The catalyst contained iron, copper, and potassium and was formulated to produce mainly hydrocarbons in the gasoline range with lesser production of diesel-range products and wax. The probability of chain growth α was thus deliberately kept low, hence the name "low-α" catalysts. Principal goals of the autoclave work have been to find the true activity of this catalyst in a stirred tank reactor, unhindered by heat or mass transfer effects, and to obtain a steady conversion and selectivity over the approximately 15 days of each test. This would typically require that activity be unaffected by variations of the initial wax medium or by increasing the weight % catalyst loading in the slurry. Nevertheless, slurry autoclave experiments have demonstrated a dependence on initial wax medium and on weight % catalyst loading. We report research attempting to clarify these effects. The reaction experiments were correlated with the results of Mossbauer spectroscopic analysis of the iron catalyst composition. These reactor tests were conducted using most of the same run parameters as those used in the AFDU bubble column reactor.

Slurry autoclave testing of a "low-α" catalyst in heavier waxes also allows insight into operation of larger slurry bubble column reactors. The hydrodynamic properties of the slurry liquid should, under these conditions, resemble the properties in a reactor containing either a "high-α" catalyst or a "lower-α" catalyst initially charged with a typical FT wax. (After a short time, the heavier wax products from a "high-α" catalyst displace the initial wax.) Thus, the stability of reactor operation in these experiments, particularly at loadings exceeding 20 weight %, suggests the likely stability of operations on a larger scale.

APPROACHES

The catalyst was prepared at United Catalysts Inc. (UCI). The catalyst contained 86.6% by weight Fe_2O_3, 12.5% CuO, and 0.05% K_2O. There was also 0.37% sulfur present as an impurity. The catalyst was formed by spray drying and no binder was added. The agglomerates were submicron to 60 microns in diameter, and broke down further inside the reactor.

Either 36.5 g (9 weight % catalyst in slurry wax) or 86.6 g (23 weight %) of catalyst were added initially to 290 or 370 g of wax in the reactor. One of three different waxes were loaded initially in the reactor: purified n-octacosane, (C_{28}), a heavier wax composed of linear polyethylene chains (Polywax-655) made by Petrolite Corporation or another heavy wax obtained from Allied-Signal, #AC1702, which had its lightest compounds distilled off at the University of Kentucky, CAER. All the tests were conducted in a 1-L Autoclave Engineers (AE) stirred tank reactor with either the original hollow shaft and stirrer or with a larger diameter hollow shaft and stirrer obtained from Pressure Products Industries (PPI). Figure 1 shows the internals of the reactor. Gas was introduced through a 1/8" tube at the bottom of the reactor while stirring was maintained at 1000 rpm (except where otherwise noted). Other experimental details are given in our previous work [1,2,3].

The catalyst was activated in 1.4 L CO/g Fe hr at 270° C and 1.31 MPa for 22 hours. The synthesis was conducted for up to 15 days at 1.31 MPa and 270° C, using a H_2/CO ratio of 0.70. The flowrate was 2.4 L syngas/g Fe hr. The volatile liquid products were collected continuously in a trap maintained at 20° C and vaporized wax was collected in a 200° C trap, while the heavier wax products remaining in the reactor were sampled for analysis. Samples for Mossbauer analysis of catalyst composition were obtained from these reactor samples. The gaseous products were analyzed every 24 hours by an on-line gas chromatographic (GC) system. A material balance based on weights of reactants and products was calculated for each 24-hour period. From this, the conversions and selectivities were determined. Mossbauer analyses gave the iron composition present in the catalyst at various points in the tests [4].

CURRENT STATUS

One initial wax tested was purified $C_{28}H_{58}$, n-octacosane. The higher flow rate used in the experiment with high weight % catalyst caused rapid loss of wax from the reactor and a substantial decrease in the reactor liquid level. The conversions are shown in figure 2. Approximately 71 grams of 270 grams of n-octacosane loaded initially was lost by the end of 75 hours. It is assumed that the drop off in conversion was related to the loss of liquid from the reactor.

In order to limit the loss of reactor wax in experiments with "low α" catalysts, other heavier waxes were considered for the initial medium, some commercially prepared and some from F-T reactors. Use of heavier waxes required the development of a new method for wax analysis. This is because the gas chromatograph used at this laboratory for wax analysis was not a high temperature apparatus and could only elute peaks up to a carbon number of 42, although many of the waxes considered had a significant weight % exceeding C_{42}. The new method was to dissolve the starting waxes in solvent as before, but then spike the solution with a known weight of a branched C_{19} compound, and inject the spiked liquid onto the chromatographic column. The weight % values for compounds $\leq C_{42}$ can then be obtained from the internal standard. The weight %'s $\leq C_{42}$ determined for each prospective wax are given in Table 1, along with the average carbon number if known. Polywax-655, with a nominal average carbon number of C_{48}, has 25.9 % of wax $\leq C_{42}$ and is clearly much heavier than n-octacosane. It resembles an FT wax, with straight, but only even carbon number chains. It is similar to an end-of-test Mobil wax from a "high-α" FT run (CT256-4+7), which has 24.3 % C_{18}-C_{42}. The Allied-AC1702 wax had very little hydrocarbon $\leq C_{42}$. The distillation by Burt Davis' group at Kentucky CAER [5] yielded the heaviest wax seen in this study.

The F-T synthesis was conducted at 10 % wt catalyst with three different initial waxes. In figure 3, the effect of initial wax composition on (H_2+CO) conversions is shown. The most stable conversions resulted when the lightest wax, n-octacosane was used. When the heavier Polywax-655 was used, the conversions were initially as high but decreased to 60 % in 13 days. When the heaviest wax, distilled Allied-AC1702 was used, conversions were initially lower and decreased to 60 % in 12 days. These results with the Allied wax matched results previously reported at Kentucky CAER [5]. Clearly the wax medium affected the conversion. However, two other parameters were varied in these tests. The Autoclave Engineer's shaft and stirrer, rather than the PPI shaft and stirrer, were used for the test in n-octacosane. Only 290 grams, rather than 370 grams, of initial wax was loaded of distilled Allied wax.

To ensure that the trend in figure 3 was due to the effect of initial wax, the test in n-octacosane was repeated with the PPI stirrer and shaft. These conversions are shown in figure 4 and can be compared to those shown in figure 3. The conversions in n-octacosane were similar to those in the initial test in n-octacosane with the A.E. shaft and stirrer. They would likely have remained steady above 80% out to 300 hours. The test in distilled Allied wax was repeated but with 370 grams rather than 290 grams of wax, and there was some small improvement in conversion. Perhaps this was due to the increased residence time of the bubbles compared with the test in 290 grams. There was again the same trend of a sharp drop in conversion with the two heavier waxes.

Chao and Lin [6] report solubilities of reactants and product gases in four waxes: C_{28}, C_{36}, Sasol Arge wax, and Mobil-CT-256-7 FT wax. The solubilities of the gases H_2, CO, CH_4, CO_2, and C_2H_6 are shown in Table 2. The waxes are shown in order of increasing carbon number. Solubilities do decrease as the wax becomes heavier. Solubilities in Mobil wax (average carbon number 61) are 70-75 % those in C_{28} wax.

One might propose a simple model which states that: because the solubilities of the reactant gases are lower in a heavier wax than in a lighter wax, the conversions would be proportionately lower. This would assume a simple first-order reaction rate. It would be assumed that the number of active sites are constant no matter what wax is used. Figure 5 plots actual data in C_{28} wax, and two "guesses" for reaction behavior in the heavier waxes in which the C_{28} data is corrected for lower solubilities. This simple model clearly does not work. It predicts lower activity throughout the life of a run, while figures 3 and 4 show that the initial conversions in the three waxes are nearly the same, while the deactivation rates are different.

This raises the question of what is causing the timing and severity of the deactivation among the different waxes. Mossbauer spectroscopy was used to identify iron phases on samples withdrawn from the reactor at various times during the activation and syntheses for several tests. Figure 6 shows the results of the test conducted in Polywax-655. After 22 hours of activation in CO, the iron oxide was converted to 81 % χ-carbide. After 6 days of synthesis some of the χ-carbide has converted back to Fe_3O_4, perhaps due to the presence of oxidizing product gases. The χ-carbide has reached a steady value of 50%, while the other 50% is made up of Fe_3O_4 and super-paramagnetic particles (probably composed of α-FeOOH). In previous work [4] it was proposed that the level of conversion is related to the amount of χ-carbide formed during activation and is best when the χ-carbide starts high, at 80% to 90%, and then is converted to include some Fe_3O_4. A poorer form of the catalyst is found in activations that yield a moderate amount of χ-carbide, say 50%, which grows to a higher amount during synthesis. Our Mossbauer results indicate that catalysts are being activated to the same extent in either the C_{28} or the Polywax media after the 22 hour activation (carbiding) period. However, in the distilled Allied wax, the catalyst was carbided to a lesser extent, 64% after activation. It reached only 42% during synthesis. Whether this has any correlation with the deactivation rate is not yet known.

In one other way, the activations in the three waxes were not totally identical. The cumulative amounts of CO_2 made from CO during the 22 hour activations were different. The legend in figure 4 shows these differences as a theoretical percentage. If all the Fe_2O_3 had been converted to χ-carbide and if all the CuO had been converted to Cu, the amount of CO_2 produced would have been equal to a certain number of moles which was called 100%. In C_{28} wax, where CO is most soluble, 250% of the theoretical CO_2 was made in carbiding and carbon formation. However, in the Polywax-655 and the distilled Allied wax, only 150% of the theoretical CO_2 was made. So the catalyst activated in C_{28} wax might have had a greater amount of surface carbon produced. Whether this had any influence on the drop in conversion rate is not yet known. (Latest tests show these results may be an artifact of the experiments.)

The rate of the water gas shift (WGS) reaction ($H_2O + CO \rightarrow H_2 + CO_2$) decreased along with the overall rate of syngas conversion. It is difficult to separate the influence of each reaction on the other. The decrease in the WGS conversion may be influencing the decrease in the FT conversion since the WGS reaction may be catalyzed by different sites than is the F-T reaction, perhaps by Fe_3O_4 versus χ-carbide sites. Or both reactions may be decreasing simultaneously. The apparent shift constant, R, begins near the equilibrium value of 62 for the WGS reaction in each of the three waxes. At this point, most of the oxygen from dissociated CO leaves as CO_2 rather than as H_2O. The shift constant decreases as syngas conversion decreases. Figure 7 shows an increase in the grams of water produced per day at lower conversions. Therefore the partial pressure of water in the reactor is actually increasing significantly over time for the heavier waxes, but not for the C_{28} wax.

Koenig et al. [7] reported FT conversions and Anderson-Schulz-Flory (ASF) distributions on iron foils with and without potassium and with and without water vapor added. They concluded that catalyst sites promoted with potassium "are more stable with respect to oxidation (deactivation) by water than unpromoted sites." They did not speculate whether the WGS sites are the same as the FT catalytic sites. This catalyst clearly has very few sites promoted with potassium compared with other previously tested FT catalysts. The catalyst may be subject to a more rapid deactivation by water than those FT catalysts with higher loadings of potassium. However, one must then explain why more water would be formed in the case of the heavier waxes.

Figures 8 and 9 show the effect of stirrer speed on conversion, using 11 weight % catalyst in Allied wax. This technique tests for gas/liquid or film mass transport limitations. Rpm's and flows were varied in the same test. Figure 8 shows that at 1.5 times the baseline flow, the conversion dropped as stirrer speed went below 500 rpm. This behavior was expected. In going from the baseline stirrer speed of 1000 rpm to 1200 rpm, the conversion reached a plateau. There can then be said to be no apparent gas/liquid or film mass transfer limitations in this wax. A few days of test were run at the normal flow, shown in figure 9, where the conversions were up near 85% and again there was little change in going from 1000 rpm to 1200 rpm. This, however, does not rule out all mass transfer or diffusion limitations in the heavier waxes.

In figure 10, conversions are plotted for a loading of 19 weight % of the LaPorte FT-II catalyst in 370 grams of Polywax-655.

Conversions started high, near 83 %, and decreased to 60 % by the end of 7 days. This decrease was more severe than that seen for 9 weight % catalyst in Polywax-655. Only a cumulative total of 5 grams of Polywax-655 was lost over 8 days for the figure 10 results. Therefore the loss of a sufficient liquid level cannot be blamed for this sharp decrease, as was suggested for the figure 2 results. How much of this drop in conversion was due to the use of a heavier wax and how much was due to additional mass transfer limitations at the higher weight loading and higher flow still need to be determined.

PLANS

The reasons for the conversions' deactivation in Polywax-655 and Allied wax still need to be explored. We also plan to retest this catalyst at a high weight loading with the C_{28}, light wax. This retest will involve modifying the unit to allow daily addition of C_{28} wax to the reactor to maintain the liquid level. If wax addition is successful at 10 weight % catalyst loading, we will go to $\geq$20 weight % catalyst loading and hope to obtain a steady conversion lasting about 15 days.

CONCLUSIONS

In general, Polywax-655 and distilled Allied wax have the same advantage over n-octacosane in their slow rate of leaving the reactor at high flows. Conversions using these two heavier waxes, however, show more of a decrease over time than conversions in n-octacosane. Reasons for these trends still need to be understood. Catalysts with 0.05 wt% K_2O could be very sensitive to the partial pressure of water present in the reactor.

REFERENCES

1. "A Study of Iron Fischer-Tropsch Catalysis," M.F. Zarochak and M.A. McDonald, 7th DOE Indirect Liquefaction Contractors' Review Meeting, Pgh. Pa., Dec. 8-9, 1987.

2. "Slurry Phase Fischer-Tropsch Catalysis," R.J. Gormley and M.F. Zarochak, 11th DOE Indirect Liquefaction Contractors' Review Meeting, Pgh. Pa., Sept. 3-5, 1991.

3. "Testing Low-Alpha Fischer-Tropsch Catalysts," R.J. Gormley and M.F. Zarochak, P.W. Deffenbaugh, and K.R.P.M. Rao, DOE Coal Liquefaction and Gas Conversion Contractors' Review Conference, Pgh. Pa., Sept. 7-8, 1994.

4. "Mossbauer Spectroscopy Study of Iron-based Catalysts used in Fischer-Tropsch Synthesis," K.R.P.M. Rao, F.E. Huggins, G.P. Huffman, B. Davis, R.J. O'Brien, R.J. Gormley, and D.B. Bukur, ACS National Meeting, Div. of Fuel Chem., Anaheim, CA, Apr. 2-7, 1995.

5. "Technology Development for Iron Fischer-Tropsch Catalysts,"

B.M. Davis, F.L. Tungate, L. Xu, R.L. Spicer, D.J. Houpt, R.J. O'Brien, R. Lin, D.R. Milburn, S. Chokkaram, and K. Chary, DOE Coal Liquefaction and Gas Conversion Contractors' Review Conference, Pgh. Pa., Sept. 27-29, 1993.

6. "Synthesis Gas Solubility in Fischer-Tropsch Slurry," K.C. Chao and H.M. Lin, Purdue Univ., Final Report to U.S. Dept. of Energy, Contract No. DE-AC22-84PC70024, July 20, 1987.

7. "The influence of water and of alkali promoter on the carbon number distributions of Fischer-Tropsch Products Formed over Iron Catalysts," L. Koenig, J. Gaube, W Meisel, P. Gutlich, W. Gerhard, and C. Plog, Ber. Bunsenges. Phys. Chem., 91, 116-121, 1987.

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Table I

GAS CHROMATOGRAPHIC ANALYSES OF COMMERCIAL OR F-T WAXES

WAX	WT % $< C_{42}$	REPORTED AVG C #
N-OCTACOSANE	100.0 %	PURE C_{28}
DRAKEOL-10	-	C_{30},??
ETHYLFLO-164	-	$C_{30,40}$
$C_{36}H_{74}$	104.0 %	C_{36}
POLYWAX-500	59.2 %	C_{36}
SASOL-7-91	49.2 %	C_{43} OR 47
ETHYLFLO-170A	40.4 %	$C_{40,50}$
LAPORTE-I–ROSE-383A	37.9 %	
POLYWAX-655	25.9 %	C_{47}
MOBIL-CT256-4+7	24.3 %	C_{61} OR 85
ALLIED-AC1702	7.9 %	
DIST. ALLIED-AC1702	3.4 TO 5.4 %	

All spiked with tetra Me-C_{15}, and dissolved in CS_2 or decalin

Table II

GAS SOLUBILITIES IN DIFFERENT WAXES *

MOLES GAS / KG WAX @ 300 ° C , 2.0 MPa

GAS	$C_{28}H_{58}$	$C_{36}H_{74}$	SASOL (Arge) Avg. C No.= 43	MOBIL CT-256-7 Avg. C No. = 61
H_2	0.155	0.133	0.130	0.111
CO	0.182	0.161	0.161	0.130
CH_4	0.288	0.254	0.247	0.208
CO_2	0.352	0.316	0.305	0.271
C_2H_6	0.504	0.463	0.409	0.350

* Chao and Lin, Purdue U., Final Report DE-AC22-84PC70024, 1987.

MODIFIED REACTOR
WITH LARGER HOLLOW SHAFT / STIRRER FOR GAS RECYCLE

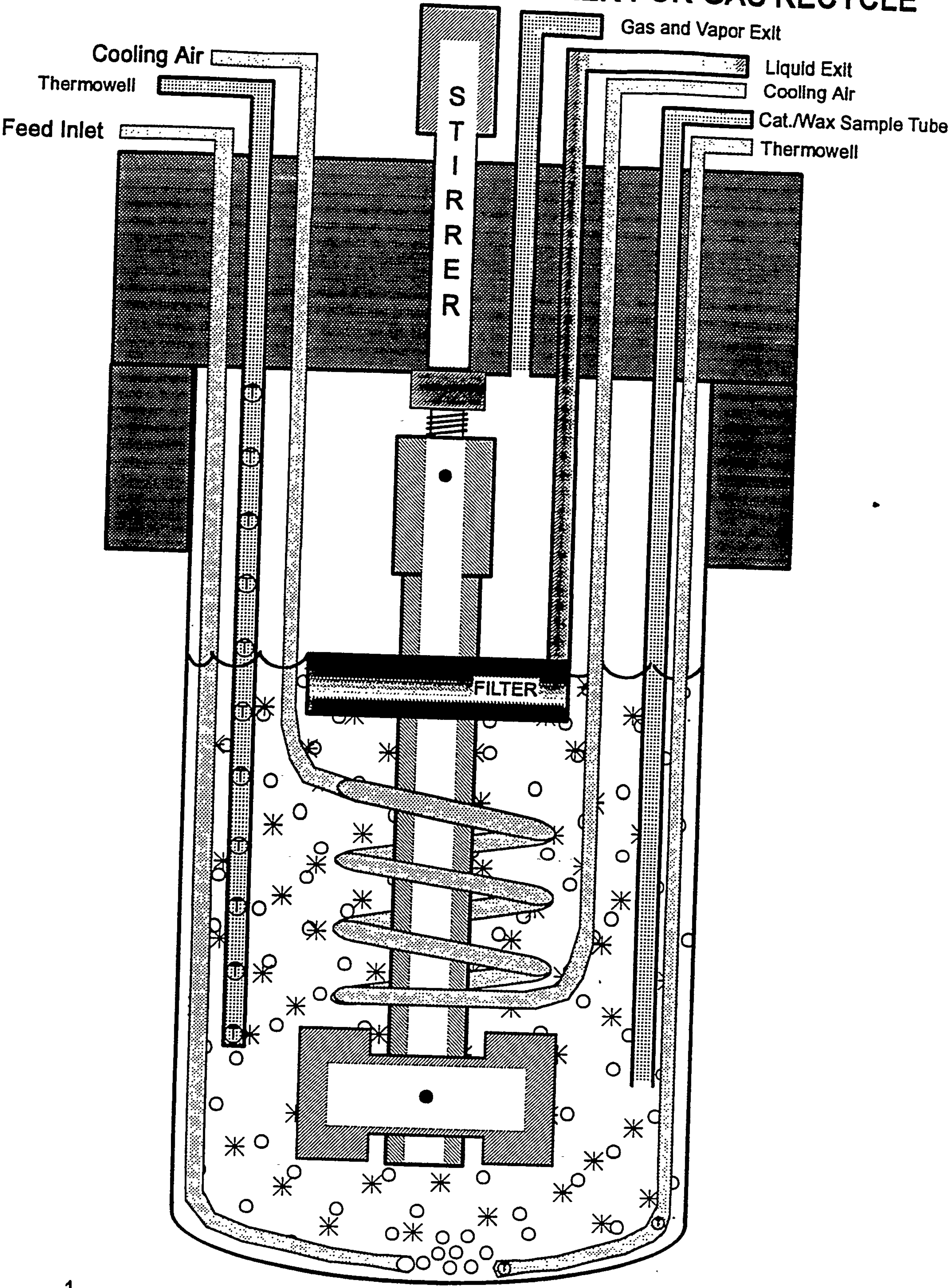
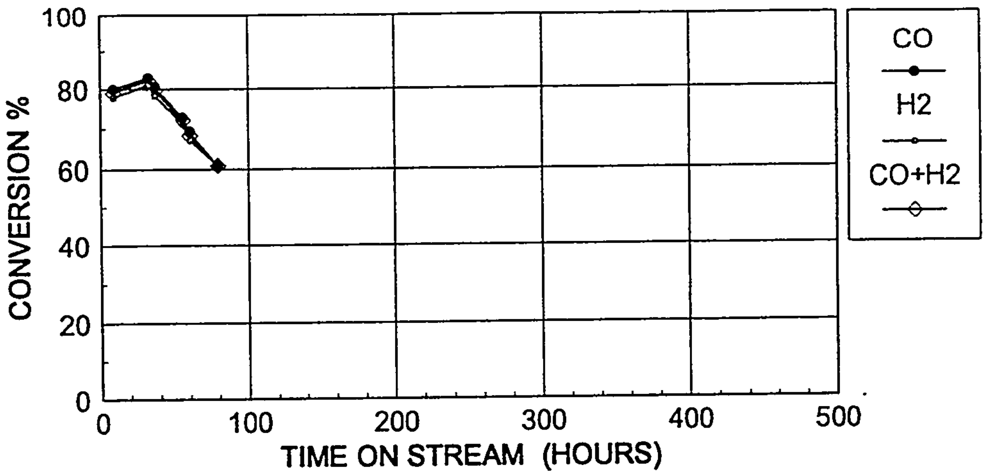


Figure 1

CONVERSIONS FOR 23 WT % LaPorte II CATALYST in 290 gm C28 WAX

Increased Wt % with proportionately higher flow



PETC TEST S3-09, A.E. STIRRER, 7 HR CO ACTIVATION

CUMULATIVE WAX LOST = 71 GM

Figure 2

EFFECT OF INITIAL WAX COMPOSITION ON CONVERSION 9 OR 11 Wt % LaPorte II Catalyst

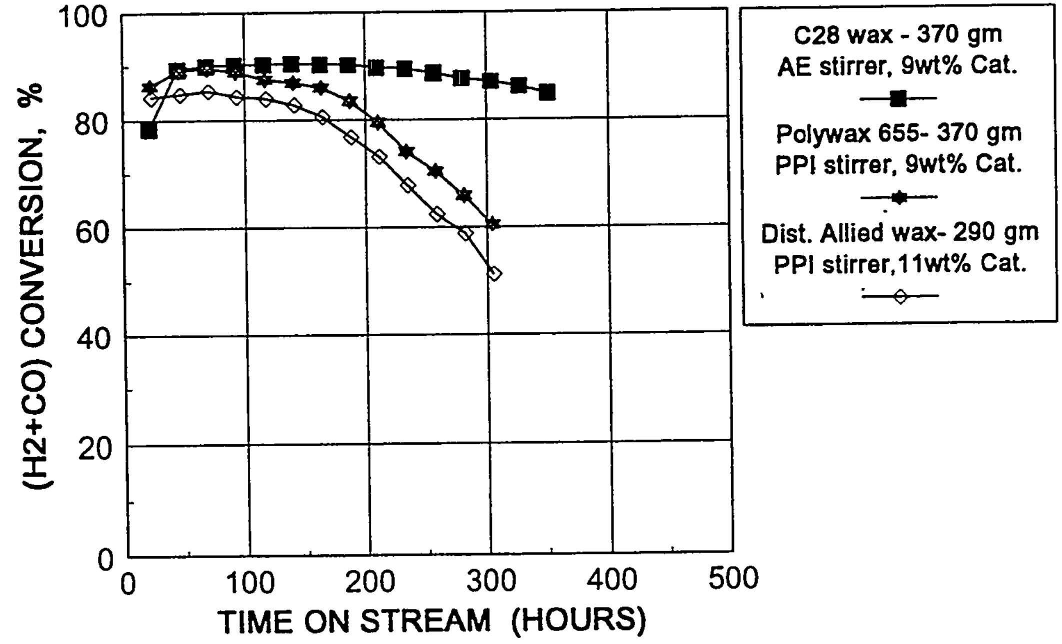
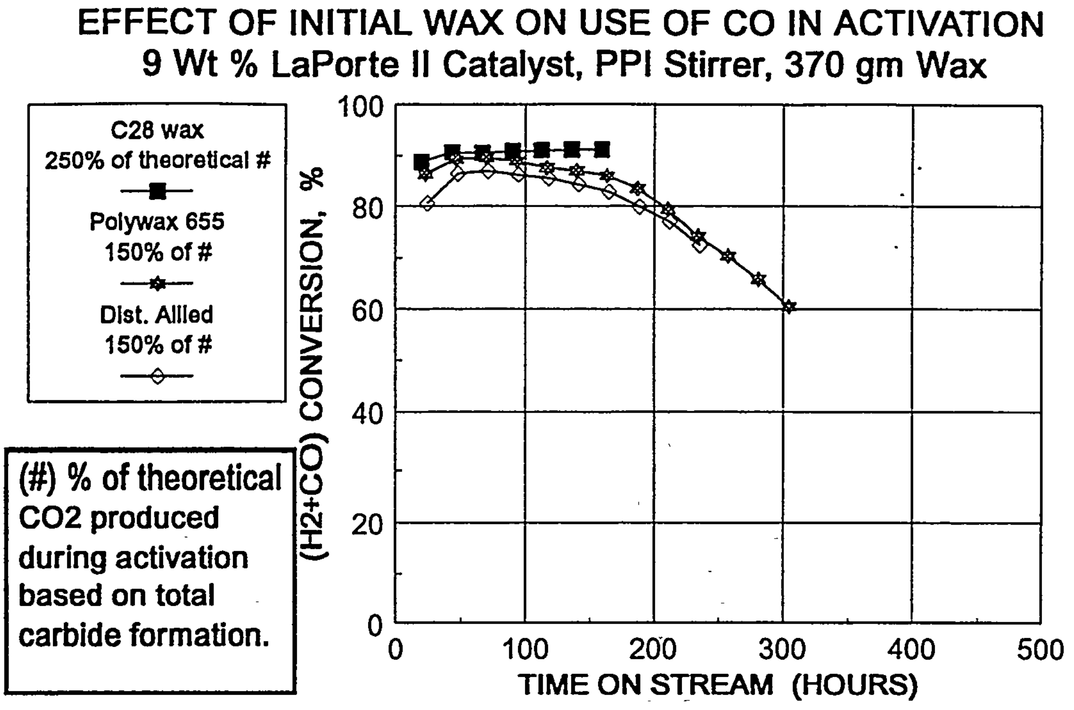


Figure 3



(#) % of theoretical CO2 produced during activation based on total carbide formation.

Figure 4

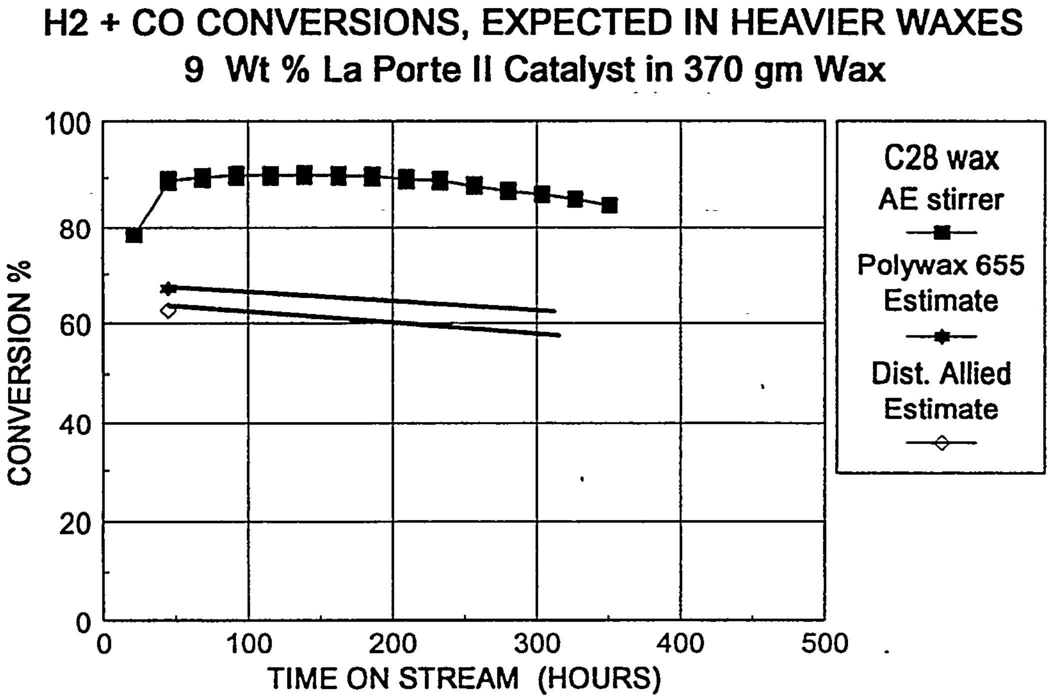
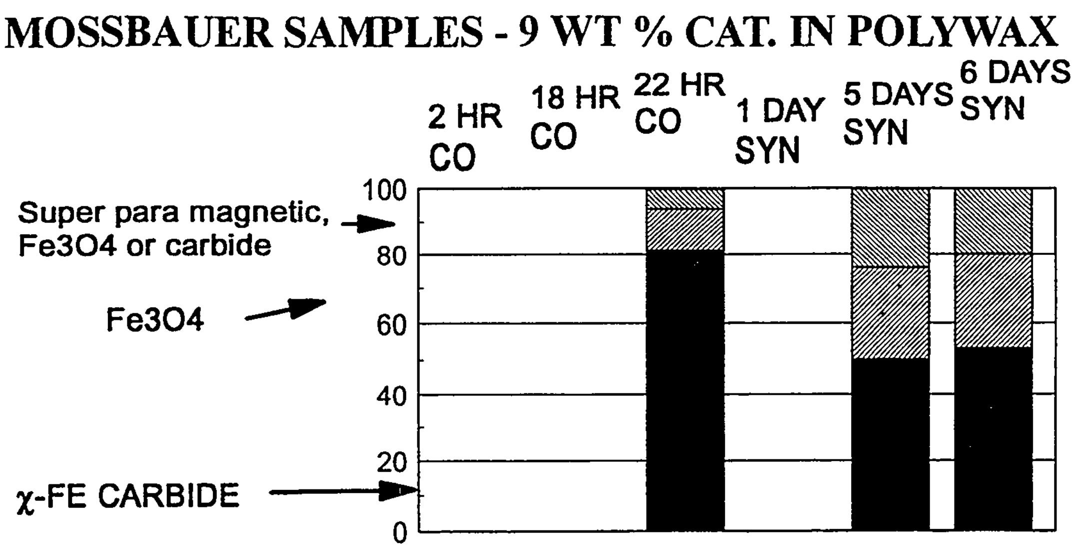


Figure 5



	2 hr CO	18 hr CO	22 hr CO	1DAY SYN	5 DAYS SYN	6DAYS SYN
chi carbide ■			81		50	53
Fe3O4 ▨			13		26	27
SPM Fe3O4 (or carbide) ▧			6		24	22
epsilon carbide ▩			0		0	0

Figure 6

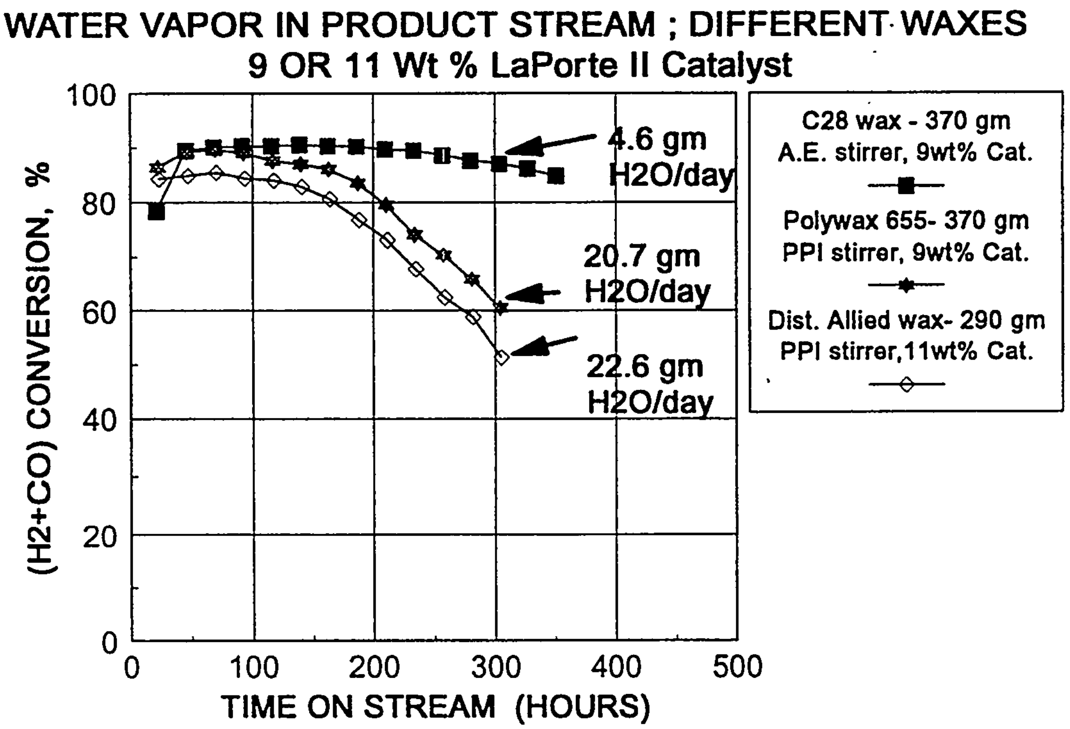


Figure 7

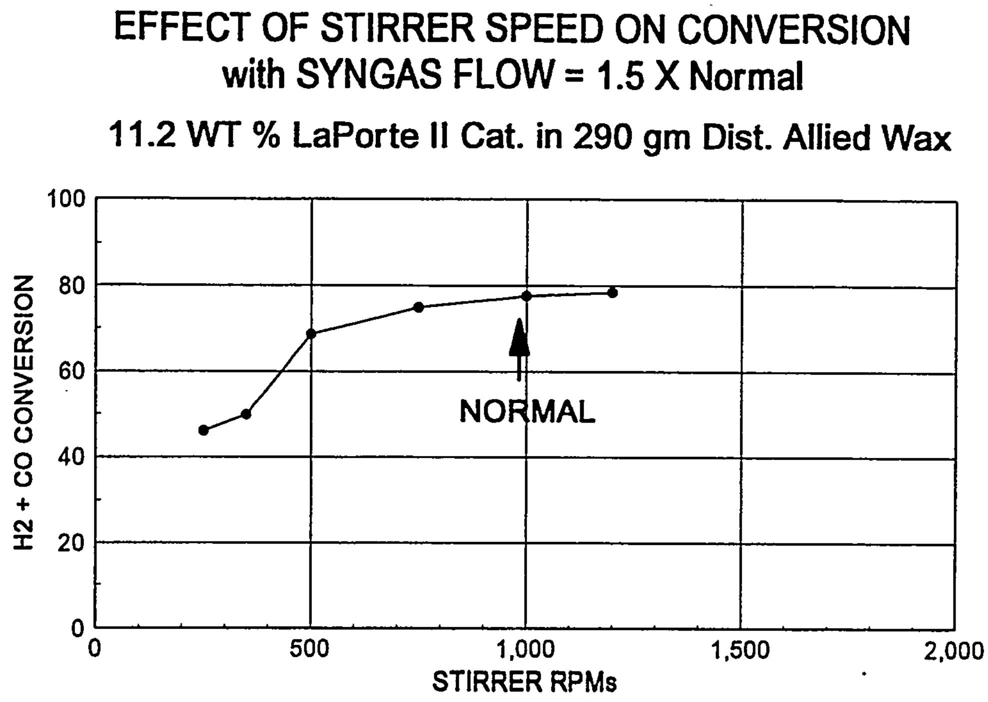


Figure 8

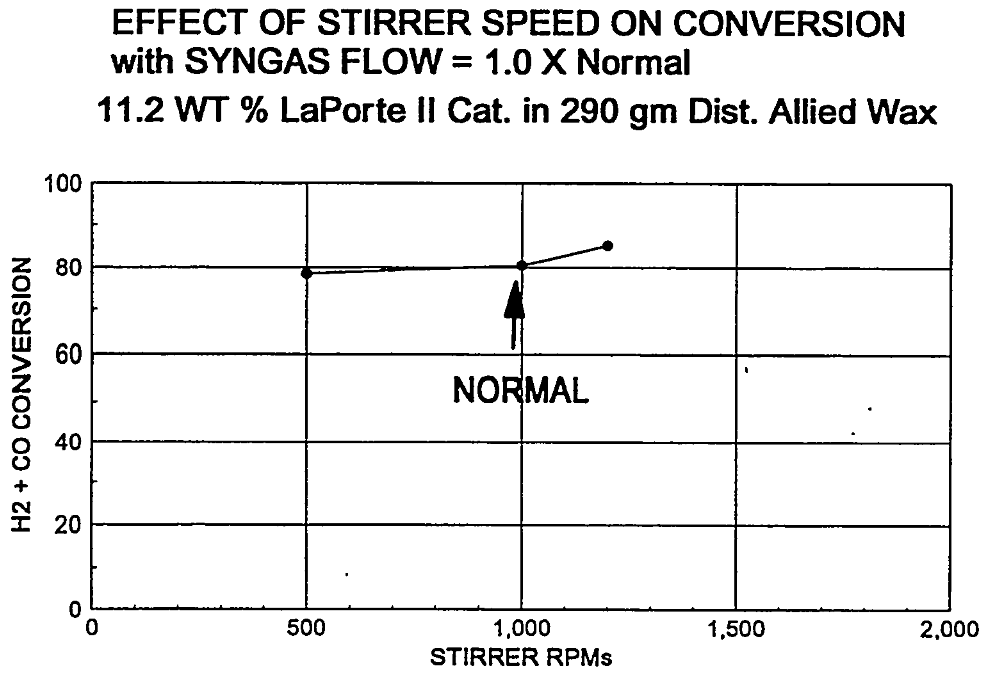
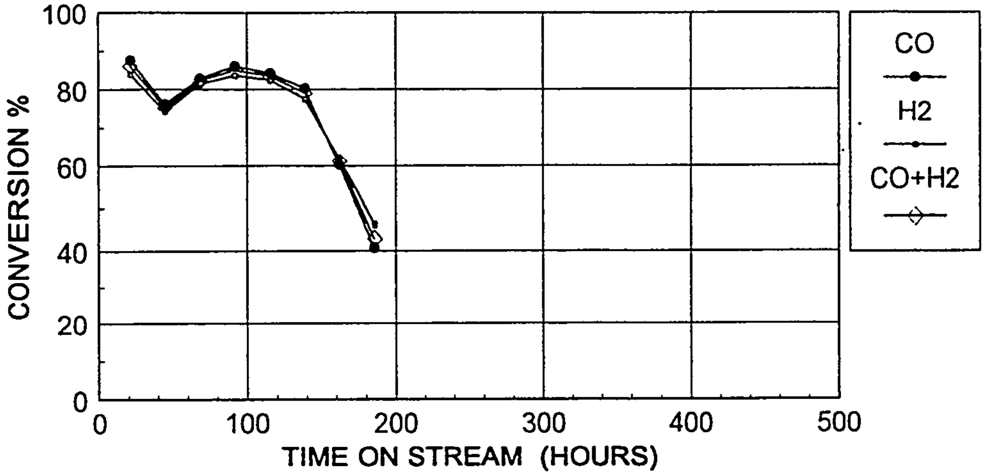


Figure 9

CONVERSIONS FOR 19 WT % LaPorte II CATALYST in 370 gm POLYWAX-655

Increased Wt % with proportionately higher flow



PETC TEST S3-14 , PPI STIRRER, 22 HR CO ACTIVATION
CUMULATIVE WAX LOST= 5 GM

Figure 10