during both reduction and synthesis. The gas chromatograms of fresh Syltherm 800 and the used slurry liquid were quite different; apparently synthesis conditions were too harsh for this liquid. The liquid recovered in the traps was presumably the products of the degradation of Syltherm 800. During synthesis, reactant conversions were very small, and the only products observed were trace amounts of gaseous C_2 and C_3 hydrocarbons.

Dow Corning 210H fluid is also a silicone polymer, similar to Syltherm 800, but with a lower vapor pressure at elevated temperatures and improved oxidation stability (16). It is used as a lubricant or as the fluid in various mechano-fluid devices. It may be used at temperatures up to 299°C. This liquid did not appear to break down during reduction or synthesis. Unfortunately, reactant conversions were very slight, with synthesis products again limited to trace amounts of C_2 and C_3 gases. Both of these silicon fluids were eliminated from further consideration because they have an adverse effect on the activity of the catalyst.

The two pure normal paraffins were selected as slurry liquid candidates because of their similarity to typical Fischer-Tropsch products. The contamination of Fischer-Tropsch product with a dissimilar slurry liquid may require an extra, undesirable separation step. Additionally, both of these paraffins are easily analyzed on a gas chromatograph. During the synthesis testing of these liquids, the activity of the catalyst appeared normal; however, slurry liquid attrition due to evaporation was substantial in both cases. The pure liquids, particularly n-eicosane, offered a unique opportunity to look for cracking products during reduction. Gas chromatograph analysis of the slurry liquid after reduction showed only trace amounts of hydrocarbons lighter than the fresh liquid, indicating that cracking of the liquid occurred only to a negigible extent during the course of the reduction.

There is some precedent to the use of Fischer-Tropsch product as the slurry liquid, but in the cases reported in the literature, the higher boiling fractions (waxes) were used (21,28). In order to use uncut product, liquid must be added to the reactor during synthesis in order to maintain a constant slurry level in the reactor. In the test of this liquid, fresh Fischer-Tropsch product was pumped from a storage tank into the reactor as needed to keep the level of slurry in the reactor constant.

Boiling was another difficulty encountered when using uncut Fischer-Tropsch product. At 160 psig, the fluidized bed product began to boil at about 250°C, leading to very high rates of liquid loss from the reactor. Although limited by temperature, the activity of the catalyst appeared normal during the test.

For long term, continuous operation of a slurry reactor, the use of Fischer-Tropsch product as the slurry liquid is an attractive alternative to other liquids because it eliminates any complications associated with mixing product and slurry liquid. A continuous system would require a partial condenser on the reactor outlet to condense the aqueous phase and heavier hydrocarbons. After separation of the two phases, a portion of the organic phase would be recycled back to the reactor in order to maintain a constant slurry level. Over a period of time, the slurry liquid in the reactor should become rich with heavy product, which should lead to lower rates of slurry liquid loss and increase the boiling point of the liquid. A system similar to that described has been tested successfully on a larger scale at ASU.

On a small scale, a better alternative was the continued use of paraffin wax as the slurry liquid.

With iron based catalysts, at reasonable operating temperatures, the cracking of the wax to lighter hydrocarbons is insignificant compared to typical rates of product formation. Also, at any temperature, the Chevron Refined Wax 143 will exert a lower vapor pressure than the other hydrocarbon liquids tested due to its higher average molecular weight. Also, the maximum synthesis temperatures will not be limited by the boiling point of the wax. These factors combined lead to small, but acceptable, amounts of wax in the recovered Fischer-Tropsch product.

3. Factor Study.

The performance of the iron-kieselguhr catalyst/ Chevron Refined Wax 143 combination was further studied by conducting a set of two level factorial experiments. Four factors were considered for this study: the reaction temperature and pressure, the weight fraction catalyst in the slurry, and the molar hydrogen/carbon monoxide feed ratio. A full factorial was performed, totaling $2^4 = 16$ experiments, plus three base point experiments.

Ranges as wide as possible were chosen for each factor. For temperature, the base point was taken at

$260^{o}C$, with a range of +/- $40^{o}C$. The base point pressure was 160 psig, with a range of +/- 40 psi. Up to 0.2 weight fraction catalyst slurries have been used successfully in similar reactor designs at ASU, so this value was used as the upper limit for catalyst concentration. For the lower limit, a 0.05 weight fraction catalyst slurry was used. Based on previous experience, this amount of catalyst should give measureable yields and conversions within the temperature range specified. The hydrogen/carbon monoxide data for simulated pyrolysis gas was available in the range of 0.5 to 2.5 mole ratios, which was used as the limits in the factorial design. The total gas composition of the feed at each hydrogen/carbon monoxide ratio appears in Table 6.

The total flowrate of the inlet gas was again limited by the capacity of the mass flowmeters, and was maintained at a value of 1 cm/s superficial velocity at the reactor inlet at synthesis temperature and pressure. The weight of wax in the reactor, which largely determines the volume of slurry in the reactor, was held constant at 2000 g for all experiments. The operating conditions for the factorial experiments are summarized in Table 7.

Table 6. Feed gas compositions as a function of the molar hydrogen/carbon monoxide feed ratio used in the factorial experiments.

Hydrogen/Carbon Monoxide (Molar Ratio)	0.5	1.5 (base pt)	2.5
Mole Fraction:			
Hydrogen	23.3	38.6	41.7
Carbon Monoxide	46.7	25.7	16.7
Carbon Dioxide	8.8	16.6	25.0
Methane	21.2	19.1	16.6

Table 7. Summary of operating conditions for factorial experiments.

Experiment Name	Treatment	T(°C)	P (psig)	H_2/CO (molar)	Wt Fraction catalyst
0	(1)	220	120	0.5	0.05
8	T	300	120	0.5	0.05
4	P	220	200	0.5	0.05
C	T P	300	200	0.5	0.05
2	F	220	120	2.5	0.05
A	T F	300	120	2.5	0.05
6	P F	220	200	2.5	0.05
E	T P F	300	200	2.5	0.05
1	X	220	120	0.5	0.20
9	T X	300	120	0.5	0.20
5	P X	220	200	0.5	0.20
D	T P X	300	200	0.5	0.20
3	F X	220	120	2.5	0.20
B	T F X	300	120	2.5	0.20
7	P F X	220	200	2.5	0.20
F	T P F X	300	200	2.5	0.20
R1	BASE POINT	260	160	1.5	0.125

Superficial inlet velocity at T and P: 1 cm/s.
Catalyst: 48 Fe/4.8 Cu/47.2 Kieselguhr
Weight Chevron Refined Wax 143: 2000 g

The conversions and yields obtained for the factor study experiments appear in Table 8. Data was taken over a long enough time period to insure steady state operation, which was typically greater than 8 hours. There was no indication of any appreciable catalyst deactivation during any of the experiments. A plot of conversion versus time for one of the three base point runs appears in Figure 21.

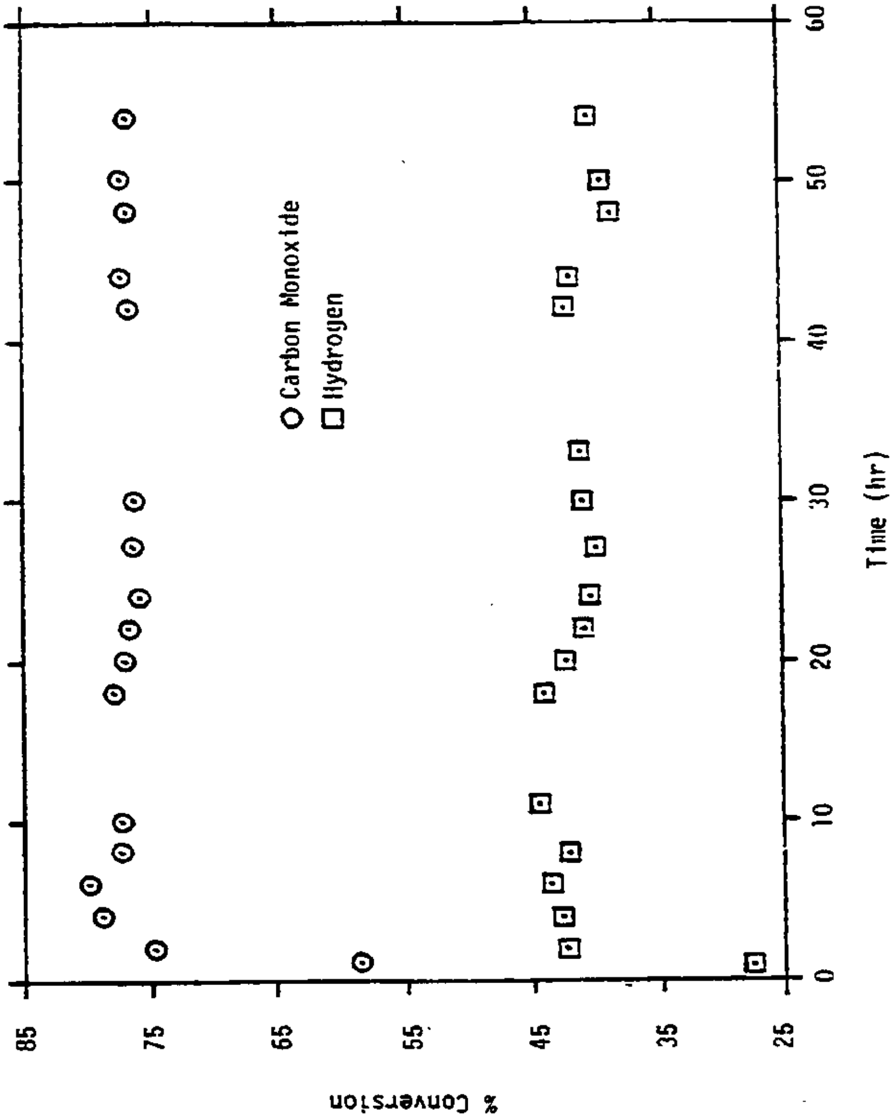
The two major sources of error in the results are the gas analysis and the calculation of actual liquid product yields. The performance of the gas chromatographs used to analyze the reactor feed and outlet streams tended to vary with time, sample composition, and the chromatograph used. To minimize the error in the gas analysis, only one chromatograph was used for all samples during a run, samples were taken as consistently as possible, and the calibrations were checked regularly during the course of a run. Actual product yields were taken as the observed yield less the time averaged slurry liquid loss from the reactor. The method does not account for slurry losses due to cracking to gaseous products; hence, the yields reported are systematically conservative estimates.

Table 8. Conversions, yields and ranking of factors for factorial experiments.

Experiment Name	Treatment	Conversions (%)		Yield (mg/g-cat/hr)	Ranking
		H_2	CO		
0	(1)	5.16	0.09	0.89	NA
8	T	66.4	44.4	31.7	1
4	P	1.07	1.10	2.21	11
C	T P	71.0	46.9	118.	9
2	F	1.20	3.57	1.42	2
A	T F	32.2	76.7	8.51	3
6	P F	1.52	5.06	0.71	7
E	T P F	43.3	88.5	4.97	5
1	X	2.44	9.99	6.60	10
9	T X	68.4	24.2	8.93	4
5	P X	5.41	0.95	2.83	12
D	T P X	54.1	54.9	28.8	14
3	F X	11.3	18.7	5.24	6
B	T F X	26.6	50.5	11.5	8
7	P F X	8.99	19.7	3.77	13
F	T P F X	45.7	49.8	5.70	15
R1	BASE POINT	41.0	77.0	30.3	NA
R2	BASE POINT	56.0	81.0	31.6	NA
R3	BASE POINT	38.1	87.9	26.2	NA

Average: 29.4
Standard Deviation: 2.81
Error: 4.60 %

Figure 21. Reactant conversions versus time for Base Point Run 1.



The relative importance of factors, based on a Yate's analysis of the experimental yields (10) were, temperature (most important), hydrogen/carbon monoxide feed ratio, weight fraction catalyst in the slurry, and pressure. The range of yields was large, 117 mg/g-cat/hr, with an error of 4.6%. The average yield of the base point runs was 29.4 mg/g-cat/hr, with a standard deviation of 2.8 mg/g-cat/hr.

4. Optimization.

An attempt was made to locate an optimum set of operating conditions within the ranges used in the factor study. It was not deemed appropriate to search for an optimum beyond the range of available data. Since seventeen different sets of operating conditions were used, equations containing up to seventeen constants could be used to represent the data; the equations actually used for optimization were polynomials, containing 8 to 16 linear constants.

Table 9 and Table 10 lists some of the equations and their constants which were fit to the experimental yields via linear regression. The correlations of the 8 and 12 constant equations, Table 9, are poor. Fourteen

Table 9. Optimization equations with 8 and 12 constants.

	Equation			
Term	8A	8B	12A	12B
1	-139	125	-94.2	-110
2	156t	-108/t	$-103t^2$	$-81.3t^2$
3	-344p	$-431p/t^2$	$-232p^2$	$-200p^2$
4	180f	$203f/t^2$	$13.9f^2$	$10.9f^2$
5	159x	$172x/t^2$	$-3.48x^2$	$-9.67x^2$
6	369tp	461p/t	510tp	463tp
7	-195tf	-220f/t	-65.3tf	-36.8tf
8	-169tx	184x/t	-39.3tx	-10.9tx
9	0	0	1.57pf	-20.1pf
10	0	0	15.2px	-72tfx
11	0	0	58.7fx	111fx
12	0	0	-38tpfx	-19.3tpfx
Correlation Coefficient	.620	.625	.684	.700

t (Temperature) = T/T_{base} (T in K)

p (Pressure) = P/P_{base} (P in absolute)

f (H_2/CO Feed Ratio) = F/F_{base} (F in mole ratio)

x (Catalyst Concentration) = X/X_{base} (X in weight fraction)

Yield (mg/g-cat/hr) $= \Sigma_i$ $(\text{Term})_i$

Table 10. Optimization equations with 16 constants.

		Equation	
Term	16A	16B	16C
1	-357	-837	-3090
2	$-226t^2$	$232/t^2$	$448/t^2$
3	$-549p^2$	$-557p^2$	$668/p^2$
4	$-28.2f^2$	$-33.7f^2$	$-225f^2$
5	$77.8x^2$	$71.2x^2$	$-113x^2$
6	1250tp	1271tp	1690tp
7	121tf	132tf	511tf
8	-99.6tx	-86.5tx	279tx
9	490pf	501pf	865pf
10	257px	270px	621px
11	-253fx	-245fx	69.9fx
12	-587tpf	-598tpf	-960tpf
13	-341tpx	-35.4px	-703tpx
14	222tfx	214tfx	-99.1tfx
15	4.48pfx	-3.61pfx	-304pfx
16	45tpfx	53.0tpfx	351tpfx
Correlation Coefficient	.988	.981	.996
Optimums			
Temperature (°C)	300	300	300
Pressure (psig)	187	186	200
H_2/CO Feed Ratio	0.5	0.5	1.3
Weight Fraction Catalyst	.05	.05	.10

t (Temperature) = T/T_{base} (T in K)
p (Pressure) = P/P_{base} (P in absolute)
f (H_2/CO Feed Ratio) = F/F_{base} (F in mole ratio)
x (Catalyst Concentration) = X/X_{base} (X in weight fraction)

$$\text{Yield (mg/g-cat/hr)} = \Sigma_i (\text{Term})_i$$

constant equations were required to bring the R^2 correlation coefficients above 0.9.

Table 10 contains three 16 constant equations which were used to determine the optimum operating conditions. The correlation coefficients of these models were all above .95. The calculated and experimental yields are compared in Figures 22 through 24. The equations were optimized using classical optimization, with a constraint check. Two models, 16A and 16B, predicted optimums at the same point. The optimum conditions predicted by these two equations were essentially the same as those used in factorial experiment C, except the optimum pressure was slightly lower (187 as opposed to 200 psig). The predicted yields were also the same as that observed experimentally.

The third 16 constant equation, 16C, suggested an optimum on the maximum temperature and pressure constraints, but with a 1.3 hydrogen/carbon monoxide feed ratio with a catalyst weight fraction of 0.101. The feed composition and catalyst loading for this optimum are very close to the base point's, while the temperature and pressure have been raised to their maximum allowable values. Since the predicted optimum yield was

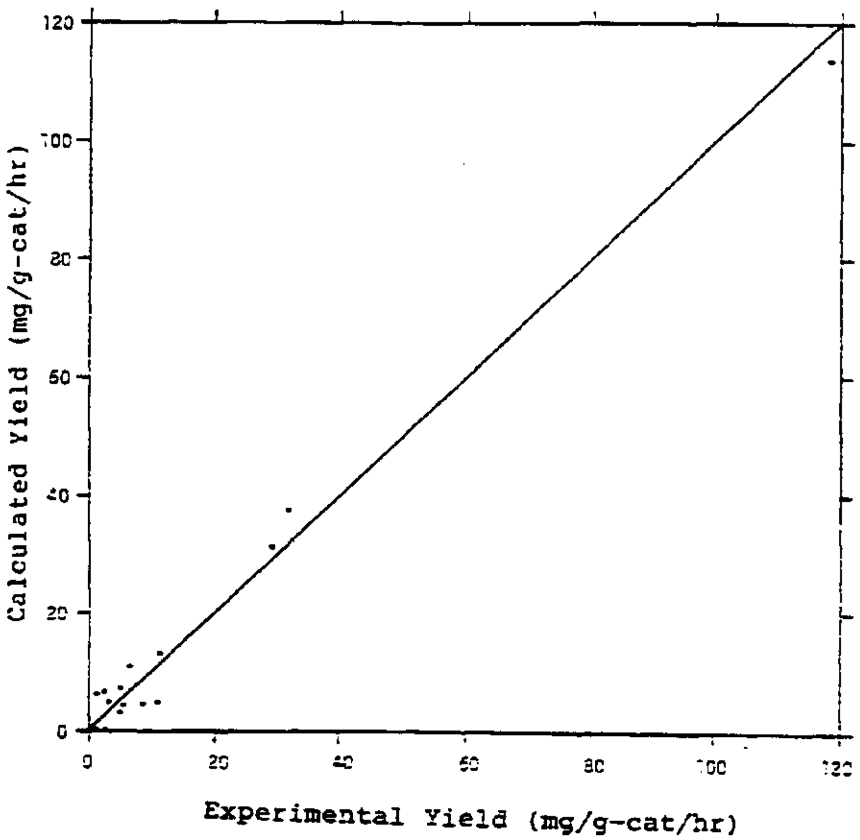


Figure 22. Experimental versus calculated yields using Equation 16A.

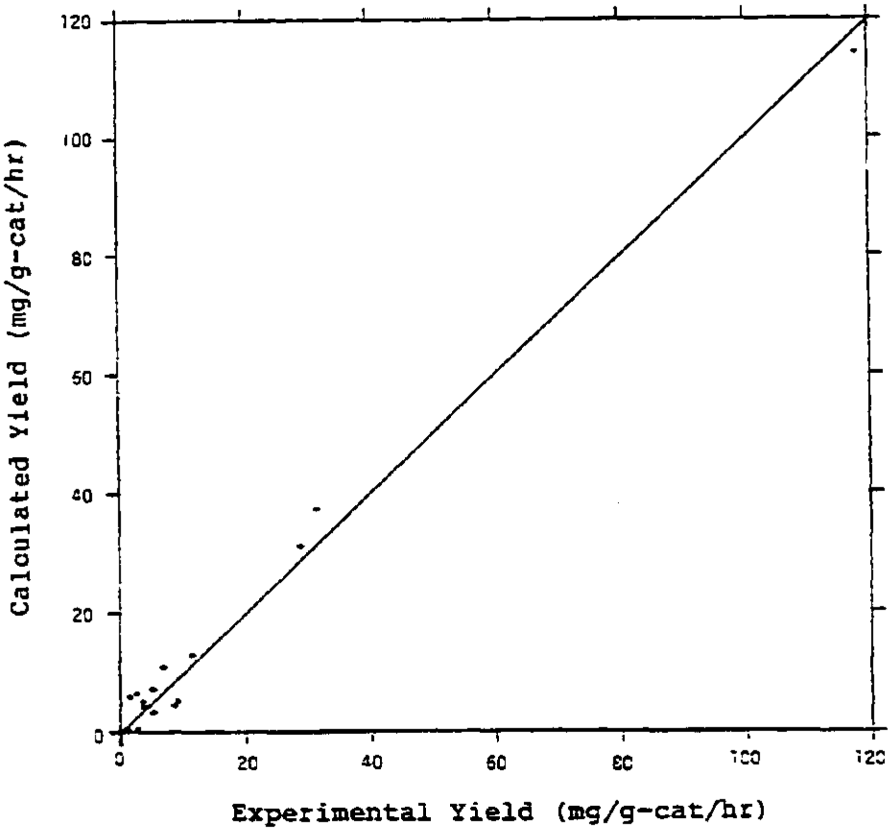


Figure 23. Experimental versus calculated yields using Equation 16B.

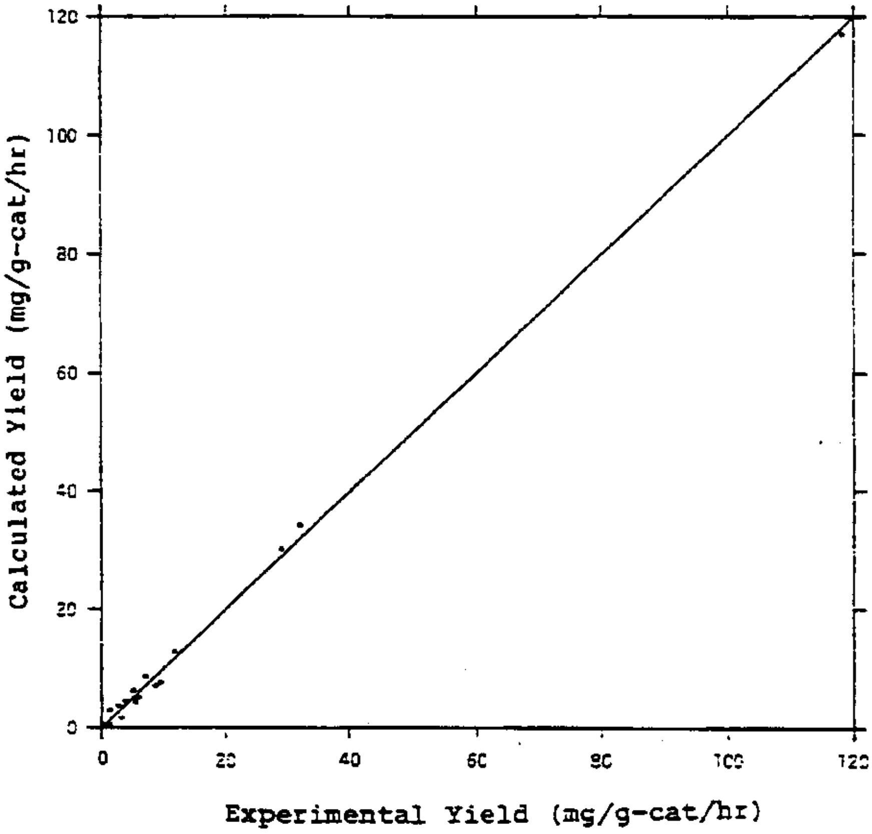


Figure 24. Experimental versus calculated yields using Equation 16C.

187 mg/g-cat/hr, a substantial improvement over the average 29.4 mg/g-cat/hr base point yield, an attempt was made to verify the predicted optimum experimentally. Unfortunately, the yield measured experimentally was only 47.2 mg/g-cat/hr at the optimum conditions.

The inability to confirm the predicted optimum is due to the shortcomings of the equation optimized, rather than the limitations of the physical system. The hydrogen and carbon monoxide conversions were 64.3% and 92.3%, respectively, indicating a high level of catalyst activity. The equation optimized did not account for a limited availability of reactants, or for catalyst selectivity; a more sophisticated model, (theoretical or semi-theoretical), needs to be developed to make a priori estimates of product yields at optimum operating conditions.

A material balance for the optimum verification run appears in Table 11. The composition of the aqueous product appears in Table 12. The organic product distribution is shown in Figure 25. Based on the data available, the best set of operating conditions lie at the intersection of constraints as per factorial experiment C, i.e., 300°C, 200 psig, 0.05 weight fraction

Table 11. Material balance for optimum verification run.

T = 300°C Molar H_2/CO Feed Rate = 1.3
P = 200 psig 10.1 wt% catalyst slurry

Component	Metered Inlet Flow (g/min)	Measured Outlet Flow (g/min)	Comments
H_2	0.28	0.10	64.3% Conversion
CO	2.99	0.23	92.3% Conversion
CO_2	3.22	4.77	48.1% Increase
CH_4	0.95	1.06	11.6% Increase
C_2H_4	0	0.01	
C_2H_6	0	0.09	
C_3H_6	0	0.27	
C_3H_8	0	0.28	
C_4H_8	0	0.26	
C_4H_{10}	0	0.13	
C_5H_{10}	0	0.06	
C_5H_{12}	0	0.08	
Aqueous Liquid	0	0.33	
Organic Liquid	0	0.23	60.3 mg/g-cat/hr Yield Observed
Subtotal	7.44	7.90	6.2% Difference
Slurry Loss	(averaged)	-0.05	60.7g over 20 hours
Total	7.44	7.85	47.2 mg/g-cat/hr Yield Corrected

Table 12. Aqueous liquid product composition for optimum verification run.

Compound	Weight Fraction
Water	.902
Ethanol	.014
n-Propanol	.084
Butanols	Trace