THE TEXAS COMPANY

REFINING DEPARTMENT
TECHNICAL & RESEARCH DIVISION

REPORT ON

YIELDS OF OXYGENATED COMPOUNDS

MONTEBELLO SYNTHESIS RUN NO. 15

Laboratory MONTEBELLO
Report No. TDC-802-4-P
Date July 15, 1947

THE TEXAS COMPANY

MONTEBELLO LABORATORY

REPORT IV

YIELDS OF OXYGENATED COMPOUNDS
MONTEBELLO SYNTHESIS RUN NO. 15

July 28, 1947

STRICTLY CONFIDENTIAL

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HYDROCARBON SYNTHESIS

PARTIAL REPORT NO. 4

Montebello Laboratory
Report Approved July 28, 1947

Experiment TDC. 802
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YIELDS OF OXYGENATED COMPOUNDS MONTEBELLO SYNTHESIS RUN NO. 15

I. INTRODUCTION

The following report presents data on the yields of alcohols, acids and esters obtained in Synthesis Run 15, which was made at Montebello during the period April 7 through April 17, 1947.

II. ORIGINAL DATA

Preliminary operating data on Run 15 were reported on April 18, 1947 and final data are being reported currently in Partial Report No. 5. Data on the oxygenated compounds were reported in Mr. McMillan's letter of June 3, 1947 on "Analysis of Montebello Hydrocol Samples. Experiment TDC 802."

III. YIELD CALCULATIONS

The data reported by Beacon, consisted of Neutralization Numbers and Saponification Numbers of the oil and water products together with Hydroxyl Numbers for the oil products and the percentages boiling below 203°F and 208°F for the water product.

In calculating the yields of oxygenated compounds it was necessary to make several assumptions in order to translate these results into yield data. It was first assumed that all acids were acetic and that all esters were ethyl acetate. Although specific data cannot be cited, it is understood that appreciable quantities of formic acid and formic derivatives have not been found in synthesis products and that these products are largely acetic. There are, however, some quantities of propionic and butyric acids and it is therefore thought that the values calculated on the assumption of acetic are lower than the true values for acids and esters.

The alcohols were assumed to have the composition shown in the memorandum of September 23, 1946 on "A Process for the Recovery of Oxygenated Compounds from Hycosynthesis Products" as follows:

	Weight %
CH_3OH	12.52
C_2H_5OH	46.35
C_3H_7OH	14.51
C_4H_9OH	6.63
$C_5H_{11}OH$	6.63
$C_8H_{17}OH$	13.36

This composition was based on analyses of the Olean product and may not apply to Run 15, but is the only distribution data available.

It was further assumed that 90% of the material boiling below 203°F was alcohol of the above composition.

With these assumptions, the concentrations of the various products were calculated as follows:

Neutralization Number, mg. KOH per gram of sample, times 60/56.1 times 1/10, or Neut. No. x 0.107 equals Wt.% Acetic Acid.

Saponification Number, mg. KOH per gram of sample, times 88.1/56.1 times 1/10, or Sap. No. x 0.157 equals Wt.% Ethyl Acetate.

Hydroxyl Number, mg. KOH per gram of sample, times 62.15/56.1 times 1/10, or Hyd. No. x 0.111 equals Wt.% Alcohols.

From the concentrations of the various constituents calculated in this manner, and the measured quantities of oil and water phases produced, the production rates of the various products

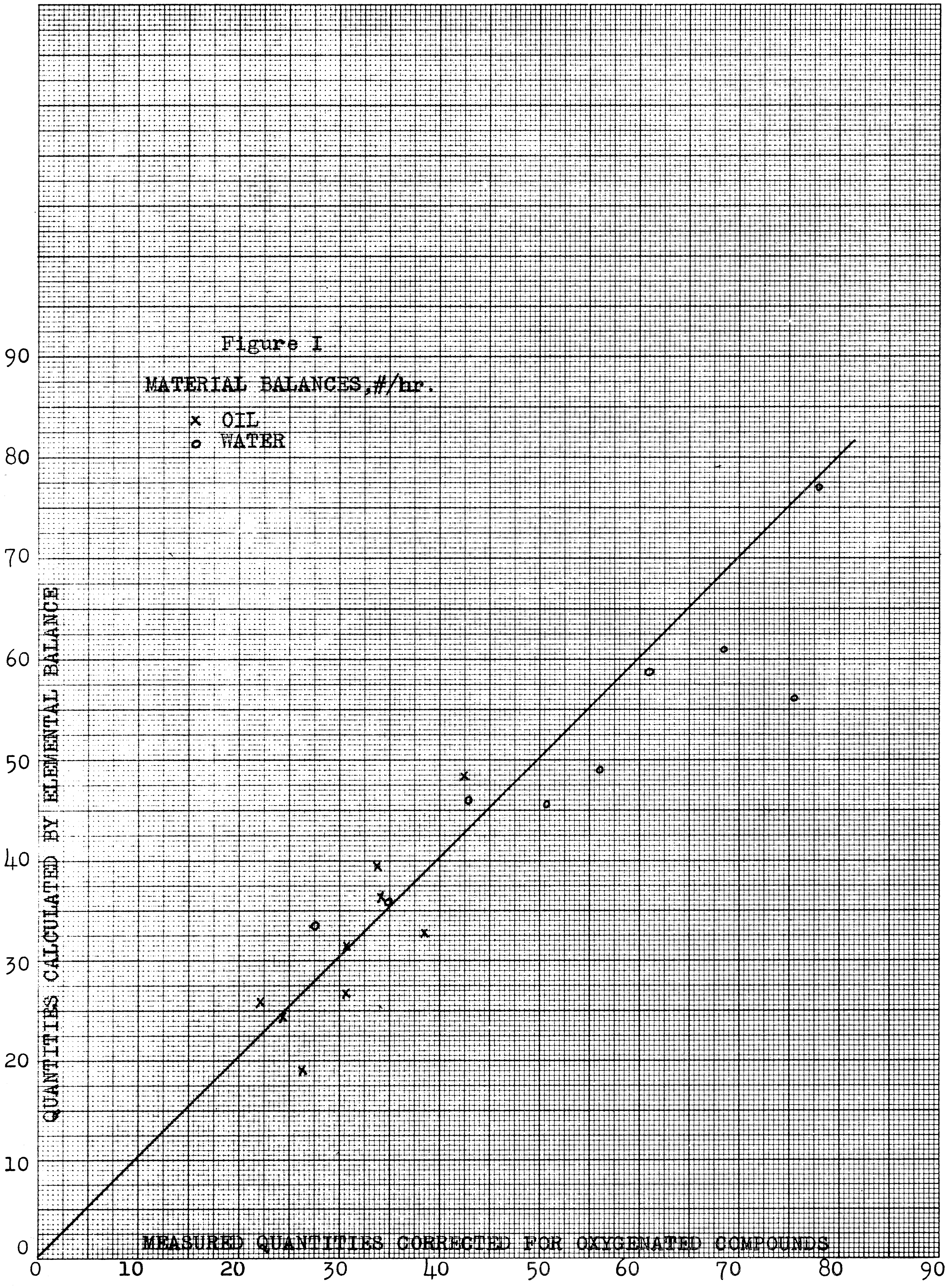

Figure I

MATERIAL BALANCES,#/hr.

were calculated, and the yields in terms of lbs/M Cu. Ft. of hydrogen plus carbon monoxide determined.

Since the primary yield calculations are based on a carbon balance for total hydrocarbon and a hydrogen or oxygen balance for total water, it was of interest to split the yields of oxygenated compounds into hydrocarbon and water fractions and check the primary yield calculations. For this purpose it was assumed that the alcohols were 66% hydrocarbon, the ethyl acetate 54% hydrocarbon, and the acid 44% hydrocarbon. The latter two figures are, of course, ambiguous in that these compounds will require additional hydrogen, but the error is not serious for the present purpose. Calculations made in this manner are given in Table II and a comparison of the yields determined by carbon and hydrogen balance with the yields determined by distributing the oxygenated compounds in the measured quantities of hydrocarbon and water is shown in Figure I. Although there is some tendency for the yields of water determined by hydrogen or oxygen balance to be lower than the values calculated from the measured water yield, the difference is not large and the results are considered satisfactory.

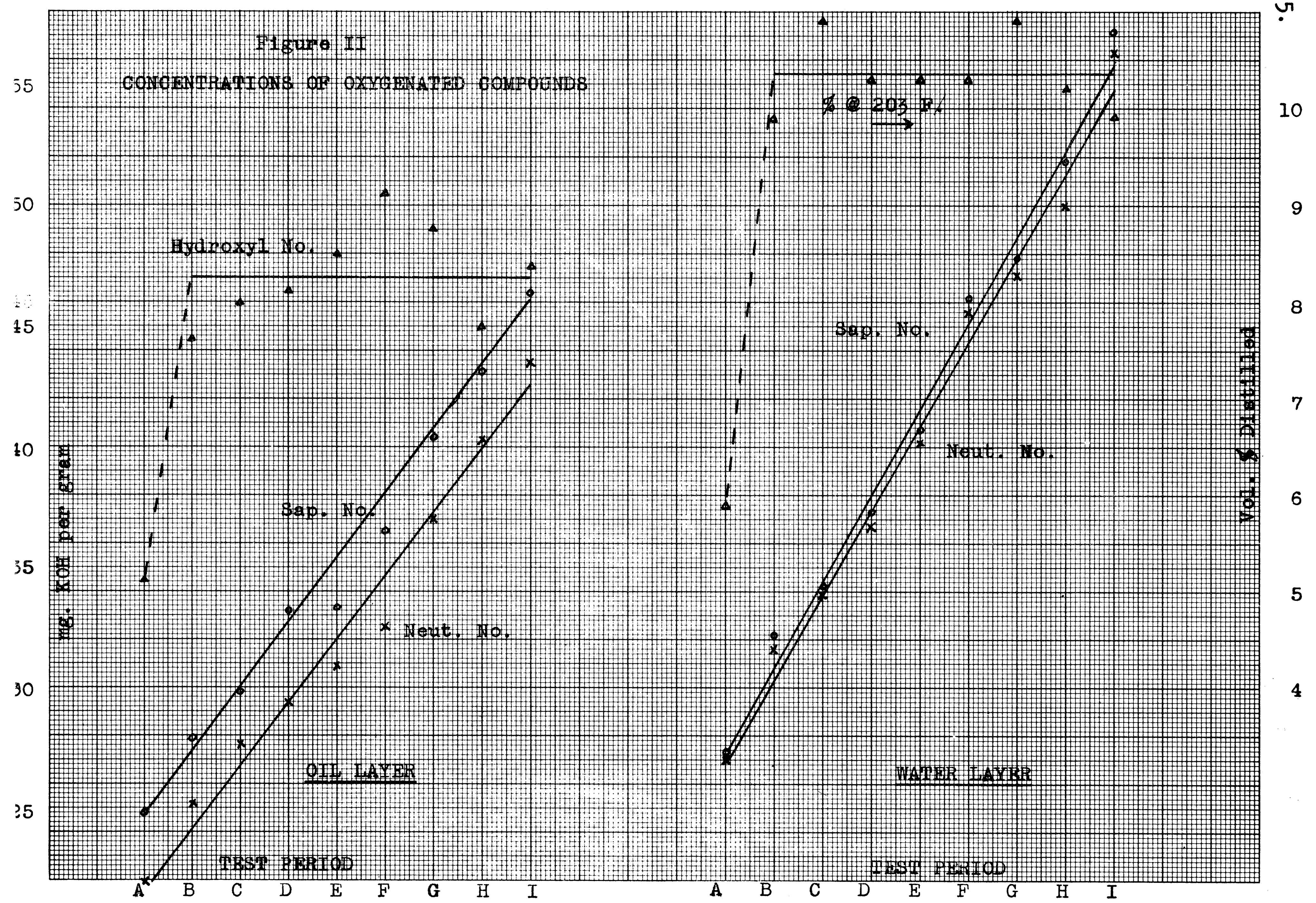

Figure II

CONCENTRATIONS OF OXYGENATED COMPOUNDS

IV. RESULTS AND DISCUSSION

As a test of the consistency of the data, the original results reported by Beacon were plotted against time, or test period, in Figure II. It will be noted that identical trends are shown by the data for the oil and water layers, namely that the neutralization and saponification numbers increased steadily throughout the run and that the hydroxyl numbers and the percentages boiling below 203°F were nearly constant except for the first test period. The discontinuity between the first and the second test periods is so marked that it suggests an error in determination but this can hardly be the case since it is shown by the independently determined hydroxyl number of the oil layer and the percent boiling below 203°F in the water layer. It is therefore believed to be real and to represent either an induction period characteristic of the catalyst or, more probably, a time lag in the composition of the recycle stream to the synthesis unit.

As expected, the difference between the neutralization number and the saponification number (ester content) is higher in the oil product than in the water product, indicating that the esters are concentrated in the oil phase. The nearly constant relationship between the tests on the oil and water phases shows that the distribution of alcohols, acids and esters is approximately constant. It further implies that there was no material shift in the distribution of these compounds with respect to molecular weight, since the distribution coefficients vary with molecular weight.

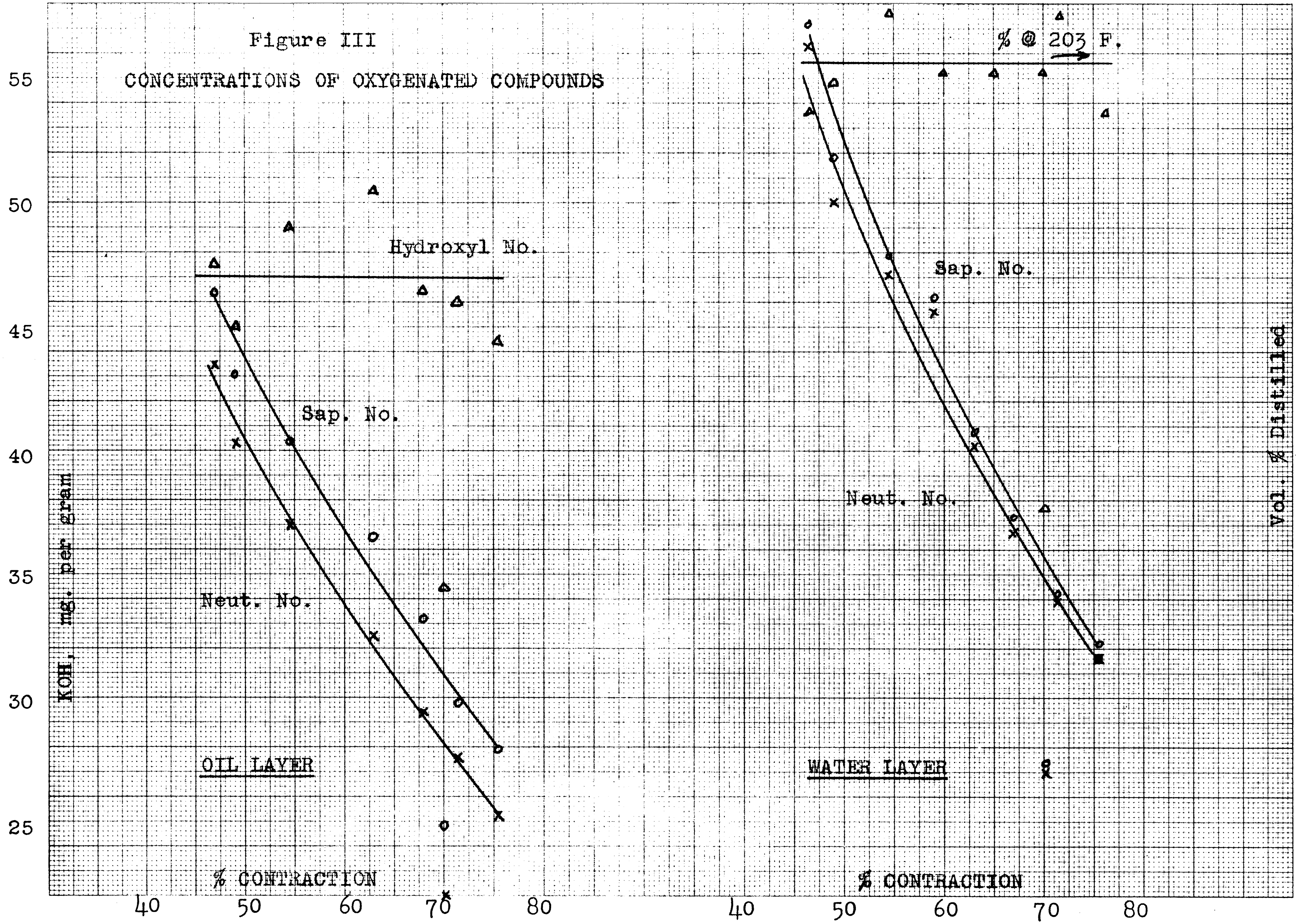

Figure III

CONCENTRATIONS OF OXYGENATED COMPOUNDS

These same test data have been plotted against conversion level, as measured by gas contraction, in Figure III.

Here again there is a marked discontinuity between the data for the first test period, at 70.1% contraction, and the remaining data, which show a consistent trend with conversion level.

It is apparent that there is a large increase in the acidity of the products at low conversion, relative to high conversion, and that the alcohol concentrations are substantially independent of conversion.

Figure IV

TOTAL PRODUCTION OF OXYGENATED COMPOUNDS

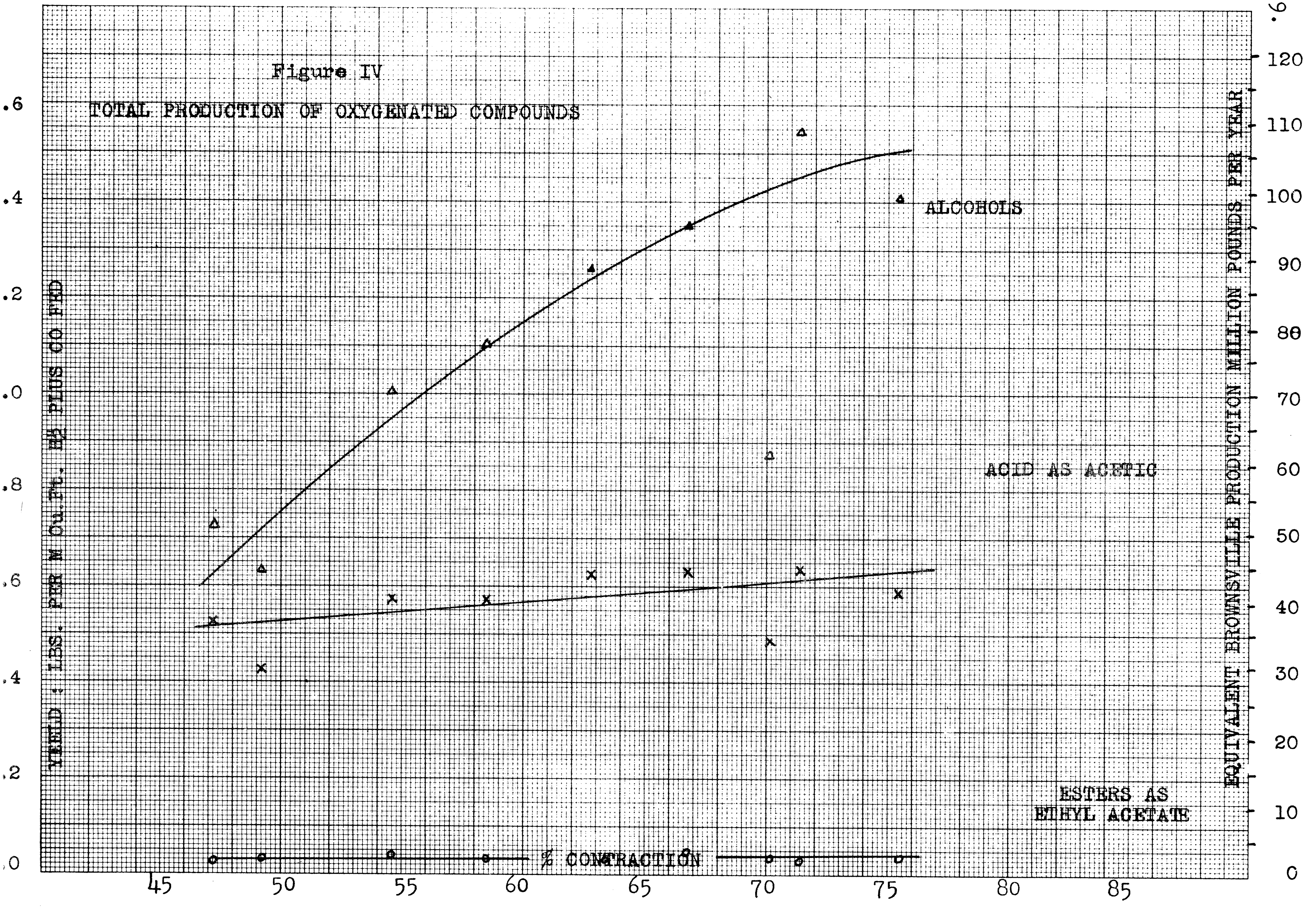

Figure IV is a plot of the yields of alcohols, acids and esters expressed as pounds per thousand cubic feet of hydrogen plus carbon monoxide plotted against conversion as measured by gas contraction. It will be noted that the relationships are reversed as compared with the plots of concentration, the acid and ester yields being substantially constant whereas the alcohol yields increase with conversion. This results from the fact that larger quantities of oil and water are produced at the higher conversion levels, the decline in acid and ester concentrations being offset by the greater liquid yields. The constant alcohol concentrations, on the other hand, result in increased alcohol yields at the higher conversion levels.

The data for the first test period, at 70.1% contraction, again differ markedly from the rest of the data and part of the run.

An auxiliary scale has been shown in this plot giving the production rates for Brownsville corresponding to the Run 15 data, using the Case IV feed rate of 8,888.8 M Cu. Ft. per hour of hydrogen plus carbon monoxide and an operating time of 330 days per year. At the conversion level of the Case IV Design, the indicated production rates in millions of pounds per year are:

	Present Data	Sept. 1946 Estimate
Alcohols	110	121
Esters	3	Not estimated
Acids	41	16
Aldehydes	Not determined	7
Total	154	144

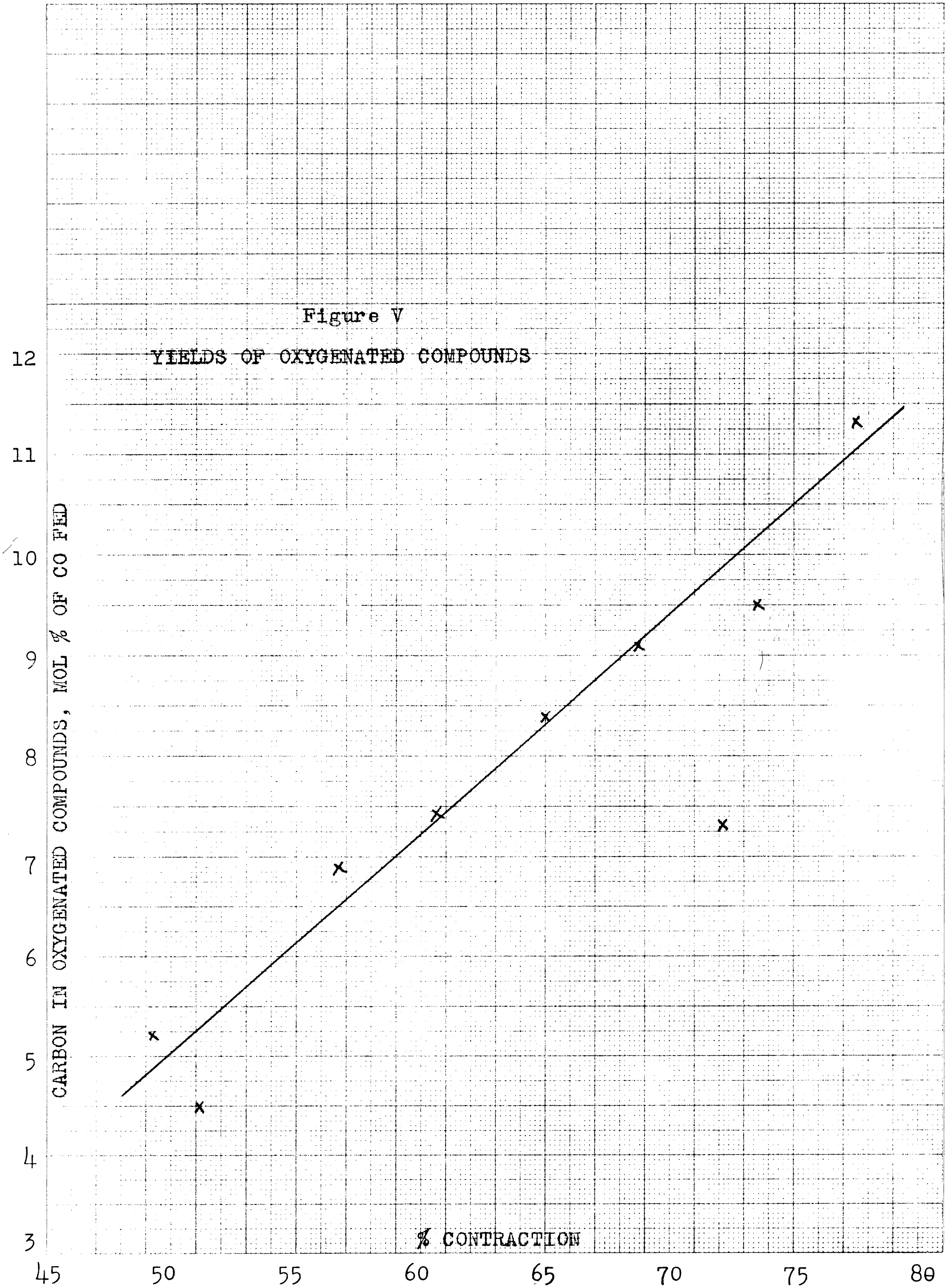
Figure V

YIELDS OF OXYGENATED COMPOUNDS

It is emphasized that the present figures are based on arbitrary assumptions as to the compositions of the alcohol, acid and ester fractions. They should be recalculated at such time as more reliable breakdowns are available.

These same date have also been calculated in terms of the mol % of the carbon in the carbon monoxide fed to the reactor which is converted to oxygenated compounds, and the results plotted in Figure V. Again, with the exception of the data for the first test period, the results are quite consistent with the conversion level.

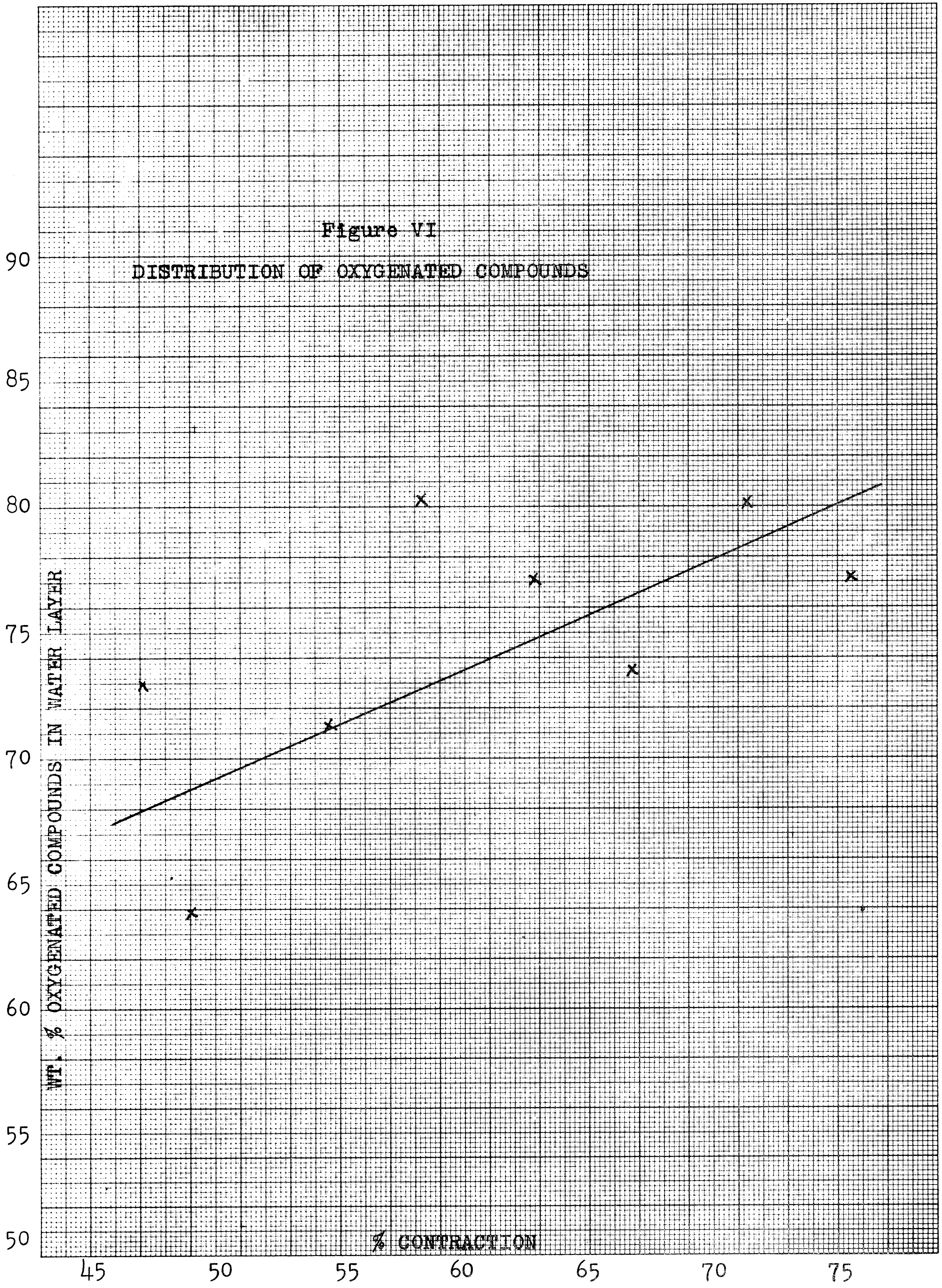

Figure VI

DISTRIBUTION OF OXYGENATED COMPOUNDS

A plot of the weight percent of the total oxygenated compounds found in the water phase, is shown in Figure VI. Although there is some scatter in the data, it is evident that these fractions are largely to be found in the water phase, particularly at high conversion levels.

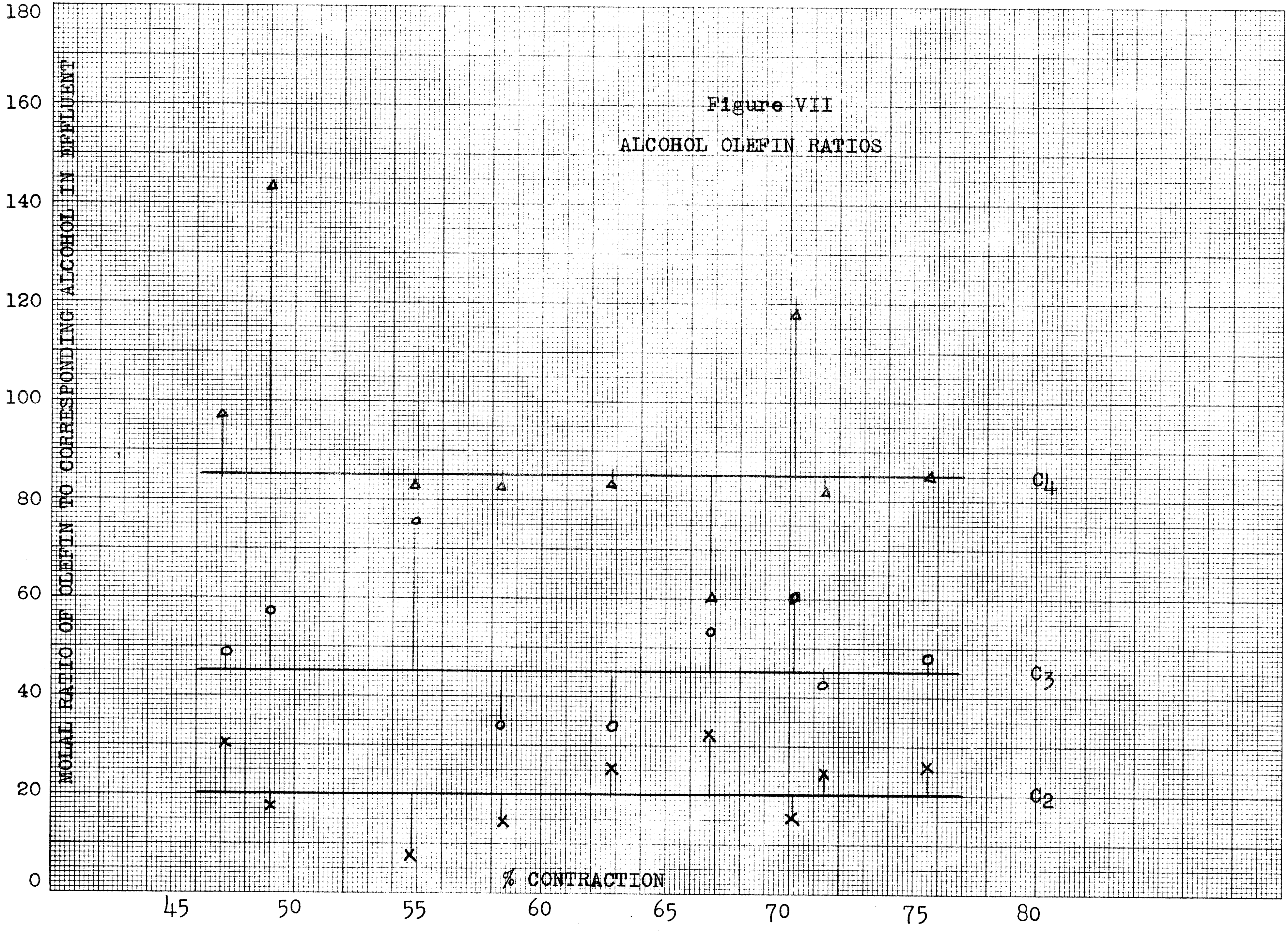
Figure VII
ALCOHOL OLEFIN RATIOS
MOLAL RATIO OF OLEFIN TO CORRESPONDING ALCOHOL IN EFFLUENT
% CONTRACTION
180
160
140
120
100
80
60
40
20
0
45
50
55
60
65
70
75
80
C_4
C_3
C_2

Since it might be expected that the alcohols could be formed by the direct hydration of the olefins present in the reactor system, values for the fraction:

$$\frac{\text{(olefin) (water)}}{\text{(alcohol)}}$$

were calculated for the reactor effluent stream. These calculations gave values which varied about three fold over the conversion range of Run 15 and therefore indicate that this equilibrium was not reached. It was noted, however, that the ratio of olefin to alcohohol concentration was constant throughout as indicated by the data plotted in Figure VII. It is of interest to note that the data for the first test period are in better agreement on this plot than in some of the previous plots, indicating that the time lag in the accumulation of equilibrium olefin content in the recycle system was responsible for the time lag in alcohols production.

Since the distribution between the various alcohols was arbitrarily taken as that shown in the memorandum of Sept. 1946, the numerical ratios shown may not be exact, but the general indication of a constant alcohol / olefin ratio is believed to be established. This, of course, indicates that higher alcohol yields may be obtained by increasing the olefin concentrations either by recycling or by the addition of extraneous olefins, or by changing the operating conditions to increase olefin / paraffin ratios. It has been noted, in comparing the Beacon and Montebello data, that the ethylene / ethane ratio at Beacon is very much lower than at Montebello (about 0.5 vs. 7.5) suggesting that this variable is critical to hydrogen / carbon monoxide ratio and perhaps to catalyst.

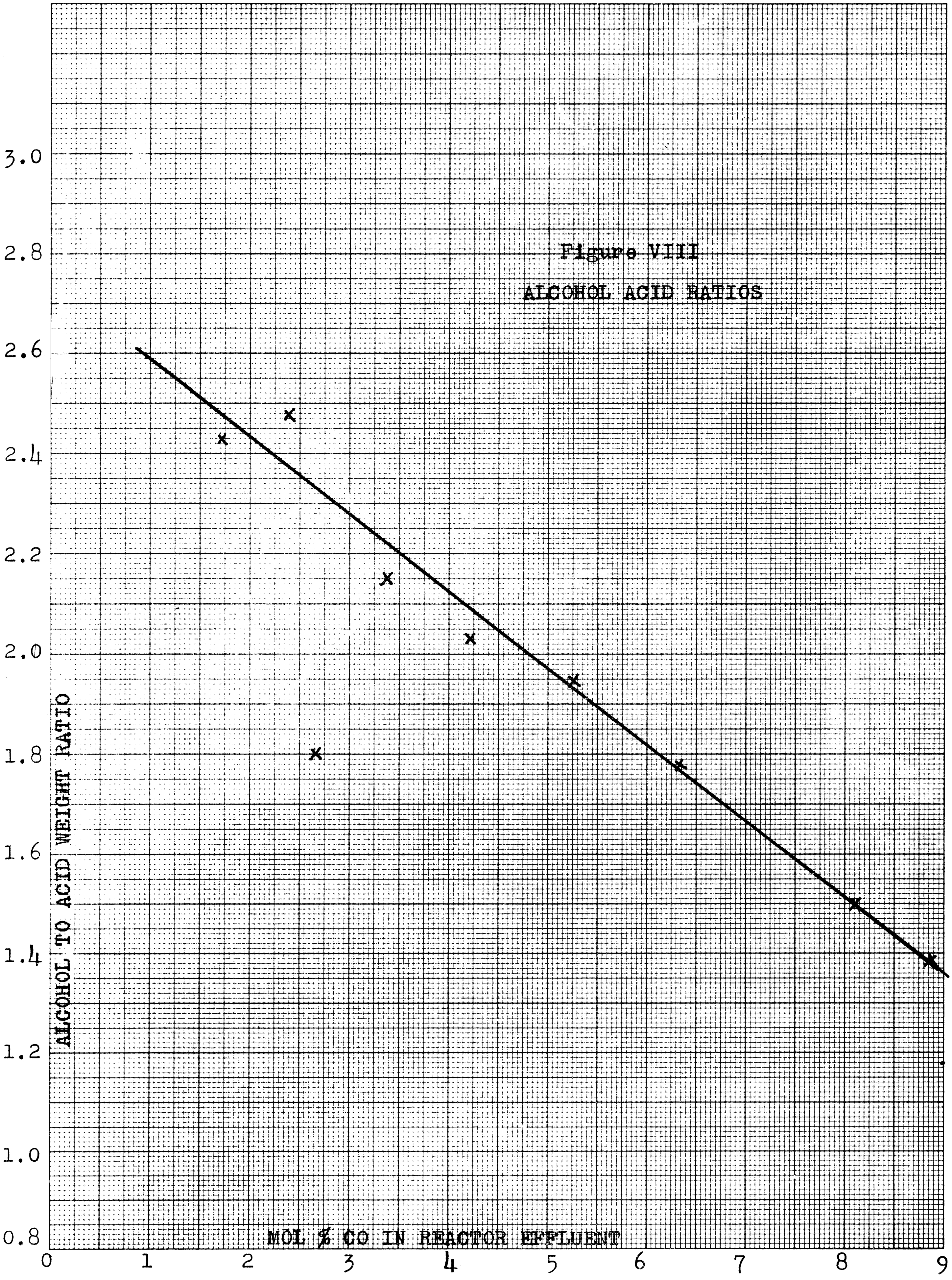
Figure VIII
ALCOHOL ACID RATIOS
ALCOHOL TO ACID WEIGHT RATIO
MOL % CO IN REACTOR EFFLUENT
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
1
2
3
4
5
6
7
8
9

The weight ratio of alcohol / acid is shown in Figure VIII plotted against the carbon monoxide concentration in the reactor effluent. The linear relationship shown suggests that acids are derived from alcohols by the addition of carbon monoxide; and that it should be possible to control this distribution by this means.

It is understood that the acid fraction is predominately acetic and it is indicated that comparatively little methyl alcohol is produced. This may reflect either a greater ease of carbon monoxide addition for methyl alcohol, or it may only indicate that the ethyl alcohol is produced by the hydration of ethylene, a reaction which has no counterpart in methyl alcohol production.

It has been shown previously, that the water gas shift reaction is at least close to equilibrium in this operation and that for this reason, carbon monoxide concentrations decline at a faster rate than hydrogen concentrations so that carbon monoxide concentrations in the reactor effluent are very low, particularly at high conversion. As the ratio of hydrogen to carbon monoxide in the fresh feed is decreased, the disproportionate decrease in carbon monoxide concentration is diminished and higher carbon monoxide concentrations are found in the effluent. If the current indications are correct, this should result in higher acid yields when processing feed stocks having a low ratio of hydrogen to carbon monoxide.

V. CONCLUSIONS

1. As conversion increased, acid and ester concentrations decreased in both water and oil products. Alcohol concentrations were approximately constant.

2. Since the quantity of oil and water product increased with conversion, the rate of production or yield of acid and ester remained approximately constant while the rate of production of alcohol increased.

3. Estimated production rates for Brownsville, based on the present data, are:

	Estimated Production Rates Millions of pounds per year
Alcohols	110
Acids	41
Esters	3
Aldehydes	Not determined
Total Weight	154

Of this total, 80 to 85% are indicated to be in the water phase.

4. The ratio of olefin to alcohol was constant throughout the run, suggesting that alcohols are formed by the hydration of olefins by a mechanism which is independent of water concentration.

5. The ratio of alcohols to acids decreased linearly with the carbon monoxide concentration in the reactor effluent, suggesting that acids are formed by the addition of carbon monoxide to alcohols.

VII. RECOMMENDATIONS

It should be borne in mind that these conclusions are based only on the results of one run and should be confirmed by later data.

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VII. APPENDIX

TABULATION OF DETAILED DATA

	15A	15B	15C	15D	15E	15F	15G	15H	15I
OIL LAYER									
Neut. No	21.8	25.2	27.6	29.4	30.9	32.5	37.0	40.3	43.5
Sap. No	24.8	27.9	29.8	33.2	33.3	36.5	40.4	43.1	46.4
Hydroxyl No	34.5	44.5	46.0	46.5	48.0	50.5	49.0	45.0	47.5
Weight %									
HAC	2.33	2.70	2.95	3.15	3.31	3.48	3.96	4.31	4.66
Et Ac	0.47	0.42	0.35	0.60	0.38	0.63	0.53	0.44	0.46
Alcohols	3.82	4.93	5.11	5.16	5.32	5.61	5.43	5.00	5.27
Total	6.62	8.05	8.41	8.91	9.01	9.72	9.92	9.75	10.39
#/hr oil layer	31.00	37.68	29.03	34.76	26.91	20.51	27.88	25.03	20.04
HAC	0.722	1.017	0.856	1.095	0.891	0.714	1.104	1.079	0.934
Et. Ac	0.146	0.158	0.101	0.208	0.102	0.129	0.148	0.110	0.092
Alcohols	1.184	1.858	1.484	1.794	1.432	1.151	1.514	1.251	1.056
Totals	2.052	3.033	2.441	3.097	2.425	1.994	2.766	2.440	2.082
MCFH H_2+CO	6.142	6.556	5.629	5.788	5.539	5.933	5.969	6.217	6.016
#/MCF									
HAC	0.117	0.156	0.152	0.189	0.161	0.120	0.185	0.174	0.155
Et. Ac	0.024	0.024	0.018	0.036	0.018	0.022	0.025	0.018	0.015
Alcohols	0.192	0.283	0.264	0.310	0.259	0.194	0.254	0.201	0.176
Total	0.334	0.463	0.434	0.535	0.438	0.336	0.464	0.393	0.346

TABULATION OF DETAILED DATA

	15A	15B	15C	15D	15E	15F	15G	15H	15I
WATER LAYER									
Neut. No	27.0	31.6	33.9	36.7	40.2	45.6	47.1	50.0	56.3
Sap. No	27.3	32.2	34.2	37.3	40.7	46.2	47.8	51.8	57.2
Azeo at 95°C	5.9	9.9	10.9	10.3	10.3	10.3	10.9	10.2	9.9
Weight %									
HAC	2.89	3.38	3.63	3.93	4.30	4.88	5.04	5.35	6.03
Et Ac	.05	.09	.05	.09	.08	.09	..11	.28	.17
Alcohols	5.31	8.91	9.81	9.27	9.27	9.27	9.81	9.18	8.91
Total	8.25	12.38	13.49	13.29	13.65	14.24	14.96	14.81	15.11
#/hr water layer	78.39	82.82	73.54	64.92	59.96	54.83	45.72	29.15	37.01
HAC	2.265	2.799	2.670	2.552	2.578	2.676	2.304	1.560	2.232
Et Ac	0.039	0.075	0.037	0.058	0.048	0.049	0.050	0.082	0.063
Alcohols	4.163	7.379	7.214	6.018	5.558	5.412	4.485	2.676	3.298
Total	6.467	10.253	9.921	8.628	8.184	8.137	6.839	4.318	5.593
#/MCF HAC	0.369	0.427	0.474	0.441	0.465	0.451	0.386	0.251	0.371
Et Ac	0.006	0.011	0.007	0.010	0.009	0.008	0.008	0.013	0.010
Alcohols	0.678	1.126	1.282	10.40	1.003	0.912	0.751	0.430	0.548
Total	1.053	1.564	1.763	1.491	1.477	1.371	1.145	0.694	0.929
Combined Product - #/MCF H_2+CO fed to Reactor									
HAC	0.486	0.583	0.626	0.630	0.626	0.571	0.571	0.425	0.526
Et Ac	0.030	0.035	0.025	0.046	0.027	0.030	0.033	0.031	0.025
Alcohols	0.871	1.409	1.546	1.350	1.262	1.106	1.005	0.631	0.724
Total	1.387	2.027	2.197	2.026	1.915	1.707	1.609	1.083	1.275
Wt.% of total in water layer	75.9	77.2	80.2	73.6	77.1	80.3	71.2	63.8	72.9
Alc/Ac.	1.79	2.417	2.470	2.143	2.016	1.927	1.760	1.485	1.376
Contraction, %	70.1	75.5	71.4	66.8	62.8	58.5	54.6	49.1	47.2

TABULATION OF DETAILED DATA

Lbs/hr	15A	15B	15C	15D
HAC	0.486	0.583	0.626	0.630
CH_3OH	0.669	1.1565	1.089	0.978
C_2H_5OH	2.478	4.281	4.032	3.621
C_3H_7OH	0.776	1.340	1.262	1.134
C_4H_9OH	0.355	0.613	0.577	0.518

Mols/hr	CF.	Effl.	CF.	Effl.	CF.	Effl.	CF.	Effl.	CF.
HAC		.00810		.00972		.01043		.01050	
CH_3OH		.0209		.0361		.0340		.0306	
C_2H_5OH		.0539		.0930		.0876		.0787	
C_3H_7OH		.0129		.0223		.0210		.0189	
C_4H_9OH		.0048		.00828		.0078		.0070	
C_2H_4	.745	.872	2.074	2.393	1.846	2.127	2.129	2.540	1.503
C_3H_6	.665	.779	.912	1.652	.770	.887	.836	.998	.473
C_4H_8	.482	.564	.605	.699	.549	.633	.347	.414	.435
H_2O		3.766		4.432		3.155		2.989	
CO_2	9.286	10.357	8.857	9.674	9.242	10.225	7.590	8.644	8.302
CO	8.281	3.027	6.341	0.395	6.228	0.786	6.414	1.162	6.765
Total	50.435	41.654	48.971	39.511	45.911	37.949	44.617	36.898	48.016

(Tabulation continued on next page)

TABULATION OF DETAILED (Continuation)

Lbs/hr	15E	15F	15G	15H	15I
HAC	0.626	0.571	0.571	0.425	0.526
CH_3OH	0.875	0.822	0.751	0.492	0.545
C_2H_5OH	3.240	3.042	2.780	1.820	2.018
C_3H_7OH	1.014	0.948	0.870	0.570	0.630
C_4H_9OH	0.463	0.435	0.398	0.260	0.289

	15E		15F		15G		15H		15I
Mols/hr	Effl.	CF.	Effl.	CF.	Effl.	CF.	Effl.	CF.	Effl.
HAC	.01043		.00952		.00952		.00708		.00877
CH_3OH	.0273		.0257		.0235		.0154		.0170
C_2H_5OH	.0704		.0661		.0604		.0396		.0439
C_3H_7OH	.0169		.0158		.0145		.0095		.0105
C_4H_9OH	.00626		.00588		.00538		.00351		.00390
C_2H_4	1.783	.660	.988	.359	.443	.545	.696	1.051	1.342
C_3H_6	.562	.434	.538	.890	1.099	.426	.544	.405	.517
C_4H_8	.517	.389	.485	.359	.443	.394	.503	.296	.378
H_2O	2.648		2.451		2.009		1.802		1.673
CO_2	9.413	8.268	9.647	8.238	9.715	8.134	9.893	7.563	9.208
CO	1.726	7.532	2.191	7.981	2.696	8.683	3.201	8.866	3.647
Total	40.811	48.721	41.499	49.367	42.464	49.815	43.140	49.023	42.908

TABULATION OF DETAILED DATA

	15A	15B	15C	15D	15E	15F	15G	15H	15I	Total
Measured oil	31.00	37.68	29.03	34.76	26.91	20.51	27.88	25.03	20.04	252.84
Less H_2O in oil										
56% HAC	.404	.570	.479	.613	.499	.400	.618	.604	.523	
46% H_2O	.067	.073	.046	.096	.047	.059	.068	.051	.042	
34% Alc.	.403	.632	.505	.610	.487	.391	.515	.425	.359	
	.874	1.275	1.030	1.319	1.033	.850	1.201	1.080	.924	9.586
Net Oil	30.126	36.405	28.000	33.441	25.877	19.660	26.679	23.950	19.116	
Plus Oil in H_2O										
44% HAC	0.997	1.232	1.175	1.123	1.134	1.177	1.014	.686	.982	
54% Et Ac.	.021	.040	.020	.031	.026	.026	.027	.044	.034	
66% Alc.	2.748	4.870	4.761	3.972	3.668	3.572	2.960	1.766	2.177	
	3.766	6.142	5.956	5.126	4.828	4.775	4.001	2.496	3.193	40.283
Total Oil	33.892	42.547	33.956	38.567	30.705	24.435	30.680	26.446	22.309	283.54
Calc.	39.49	48.40	36.44	32.65	31.51	24.29	26.85	19.03	26.03	284.69
Measured H_2O	78.39	82.82	73.54	64.92	59.96	54.83	45.72	29.15	37.01	526.34
Less Oil to Oil	3.766	6.142	5.956	5.126	4.828	4.775	4.001	2.496	3.193	40.283
Plus H_2O from Oil	.874	1.275	1.030	1.319	1.033	.850	1.201	1.080	.924	9.586
Net Loss	2.892	4.867	4.926	3.807	3.795	3.925	2.800	1.416	2.269	30.697
Net H_2O	75.498	77.953	68.614	61.113	50.165	50.905	42.92	27.734	34.741	495.643
Calc. H_2O	56.02	77.08	60.91	58.82	48.98	45.45	46.17	33.48	35.86	462.77
Total Oxy.-HAC	2.937	3.816	3.526	3.647	3.469	3.390	3.408	2.639	3.166	30.048
Et Ac.	.185	.233	.138	.266	.150	.178	.198	.192	.155	1.695
Alc.	5.347	9.237	8.698	7.812	6.990	6.563	5.999	3.927	4.354	58.927
	8.519	13.286	12.362	11.725	10.609	10.131	9.605	6.758	7.675	90.670
Total HC in Oxy.										
HAC	1.315	1.679	1.552	1.605	1.526	1.491	1.500	1.161	1.393	
Et Ac.	.100	.125	.075	.143	.081	.096	.107	.103	.084	
Alc.	3.529	6.096	5.740	5.156	4.613	4.332	3.959	2.592	2.874	
	4.944	7.900	7.367	6.904	6.220	5.919	5.566	3.856	4.351	
Carbon Content #/hr	4,152	6.771	6.322	5.918	5.331	5.073	4.771	3.305	3.729	
m/hr	.415	.564	.527	.493	.444	.423	.398	.275	.311	
%CO Fed	7.29	11.29	9.50	9.06	8.36	7.37	6.87	4.45	5.17	