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.

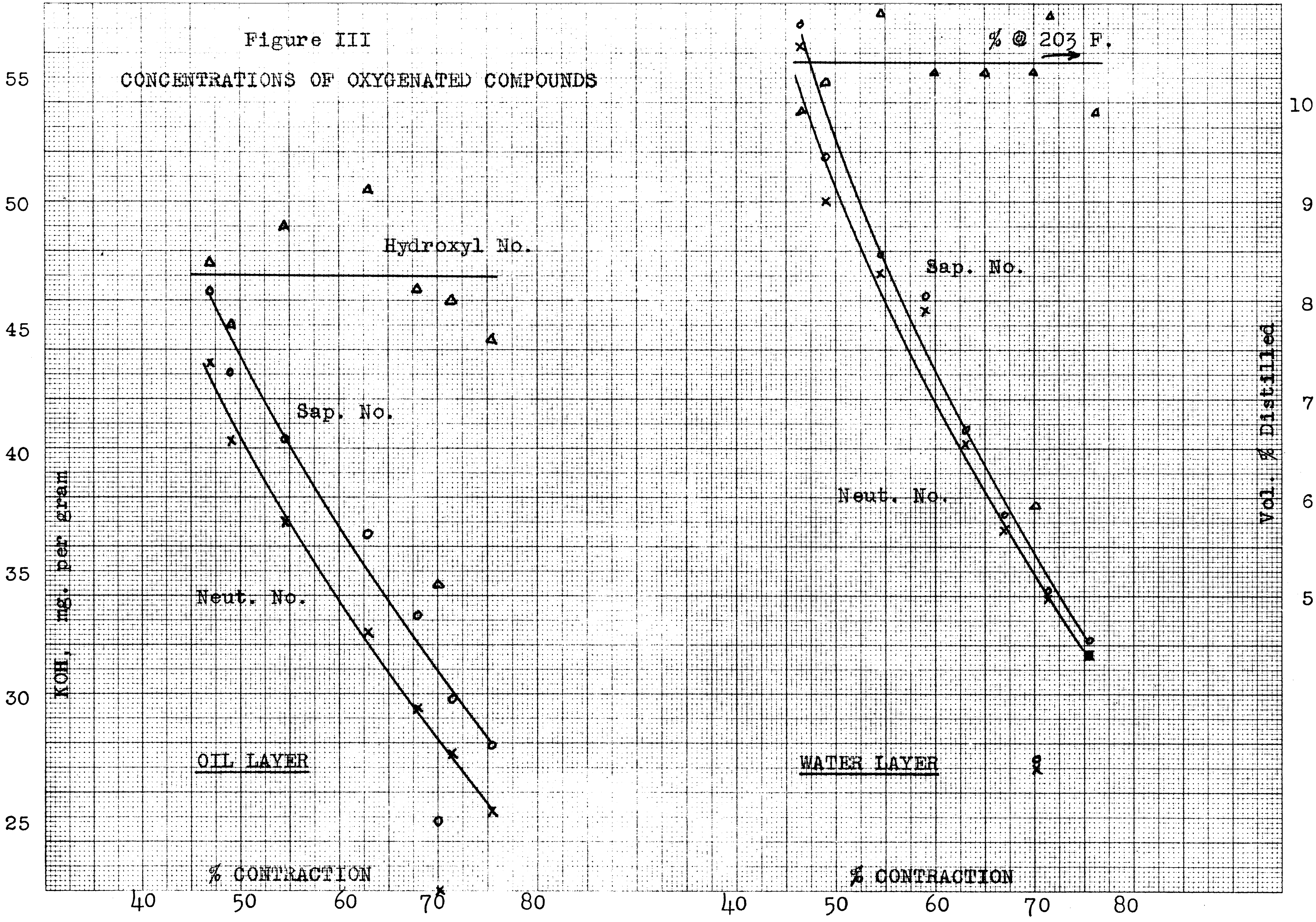

Figure III

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.

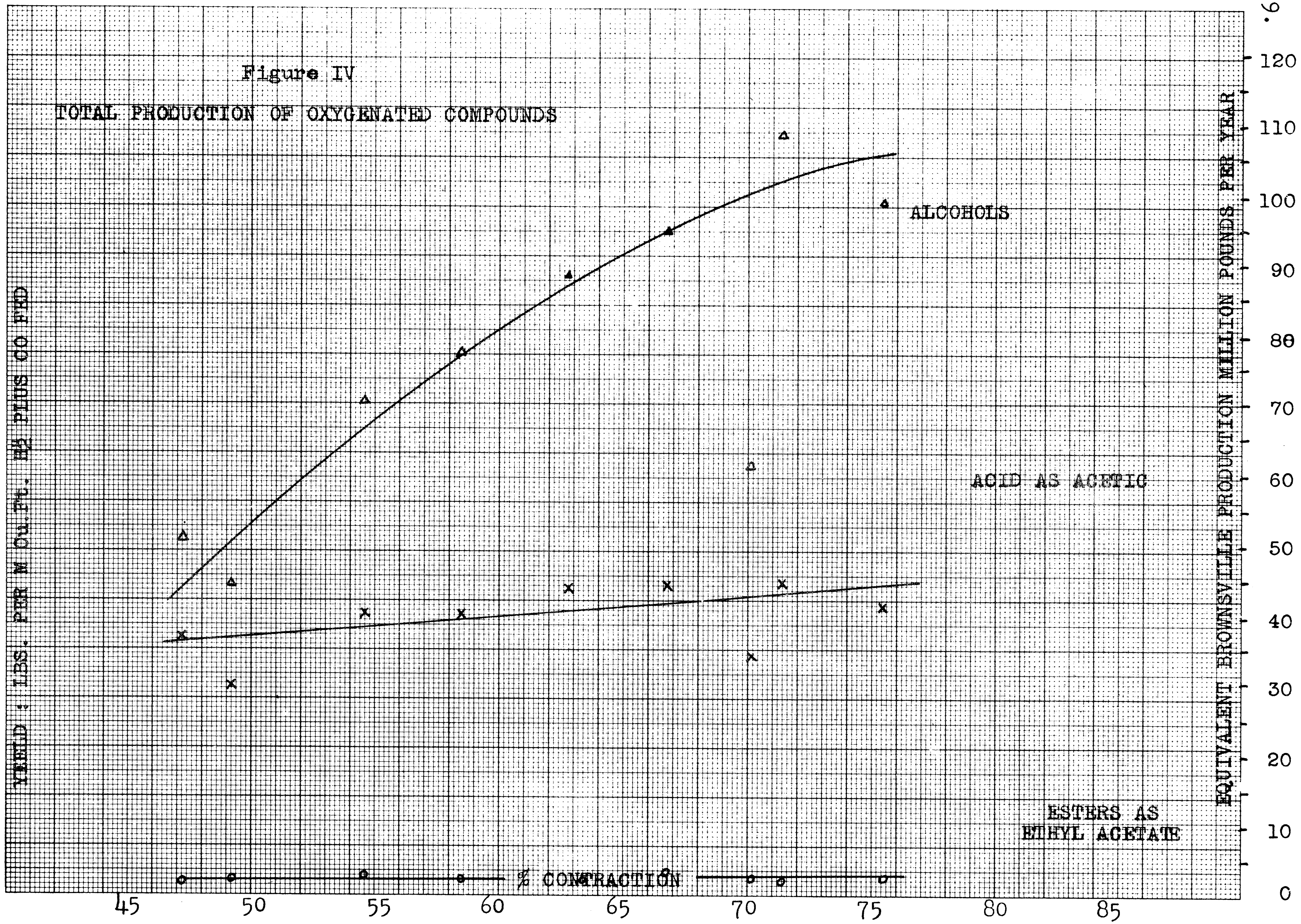
Figure IV
TOTAL PRODUCTION OF OXYGENATED COMPOUNDS
YIELD : LBS. PER M Cu.Ft. H2 PLUS CO FED
.6
.4
.2
.0
.8
.6
.4
.2
.0
EQUIVALENT BROWNSVILLE PRODUCTION MILLION POUNDS PER YEAR
.6
120
110
100
90
80
70
60
50
40
30
20
10
0
ALCOHOLS
ACID AS ACETIC
ESTERS AS
ETHYL ACETATE
% CONTRACTION
45
50
55
60
65
70
75
80
85

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

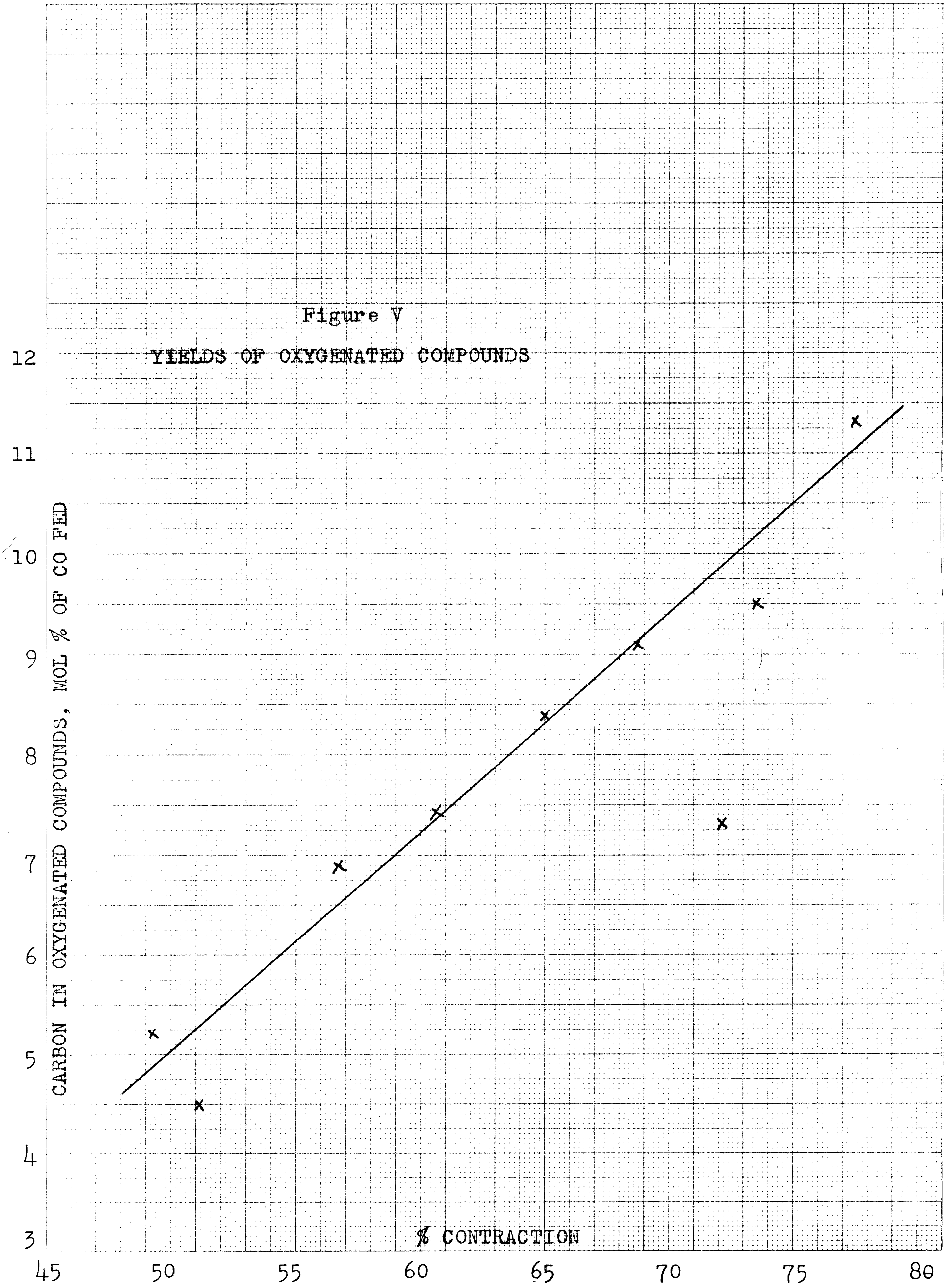

Figure V

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.

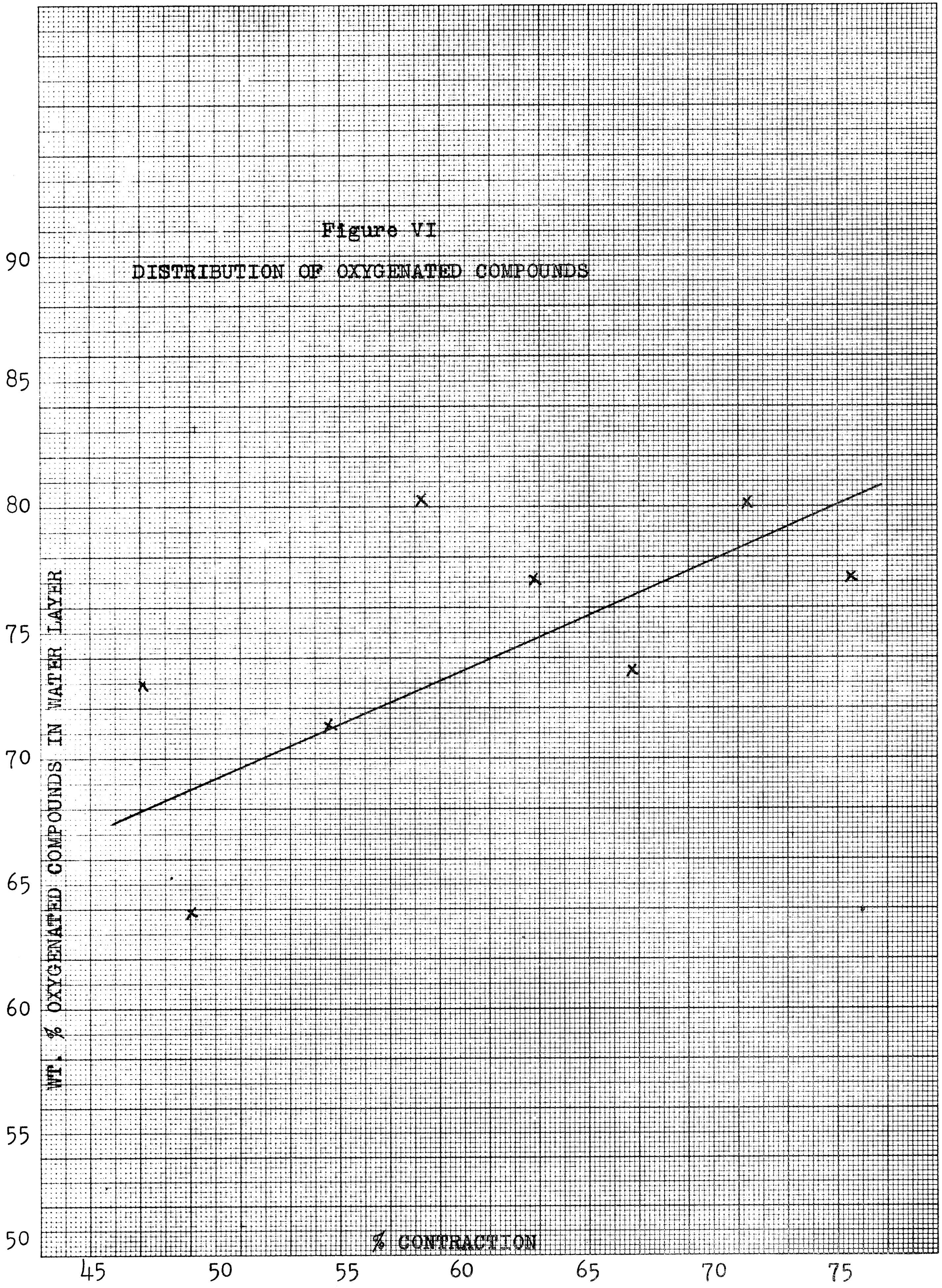

Figure VI

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.

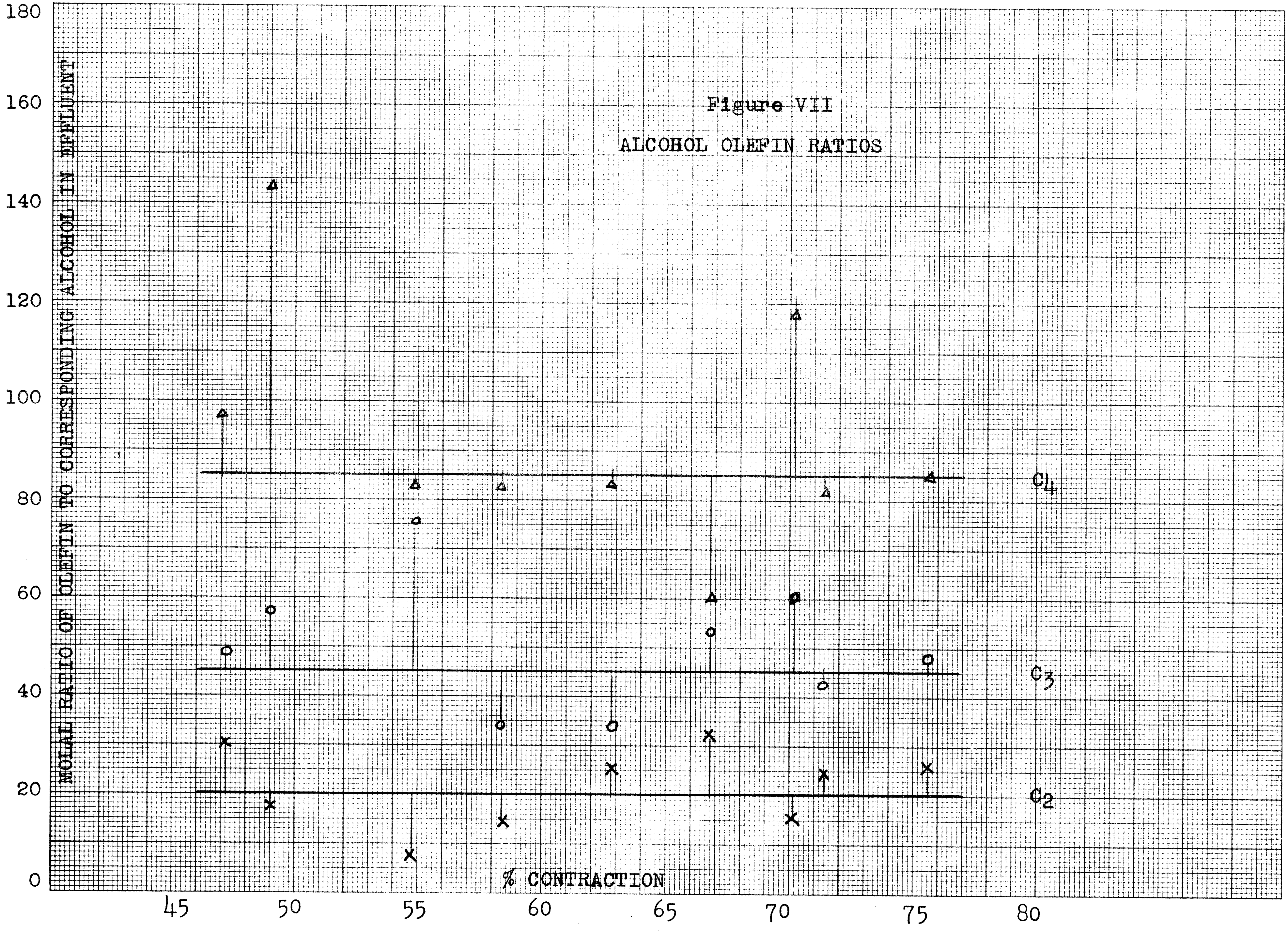

Figure VII

ALCOHOL OLEFIN RATIOS

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:

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

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.

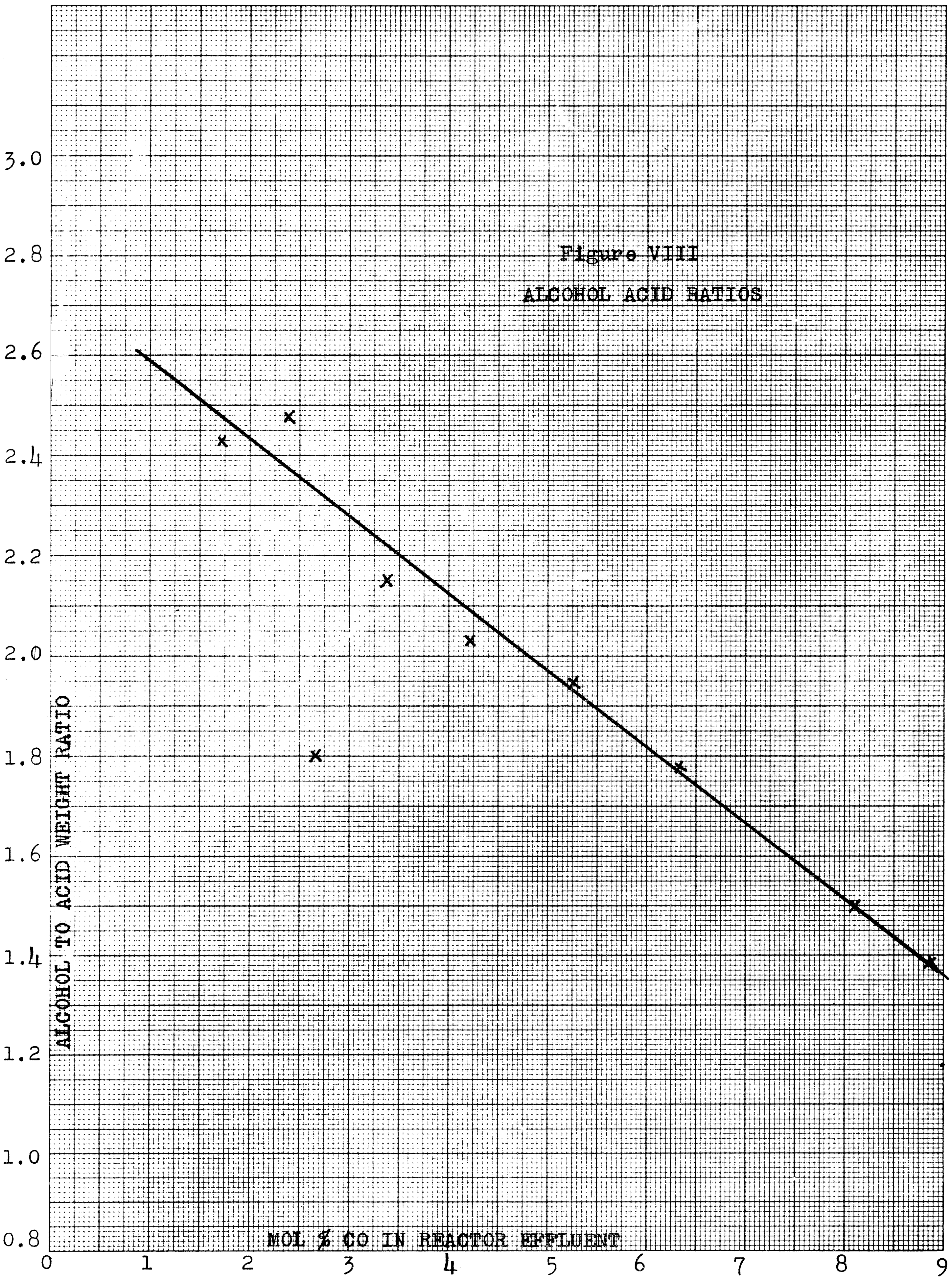

Figure VIII

ALCOHOL ACID RATIOS

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.