

VII. CORRELATIONS

A. Conversions and Distribution of Product

Until further data are obtained for the specific purpose, it is impossible to establish accurately the independent effect of many of the operating variables listed above. As a matter of fact, the magnitude of the effect of some of the factors, within the range studied, may be so small as to be well within the accuracy of the data used.

It is recognized that a more careful study of the individual points might disclose effects that went unnoticed. However, the time available, dictated that only the major effects could be studied at this time.

It has been found that for good catalysts there are certain broad relationships between degree of conversion and product distribution which appear to be independent of the conditions used to attain that degree of conversion. These broad relationships will be presented first.

Measure of degree of Conversion:

It has been found that CO disappearance is a poor index of the process efficiency. The CO disappears very rapidly in all cases even though the % H₂ disappearance is low. When catalyst activity is improved or better operating conditions are used, however, the H₂ disappearance will increase while the CO disappearance, already high, may change very little.

Better measures of degree of conversion are:

1. % Contraction (readily available on the unit)
2. H₂ Disappearance (% of H₂ in FF converted)
3. Water yield
4. Other liquid yield
5. Beyond 60% contraction with a given catalyst the CO₂ content in the product is an indication of conversion. This decreases as conversion increases.

For purpose of this correlation it has been found desirable to use H₂ disappearance expressed as % H₂ in the Fresh Feed as the measure of degree of conversion. This is called "H₂ Conversion" throughout the report.

% Contraction vs. H₂ Conversion:

The % Contraction, expressed as Fresh Feed minus Exit Gas divided by Fresh Feed, correlates reasonably well against H₂ Conversion as shown by Figs. I, IA, IB, IC & ID.

Figure IA is a plot of all the HRI data with the % Contraction calculated directly, that is, without correcting for the CO₂ or CH₄ in the Fresh Feed. (FF in SCFH - Exit Gas in SCFH divided by FF in SCFH). The H Series data correlate extremely well but the 14 Series data all show a broad scattering and a lower contraction for a given H₂ Conversion.

Since the CO₂ and CH₄ content of the Fresh Feed was somewhat higher in these H Series runs than in the others, it was felt that a better correlation could be obtained if the % Contraction were recalculated basis a pure H₂ + CO feed, that is, considering the CO₂ and CH₄ in FF inert and by removing this amount of CO₂ and CH₄ from both the fresh feed and exit gas. This was permissible because there was no evidence of CO₂ or CH₄ disappearance except in Run H-6.

The adjusted % Contractions are plotted against H₂ Conversion on Fig. IB. The deviation is less than that in Fig. IA but again there is a real difference between the 14 Series data (direct from summaries) and the H Series data. Whether this is due to the difference in method of calculation or to differences in operating variables will be considered later. Assuming the data accurate, it does indicate that in the 14 Series more of the H₂ went to gas than in the H Series.

This plot shows graphically and readily, which runs gave high conversions and which were poor. The reasons for the differences in degree of conversion will be considered later.

Fig. IC is a similar plot of % Contraction basis H₂ + CO in Fresh Feed vs. H₂ Conversion for the data supplied us by HRI which were obtained with low H₂/CO in fresh feed. In general, these data correlate well and make possible a family of curves with H₂/CO in the fresh feed as the parameter.

The solid lines of Fig. IC are reproduced on Fig. ID which is a plot of the Stanolind data, most of which were obtained with an H₂/CO

ratio in the fresh feed of 4.0 or more.

In these runs the Fresh Feed contained considerable CO₂ and CH₄ (CO₂/CO in FF = 35 to 55) and except in periods 1, 2, 3 and 14 much of the CO₂ and some of the CH₄ apparently disappeared along with some of the surplus H₂. The theoretical relationship between H₂ Conversion and % Contraction with and without CO₂ reacting is shown below.

<u>H₂/CO</u> <u>in FF</u>	<u>CO₂/CO</u> <u>in FF</u>		<u>% Contraction</u>		
			<u>H₂ Conv.</u>	<u>Theor.*</u>	<u>Actual</u>
1	0	3H ₂ + 3CO → 2CH ₂ + CO ₂ + H ₂ O	100	83.3	75.0
		3H ₂ + 3CO → 1.5CH ₂ + 1.5 H ₂ O + 1.5CO	100	75.0	
2	0	2H ₂ + CO → CH ₂ + H ₂ O	100	100.0	95.0
4	0	4H ₂ + CO → CH ₂ + H ₂ O + 2H ₂	50	60	-
				60 (Adj.)	
4	0.5**	4H ₂ + CO + 0.5CO ₂ → CH ₂ + H ₂ O + 2H ₂ + 0.5CO ₂	50	54.5	
4	0.5	4H ₂ + CO + 0.5CO ₂ → 1.5CH ₂ + 2H ₂ O + 0.5H ₂	87.5	90	

The dotted lines on Fig. 1D are those representing the above theoretical relationships with and without CO₂ reacting. It will be evident that in these runs the % Contraction was in general not as high as would be expected if all CO₂ were to disappear. This may indicate that CO₂ disappearance is not as rapid as CO or that more gaseous product is made when there is a surplus of H₂ in the Fresh Feed. On the other hand the deviations may be due largely to experimental error or an error in our interpretation of the Stanolind data.

Fig. 1 shows the Beacon data compared with the correlation of Figs. 1B and 1C. In this case the fresh feed contained no CO₂ or CH₄ except in the series 14, 15, 18 and 22 but these were adjusted to CO₂ free basis because no net disappearance of CO₂ occurred. (The runs with CO₂ added were all once through).

The following will be noted from Fig. 1.

1. The once through runs with CM&S reduced catalyst (7, 23, 35A and 35B) are a good check on each other and the once through results are only 63% H₂ Conversion and 58% Contraction.

2. H₂ Conversion is increased to 88% and contraction to 78% by

*Assuming all CH₂ is liquid.

**No CO₂ reacted.

recycling with a R/FF of 1.0 (Runs 24, 27 & 8001). The contraction here however was less than experienced by HRI.

3. Lowering the temperature to 600°F. (Run 7005) more than offsets the beneficial effect of recycling at 0.5 R/FF.

4. CM&S unreduced catalyst at 1.0 R/FF results in an H₂ Conv. and % Contraction little better than those obtained without recycling with the same catalyst reduced.

5. Adding CO₂ to the feed increase H₂ Conversion and % Contraction slightly.

6. C.I. Powder is not a suitable catalyst.

7. Limonite with KF is better than Limonite with K₂O but both are very poor when compared to the CM&S reduced catalyst used at the same R/FF in Runs 24 and 27.

These two catalysts apparently convert H₂ faster than the others indicating a tendency to produce more CH₄, more H₂O and a more saturated hydrocarbon fraction.

8. The correlation of Fig. I, that is the line for H₂/CO = 2.0, is satisfactory for the purpose of currently estimating the H₂ conversion from the % contraction which can be determined easily on the unit as the run progresses.

9. Of all the runs included here only five, Runs 7024, 7027, 8001, 8003 and 8004 attained a degree of conversion comparable to those obtained in several runs at Olean.

10. The three runs on unit #8 with special catalysts will be discussed separately under "Effect of Catalysts".

H₂ Conversion vs. CO Conversion

Fig. IIA is a plot of % H₂ in FF Converted vs. % CO in FF Converted for all the HRI data which it will be remembered were obtained with the fresh feed having an H₂/CO = 2.

It will be noted that in general the 14 Series data show a lower CO Conversion for a given H₂ Conversion than the H Series. This may be due partly to the fact that the CO₂ content of the Fresh Feed was higher (6%) in the 14 Series than in the H Series (0.2%).