

Fig. VIB shows the HRI 2/1 Line for methane yield when the $R/FF = 3.0$ compared with the Laboratory B 2/1 data obtained at the R/FF ratios ranging from 2.0 to 4.6. The Fresh Feed compositions (approx. averages) of the HRI and Laboratory B data shown are compared below.

| | <u>HRI</u> | <u>Laboratory B</u> |
|-----------------|------------|---------------------|
| H_2/CO in FF | 2 | 2 |
| CO_2/CO in FF | 19 | 28 |
| CH_4/CO in FF | 11 | 8 |

Some of the Laboratory B data check the HRI Line but in general the methane yield was higher than obtained in the HRI runs perhaps because the CH_4 in the fresh feed was a little less. Since the CO_2 in the FF was greater in the Laboratory B runs, this indicates that CH_4 content of the FF has a more profound effect on CH_4 formation than the CO_2 content.

Fig. VIC is a plot of all the Laboratory A data where the H_2/CO ratio in the fresh feed was 1.0. No sensible correlation has been found for these data but it will be noted that in general the methane yield for a given conversion was as high or higher than in the HRI runs with 2/1 H_2/CO in the feed. Perhaps this is because the recycle ratio was almost always high in the Laboratory A runs. On the other hand, it is indicated that when H_2/CO ratio in the FF is low, factors other than recycle rate may control methane formation.

An inspection of the data where the fresh feed H_2/CO ratio was between 1.0 and 2.0 indicates that within this range methane formation is not a function of H_2/CO ratio in the feed.

With the Stanolind high H_2/CO ratio feeds the methane yield varies all over the lot. (As shown on Fig. IVD) Some being very high for no apparent reason and some being very low. It is believed that these data can be considered unreliable and it cannot be concluded that high H_2/CO ratios in the fresh feed inevitably result in high methane yields.

CH_4 Yield vs. Yield of C_2S

Suspecting that the same factors which effect methane yield might also effect the yield of C_2S , a plot of one vs. the other was made for all the Beacon data in Fig. VII. The relationship is not bad for the CM&S Catalyst but breaks down with catalysts that tend to selectively promote

high methane formation.

A similar plot of the HRI data is shown on Fig. VIIB. In general, the HRI runs produced much more C_2S for a given yield of methane.

Fig. VIIC shows the same relationship for all the Laboratory A and Laboratory B data. If the earlier runs 18, 19 and 20 are discounted there is evidently a relationship for these data which falls between that for Beacon and HRI data. These Laboratory A and B data indicate that the relationship between CH_4 and C_2 yield is independent of H_2/CO ratio in the fresh feed. As this increases from 1 to 2 the CH_4 and C_2 yields both increase.

H_2 Conversion vs. Yield of C_2S

A plot of H_2 Conversion vs. yield of C_2S for the Beacon data is included as Fig. VIID. A similar plot Fig. VIIE is included for the HRI data.

Yield of C_2S vs. Yield of C_3S

Fig. VIII is a plot of the C_2 yield vs. the yield of C_3S for all the data. The accuracy of determination of one or the other or both of these is not too great. Except for the few Beacon runs with special catalysts there is no good explanation for the wide deviation experienced. Run #6 of HRI is apparently in error as to C_3 or C_2 determination. The HRI 15 Series runs may actually have produced a higher ratio of C_3S to C_2S but no reason for this is conjectured. The special catalysts tried at Beacon all have a tendency to produce more C_2S as well as more CH_4 than the others but the production of C_3S was apparently in line with that experienced with other catalysts.

Yield of Methane vs. % Unsats. in C_2S

Fig. IX is a plot of methane yield vs. % unsaturates in C_2 fraction. Apparently the factors which increase methane yield also increase ethane yield since unsaturation of C_2 fraction decreases as methane yield increases.

On this plot points 27 and 1 are out of line probably because the ethane and ethylene were erroneously reversed when the data was reported. The other points out of line are those obtained with cast iron powder catalyst and one of the catalysts made at Beacon. These it seems tend to

selectively saturate the C₂ fraction.

Fig. IXA is a plot of the corresponding factors for the HRI data. The Beacon line of Fig. IX is reproduced for comparison.

Again the relationship appears to hold fairly well except for Runs H5, H6, H25 and part of the 14 Series. Why these particular runs are out of line is not evident.

The % Unsaturation of the C₂ fraction for a given methane yield was considerably lower in the HRI runs than in the Beacon runs. This may be significant but the reason is not obvious. It may be due to consistent error in analyses.

% Unsats. in C₂S vs. % Unsats. in C₃S and % Unsats. in C₄S

Fig. X shows the relationship between unsaturation of C₂ fraction and that of the C₃ fraction for all the runs on which such data was available. Bearing in mind the large possibility of error in the determinations, the relationship is good for all but 4 or 5 pts. In addition, two or three of the points representing runs with special catalysts show a lower % unsaturation for the C₃ fraction than the others.

Figs. XI and XII show similar relationships between the unsaturation of the C₂, C₃ and C₄ fractions.

H₂ Conversion vs. H₂ to H₂O

Fig. XIII shows the relationship between H₂ Conversion vs. % H₂ in FF to H₂O (as measured) for the HRI data, the Beacon data with CM&S reduced catalyst and data from other laboratories on 2/1 feeds.

If we assume that the CO Conversion and the CO₂ yield relationships are correct, then by oxygen balance we can calculate the maximum possible H₂O yield as follows:

For H₂/CO in Feed = 1.0 (400 H₂, 400 CO)

| <u>H₂ Conv.</u> | <u>O in CO UnConv.</u> | <u>O in CO₂</u> | <u>O in H₂O</u> | <u>H₂O/H₂ in FF</u> |
|----------------------------|----------------------------|----------------------------|----------------------------|---|
| 25 | 300 | 48 | 52 | 13.0 |
| 50 | 200 | 108 | 92 | 23.0 |
| 75 | 100 | 189 | 111 | 27.7 |
| 90 | 40 | 256 | 104 | 26.0 |
| 100 | 0 | 312 | 88 | 22.0 |

For H_2/CO in Feed = 1.5 (900 H_2 , 600 CO)

| <u>H_2 Conv.</u> | <u>O in CO UnConv.</u> | <u>O in CO_2</u> | <u>O in H_2O</u> | <u>H_2O/H_2 in FF</u> |
|-------------------------------|----------------------------|-------------------------------|-------------------------------|------------------------------------|
| 25 | 375 | 139.2 | 85.8 | 9.5 |
| 50 | 150 | 313.6 | 136.4 | 15.2 |
| 60 | 76 | 334 | 190 | 21.1 |
| 75 | 40 | 372 | 188 | 20.9 |
| 90 | 16.8 | 290.4 | 292.8 | 32.6 |
| 100 | 0 | 192 | 408 | 45.3 |

For H_2/CO in Feed = 2 (200 H_2 , 100 CO)

| | | | | |
|-----|-----|------|------|------|
| 25 | 50 | 31.2 | 18.8 | 9.4 |
| 50 | 7.5 | 60.4 | 32.1 | 16.1 |
| 60 | 3.3 | 58.8 | 37.9 | 19.0 |
| 75 | 0.5 | 46.0 | 53.5 | 26.8 |
| 90 | 0.3 | 24.4 | 75.3 | 37.7 |
| 100 | 0 | 5.0 | 95.0 | 47.5 |

The latter is shown dotted on Fig. XIII. Since the calculated line includes the oxygen that went to alcohols, it is evident that the reported water yields in many of the runs may be too high.

Similar lines are shown with the Laboratory A data for feeds having H_2/CO ratios of 1 and 1.5 on Fig. XIII A.

On XIII B are shown the Beacon data for the runs other than those made with CM&S reduced catalyst.

H_2 Conversion vs. Yield of Oxygenated Compounds

It was hoped that the H_2O correlation might throw some light on the factors influencing the yield of alcohols and other oxygenated compounds. This is not the case however, and the only data on this item available at this time are those reported by HRI. These have been plotted on Fig. XIV which indicates that the yield of oxygenated compounds increases with H_2 Conversion and decreases as recycle ratio is increased.