

IV. RESULTS AND DISCUSSION

Effect of Catalyst Reduction Conditions

The yields of hydrocarbons and water-soluble chemicals have been plotted as a function of average catalyst age in Figure 1, page 5. The yields of carbon dioxide and water are shown similarly in Figure 2, opposite. It is evident that the yield structures were the same for Runs 63 through 66 when the only variables were the catalyst reduction conditions previously discussed.

H₂/CO in Effluent
 H₂/CO in Combined Feed
 H₂/CO in F.F.

5.628
 1.654
 1.604

TABLE II

EFFECT OF RECYCLE RATIO ON PRODUCT DISTRIBUTION

Run No.	55-2	55-3	55-4	55-5	66-3	66-4	66-5
Periods	L-Q	R-Z	AA-FF	GG-KK	P-T	U-X	Y-CC
Hours	235-379	379-570	570-714	714-834	296-416	416-500	500-619
Recycle Ratio	0.63	0.96	1.01	0.06	1.07	1.05	2.09
Fresh Feed, SCFH	14111	9922	14581	14776	14293	15232	15014
CO ₂ in Total Feed, ^{mol/hr.} mol %	6.23	8.22	11.74	1.57	12.39	11.37	19.78
Space Velocity, v/hr/v	1097	720	1021	1069	1125	1369	2668
Conversion of H ₂ +CO, %	73.03	83.47	76.06	73.64	79.78	72.84	72.28
Selectivity, C ₃ +C ₁ +, %	76.51	75.06	74.86	69.12	75.50	74.83	79.56
Yield of C ₁ +, lbs/MCF H ₂ +CO	9.82	11.19	10.07	8.96	10.63	9.39	9.71
Product Distribution, ^{wt %} mol %	7.65	10.67	8.35	8.26	8.48	6.96	6.36
Weight Per Cent of C ₁ +	23.79	27.61	27.59	28.42	28.56	24.24	22.80
CH ₄	12.93	12.94	12.86	18.00	13.02	13.87	10.73
C ₂ H ₄	6.32	5.95	6.83	7.64	6.28	6.37	6.06
C ₂ H ₆	4.23	6.05	5.45	5.24	5.20	4.93	3.65
C ₁ +C ₂	23.48	24.94	25.14	30.88	24.50	25.17	20.44
C ₃ H ₆	12.46	12.65	11.93	11.91	11.87	11.49	10.37
C ₃ H ₈	1.90	1.70	1.50	1.23	1.32	1.31	1.09
C ₄ H ₈	8.73	8.97	9.53	8.62	9.13	8.75	9.12
C ₄ H ₁₀	4.80	2.51	2.83	3.20	2.81	2.85	2.85
C ₅ + Recovered Oil	34.81	34.42	34.36	33.17	36.43	36.32	41.46
C ₃ +	62.70	60.25	60.15	58.13	61.56	60.72	64.89
Alcohols	10.67	11.59	11.11	9.22	10.52	10.66	10.37
Acids	3.15	3.22	3.60	1.77	3.42	3.45	4.30
Water Soluble Chemicals	13.82	14.81	14.71	10.99	13.94	14.11	14.67
Yield Basis Brownsville Design Feed Rate, 9488 MCFH H₂+CO BPD							
Liquid Hydrocarbons	4336	5051	4480	3814	4988	4301	4854
Alcohols	731	915	772	582	766	688	682
Acids	215	254	250	112	249	223	283
Total Liquid	5282	6220	5502	4508	6003	5212	5819

Effect of Recycle/Fresh Feed Ratio

The data from Run 55 also have been shown in Figures 1 and 2. During this run there were two periods of low recycle ratio, Periods 55-2 with 0.4/1 ratio and Period 55-5 with no recycle gas except the bleed gas through the pressure taps. This flow corresponds to a 0.06/1 ratio. Otherwise the conditions were similar to those of Run 63 through 66, made with a recycle ratio of 1/1 except for Period 66-5, made with 2/1 recycle ratio.

It can be seen in Figure 2 that the H_2/CO ratio in the total feed stream tended to be constant at about 2.2/1. Since the H_2/CO ratio in the fresh feed was fixed at about 1.65 to 1, the composition of recycle gas changed sufficiently, when the recycle ratio was raised from 1/1 to 2/1, to maintain the constant H_2/CO ratio in the total feed. A similar change in the opposite direction took place when the recycle ratio was decreased. Of course, when the recycle flow was practically stopped, then the total feed composition became almost the same as the fresh feed.

The period of lower recycle ratio in Run 55 showed lower yields of C_3 and heavier hydrocarbons, lower yields of water-soluble chemicals, lower yields of water, higher yields of C_1 and C_2 hydrocarbons, and higher yields of CO_2 . The effect of raising the recycle ratio in Run 66 was to increase the yields of C_3 and heavier hydrocarbons (even though the catalyst volume was less). The yields of CO_2 were decreased, but there was only a slight effect on the yield of other products.

Additional data on the effects of recycle ratio are shown in Table II, opposite. The tabulated data shown in more detail the same effects of recycle ratio shown graphically in Figures 1 and 2.

In summary, higher recycle/fresh feed ratio was beneficial in the range of 0.06/1 to 2.0/1. The yields of useful liquid product increased with recycle ratio, and the yields of methane and CO₂ were suppressed. Since the selectivity and conversion decrease with catalyst age, and the CO₂ yields increase, the beneficial effects of increasing the recycle ratio may be more pronounced as the catalyst gets older.

Effect of Addition of Potassium Carbonate

The addition of anhydrous potassium carbonate during period 65-J had no apparent effect on the synthesis reaction.