IV. RESULTS AND DISCUSSION

A. Changes in Yield with Time

Yields and operating conditions are summarized in the opposite Table I. It is evident that the yield declined very rapidly from the first two test periods reaching a substantially steady condition after about 100 hours on stream. From this point onward there was undoubtedly some further decline in yield but over the interval 104 to 257 hours average catalyst age where the conditions were held constant, the effect is too small to be measured by the present data. The value of catalyst age used here is calculated from the catalyst addition and the loss rates on the assumption that the age of the catalyst lost at any time is the average age of all the catalyst in the reactor.

This very sharp initial decline followed by a long period of relatively constant yield coincides with a very rapid initial change in catalyst composition and is also followed by a long period of relatively constant composition.

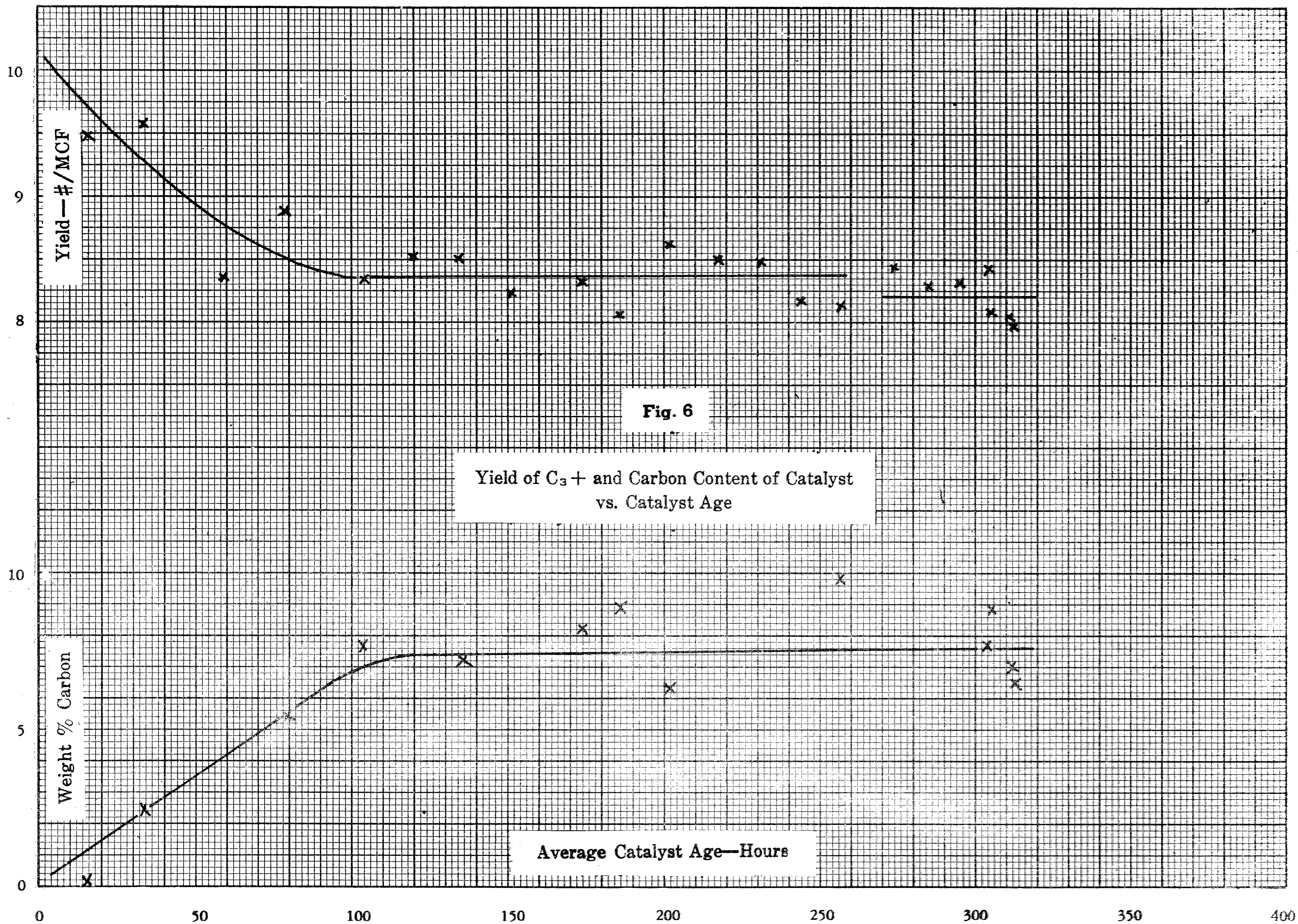
Fig. 6
Yield of C_3+ and Carbon Content of Catalyst vs. Catalyst Age
Yield—#/MCF
10
9
8
Weight % Carbon
10
5
0
Average Catalyst Age—Hours
0
50
100
150
200
250
300
350
400

These changes are shown in the opposite Figure 6 where yield and the carbon content of the catalyst have been plotted against age. The catalyst test data are detailed in Table II, following. It should not be inferred from the plot in Figure 6 that the change in yield is necessarily a result of the change in carbon content since several other catalyst properties show similar changes during this period.

The point of importance is that the catalyst required about 100 hours to adjust itself to the operating conditions used in this run. During this period yields declined rapidly and then reached a substantially steady state. This means that yield data obtained during the conditioning period, the first 100 hours in this run, are not representative of stable operation and should therefore be disregarded.

It also means that the rate of catalyst addition used in this run was unnecessarily high and that the rate of addition could have been materially reduced without serious loss in yield. This is confirmed by the Stanolind data obtained on Alan Wood catalyst in their 8-inch reactor, Run D-201-29, which are given in Table III, page 17. These data show the same very rapid initial decline followed by a nearly constant operation over a very long period. Since little catalyst was added during this run, the time on stream is nearly identical with the catalyst age, reaching a value of 695 hours at the end of the run.

Some idea of the economics of catalyst addition rate can be obtained from the Stanolind decline rate. If it is assumed that the v./hr./v. at Brownsville is 1000, the catalyst density

TABLE II
CATALYST TEST DATA - RUN 49

Test Period	Average Age-Hrs.	Wt. % Carbon	Wt.% Fe	NH_3 Value	Particle Density	X-Ray Diffraction - % Fe_2OC_9	Fe_3O_4	Fe
A	16	0.22	88.9	0.4	4.7	--	--	100
B	34	2.41	68.8	2.2	4.4	40	55	5
C	59			2.4	4.3			
D	79	5.4	66.1	7	4.3	30	65	5
E	104	7.7		21	4.4			
F	120			12	4.3			
G	135	7.2	67.8	8	4.4	40	55	5
H	151			16	4.3			
I	174	9.5/6.6	66.6	9	4.1	40	55	5
J	180	5.6		10	--			
K	186	8.9		12	4.3			
L	202	6.3		26	4.3			
M	217			15	4.2			
N	231			18	4.3			
O	244			19	4.4			
P	257	9.9		14	4.3			
Q	274			12	3.8			
R	285			10	4.3			
S	295			22	4.0			
T	304	7.7		24	4.0			
U	312	6.5		17	4.2			
V	305	8.9		4	4.2			
W	312	7.0		21	4.2			
X	316	9.8		15	3.8			
Y	301			25	4.1			

TABLE III
SUMMARY OF DATA - STANOLIND RUN D-201-29

400 psig, 650°F., Alan Wood

Test Period	Hours on Stream Avg. Cat. Age	Rates MCFH Feed	Rates MCFH Recycle	Inlet Vel. ft/sec.	Bed Depth Ft.	Space Vel. v/hr/v	Conversion % of H_2+CO Fed	Selectivity C_3+ ÷ C_1+	Yield of C_3+ #/MCF(1)	Chemicals from water #/MCF
1	21	3.62	3.75	0.47	12.5	851	90.0	80.1	9.95	1.00
2	47	3.60	3.68	0.46	12.3	866	86.6	88.0	9.63	1.08
3	119	3.62	3.64	0.46	11.8	922	87.9	72.7	8.71	1.03
4	191	3.63	3.58	0.46	11.8	926	82.4	79.1	8.54	1.18
5	263	3.65	3.66	0.48	11.0	1003	79.7	78.3	8.49	1.18
6	349	3.54	3.61	0.55	11.8	904	80.1	78.4	8.54	1.24
7	456	3.60	3.64	0.51	11.8	906	80.4	78.4	8.48	1.15
8	481	3.62	3.60	0.45	11.5	946	79.0	78.5	8.31	1.12
9	652	3.59	3.60	0.46	11.3	966	77.5	78.1	7.91	1.18
10	695	3.61	3.64	0.47	11.8	922	81.8	76.4	8.02	1.15

TABLE IV

ECONOMICS OF CATALYST REPLACEMENT RATE

Data from Stanolind Run D-201-29

Average of Periods 5 and 6 - 306 Hours Average Age

Gasoline	4,224 Bbl/Day	$5.04/Bbl	$21,289
Gas Oil	491	3.25	1,596
Waxy Bottoms	347	1.30	451
Polymer Tar	112	1.30	146
Hydrocarbons	5,174		$23,482
Chemicals from			
Gas	100	$10.00	
Oil	113		
Water	803		
	1,016		10,160
Total Products	6,190		$33,642

Average of Periods 9 and 10 - 673 Hours Average Age

Gasoline	4,085 Bbl/Day	$5.04/Bbl	$20,588
Gas Oil	430	3.25	1,398
Waxy Bottoms	303	1.30	394
Polymer Tar	102	1.30	133
Hydrocarbons	4,920		$22,513
Chemicals from			
Gas	91		
Oil	160		
Water	786		
	1,037	$10.00	10,370
Total Products	5,957		$32,883

is 125 lbs. per cubic foot and the fresh feed rate is 9488 MCFH of H2 + CO; catalyst inventory will be 600 tons. Comparing the average results of Periods 5 and 6 (corresponding to a catalyst age of 306 hours) with the average of Periods 9 and 10 (corresponding to a catalyst age of 673 hours) catalyst addition rates will be 47 and 21 tons per day respectively.

The equivalent Brownsville production rates for these periods have been calculated by the method described in the Appendix, and are listed in the opposite Table IV together with the values of the various products. The price used for the chemicals fraction is higher than the minimum guarantee carried in the Brownsville contracts but is lower than the expected return and is believed to represent a reasonable value.

This tabulation shows that an increase in catalyst addition rate from 21 to 47 tons per day will increase the value of the products at Brownsville by $759. This makes the value of the additional 26 tons of catalyst to Brownsville, $29 per ton or substantially equivalent to the cost of the catalyst.

A firm conclusion as to the economics of catalyst replacement rate should not be reached on the basis of the present very limited data, but it is clear that replacement rate is not a matter of great importance over the range of 300 to 700 hours age under the Brownsville conditions.

B. Effect of Space Velocity

Since the cost of a synthesis reactor is determined by its volume and is independent of the density of the catalyst used, throughput is properly expressed in terms of the volume of feed per unit of time per unit of catalyst volume or cubic feet of fresh feed per hour per cubic foot of catalyst. This is inconvenient because the volume of catalyst in an operating reactor is considerably more difficult to measure than the weight.

There is also evidence from pyrites runs at Montebello that conversion is actually a function of catalyst volume and independent of catalyst weight. Run 22[1], for example, showed the following results:

Test Period	Hours on Stream	Catalyst Bed Depth Ft.	Catalyst Bed Density #/CF	Fresh Feed $H_2 + CO$ v/hr/w	Fresh Feed $H_2 + CO$ v/hr/v	Conversion %	Yield of C_3+ #/MCF
A	24	3	98	29	2820	52	7.2
B	48	3	84	38	3160	61	7.2
C	72	7	90	24	2160	67	7.5
D	96	18	34	21	725	86	9.9
E	120	22	29	20	580	87	9.1
F	144	14	36	21	780	92	7.9
G	168	29	24	19	460	89	10.4
H	192	18	10	38	570	89	8.5
I	216	30	8	59	470	87	9.0
J	240	30	14	34	470	92	8.8

Conditions were unstable during this run and the results are therefore somewhat erratic but it is evident from this tabulation that the disintegration of this catalyst, which took place at about 75 hours, resulted in a three-fold change in v/hr/v, very little change in v/hr/w, and a substantial increase in both conversion and yield. This increase in yield can be considered to result either from a change in the specific activity of the catalyst or from the change in volume. Since the current data on the Alan Wood catalysts, obtained under stable conditions, show changes in yield with space velocity which are comparable to those

[1] Partial Report No. 13, Experiment No. TDC-802.

TABLE V
YIELD vs. SPACE VELOCITY

Run Number	46-1	46-2	46-3	45-1	49-2	49-1	29-3/6
Hours on Stream	108 204	204 369	369 537	96 299	341 497	104 341	119 349
Avg. Cat. Age, Hours	168	183	162	140	298	198	231
Space Vel., v/hr/v.	2825	2314	2178	1646	1215	1072	939
YIELD BASIS BROWNSVILLE, BBL/DAY							
Gasoline	2863	3362	3562	3844	4534	4721	4568 (1)
Gas Oil	363	449	454	443	628	629	496
Fuel Oil	534	467	446	462	495	448	480
Chemicals from Water	467	527	541	488	620	588	776
Total	4227	4805	5003	5237	6277	6386	6320
Conversion, % of H_2+CO fed	58.4	64.6	67.5	71.4	76.4	78.0	85.1
Selectivity, % C_3+ ÷ C_1+	80.1	82.3	81.9	77.5	82.8	82.3	77.1
C_3+ #/MCF of H_2+CO fed	5.96	6.46	6.64	7.07	8.21	8.37	8.57

(1) Includes 214 Bbls. Water Soluble Chemicals Scrubbed from Gas and Oil

observed in Run 22, there is a strong presumption that the disintegration of the catalyst was unimportant and that the essential change was the increase in catalyst volume.

The present data on the relation of yield to space velocity are given in the opposite Table V. Run 46 was made on Alan Wood catalyst under the original Brownsville design conditions: 400 psig, 650°F., 24 MCFH/sq. ft., and a bed depth of 8 to 10 feet. Run 49 was made under the same conditions except that the bed depth was increased to 20 feet. The Stanolind Run 201-29 was made under conditions similar to those used in Montebello Run 49 except that both bed depth and feed rate were one half those of Run 49. Run 45 was the first run made with the 12-inch reactor at Montebello and was made on a mill scale catalyst.

These yield data are plotted against space velocity in **Figure 7, following,** which shows a linear relationship for the Alan Wood data. The Stanolind point falls slightly below the Montebello line but is considered an excellent check in view of the large differences in bed depth, linear velocity, and the particle size of the catalyst. This implies that these are factors of small importance over the range covered.

A comparison of periods 49-1 and 49-2 which were made with recycle ratios of 1/1 and 1.5/1 shows no effect except for a slight increase in v/hr./v at the higher recycle ratio and a corresponding decrease in yield. This increase in v/hr./v resulted from the increase in inlet velocity from 1.01 to 1.37 ft./second which increased carryover and reduced the bed depth

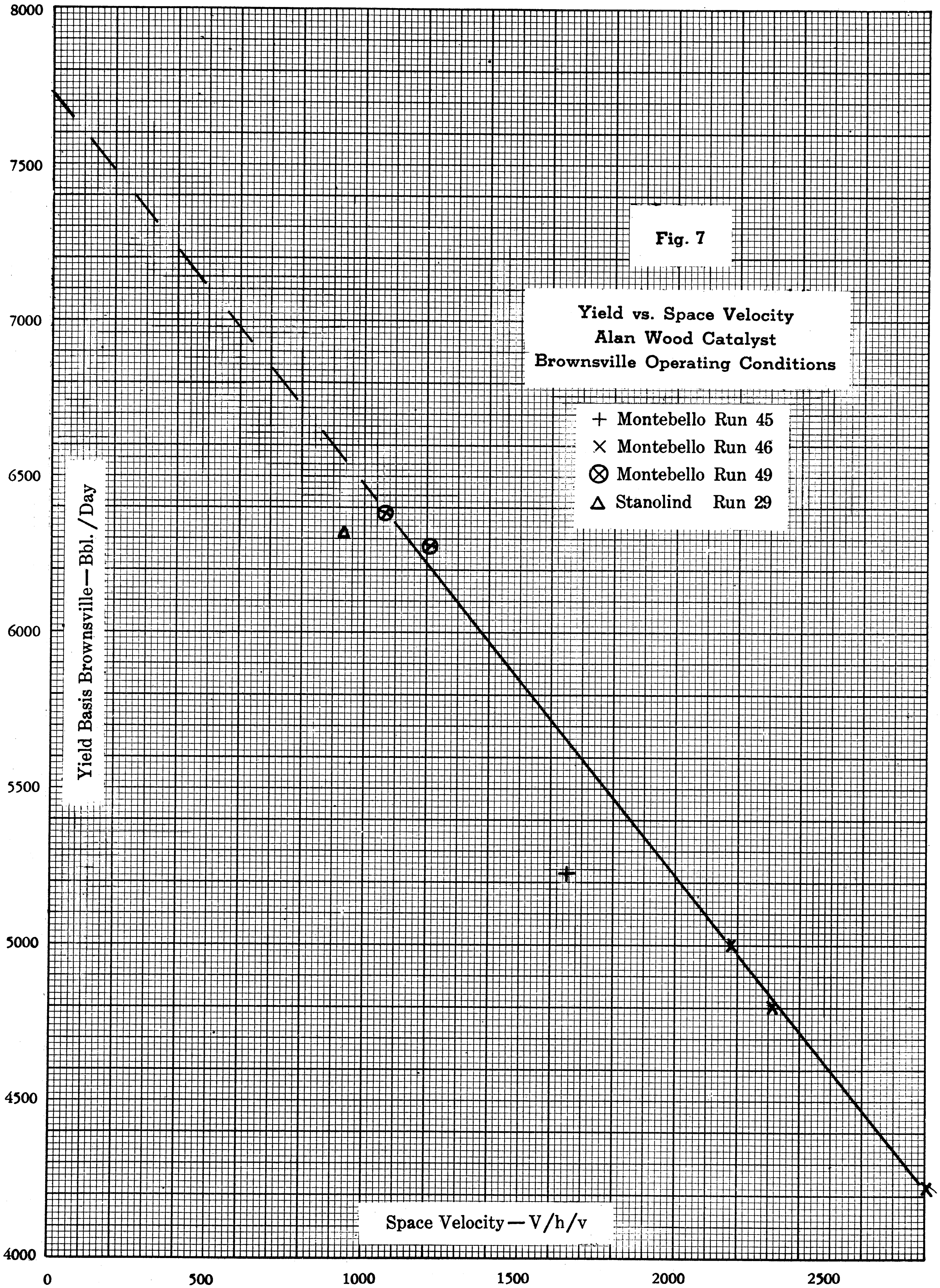
Fig. 7
Yield vs. Space Velocity
Alan Wood Catalyst
Brownsville Operating Conditions
+ Montebello Run 45
× Montebello Run 46
⊗ Montebello Run 49
△ Stanolind Run 29
Yield Basis Brownsville—Bbl. /Day
Space Velocity—V/h/v
8000
7500
7000
6500
6000
5500
5000
4500
4000
0
500
1000
1500
2000
2500

TABLE VI
COMPARISON OF YIELD DATA

Alan Wood Catalyst

	Montebello Run 49	Stanolind D-201-29	Brownsville Design
Production, Bbls/Day			
Gasoline	4,562	4,358	6,079
Gas Oil	629	496	947
Fuel Oil	448	480	198
Total	5,639	5,334	7,223
Chemicals from:			
Gas	86*	114	--
Oil	73*	96	--
Water	588	776	631
Total	6,386	6,320	7,855
Prices, $/Bbl.			
Gasoline	5.04	5.04	5.04
Gas Oil	3.25	3.25	3.25
Fuel Oil	1.30	1.30	1.30
Chemicals	10.00	10.00	3.70
Value - $/Day	$33,089	$34,060	$36,308

*Estimated Basis Stanolind Data

from 21 to 19 feet. It is possible that the effect of recycle ratio is offset in these data by the greater age of the catalyst (298 vs. 192 hours), and that the two effects are of comparable magnitude.

The yield shown for Run 45 falls somewhat below the line in Figure 7 indicating that the Finkelstein Mill Scale is slightly inferior to the Alan Wood catalyst.

C. Comparison with Brownsville Design

The yield data obtained in Run 49 and in the Stanolind Run D-201-29 are compared with the Brownsville design values in the opposite Table VI, which shows that both pilot plant results are nearly 20 per cent below the design value. Product distribution is about the same in all cases.

This dificiency is not as serious economically as it might appear from the yield data. Since Brownsville has been set up to scrub both gas and oil products to recover water soluble chemicals, the rate of chemicals production is indicated to be considerably higher than design in spite of the lower total liquid production. The chemicals fraction, furthermore, was priced at 1.1 cents per pound in the original economics, whereas it is now evident that the value is actually at least 3 cents per pound. When these differences are considered, it is seen that the actual return to Brownsville is over 90 per cent of the amount originally used.

It might appear from Figure 7, page 23, that the maximum possible yield from the Brownsville feed would be about 7700 Bbls./day since the linear space velocity-yield relation

TABLE VII
YIELDS FROM PYRITES AND STANOLIND MILL SCALE

RUN NUMBER	Montebello Run 22-G	Stanolind Run 201-2-9
Hours on Stream	144-168	215-239
Space Velocity, v/hr/v	460	1790
Catalyst	Pyrites	C. F. & I Mill Scale
YIELDS BASIS BROWNSVILLE - BBL/DAY		
Gasoline	5,571	6,522
Gas Oil	862	1,094
Fuel Oil	934	825
Chemicals	1,420	1,081
Total	8,788	9,521

extrapolates to this value at zero space velocity. It is possible that this is actually true for the Alan Wood catalyst but it is certainly not true in general for the synthesis reaction since the data in Table VII, opposite, from both Montebello and Stanolind on other catalysts show that much higher yields can actually be obtained. As stated above the Montebello Run 22 operation was very erratic and the results are not considered altogether reliable. This is not true, however, of the original Stanolind C F & I Mill Scale data from Runs D-201-2 through D-201-8 which are generally similar to the results shown for D-201-2. Unfortunately, the Colorado Fuel and Iron Company's mill where this scale was produced has been extensively altered and this mill scale is no longer available. Samples of mill scale from other sources, such as the Finkelstein mill scale used at Montebello, have been poorer than the original Stanolind catalyst and it is indicated that a further, more extensive search should be made for more active catalysts.