and Brabag catalysts, whereas the Rheinpreussen catalyst had the lowest yield. The Diesel-oil yield was lower than the gasoline yield for all of the catalysts. All of the gasolines contained 50 percent or more of olefins, the highest being 70 percent in the Brabag product. Despite a higher yield in grams per cubic meter of synthesis gas the space-time yields were about the same as those obtained in Bureau of Mines runs 42, 62, 72, and 81, using unpromoted iron catalysts precipitated from ferric nitrate solution with potassium carbonate.

NICKEL AND COBALT CATALYSTS

PRELIMINARY TESTS USING HYFLO SUPER-CEL AS CARRIER [5]; DURABILITY TEST AT 100 P. S. I. AND EFFECT OF NITROGEN IN SYNTHESIS GAS

Data on nickel and cobalt catalyst preparation conditions are given in tables 20 and 21, and on activity in the synthesis in tables 33, 34, and 35. In the group of catalysts containing nickel and cobalt only three were inactive: 36A, 38A, and 65A. (See table 33.) It may be significant that the only constituent common to all three catalysts and absent from all the others in this group was alumina.

Activities of catalysts 60A, 61A, 62A, and 64A containing nickel were measured in short tests (table 33) of not more than 4 weeks duration at atmospheric pressure. These catalysts were of low activity, the least active being 62A, which contained cobalt and whose maximum yield was only 36 grams per cubic meter. Catalysts 60A and 61A contained the same ratio of Co:Ni:ThO_2, but 61A had about 50 percent of Hyflo Super-Cel, whereas 60A had about 80 percent of this constituent. At about the same temperature the space-time yield from 61A was two to three times that from 60A. Catalyst 64A, of about the same composition as 61A (except for the content of thoria, which was about one-half that of 61A), gave the highest yield, namely, 74 grams per cubic meter.

Test 23 (see table 34), using a catalyst containing Co–ThO_2–Hyflo Super-Cel, 100:18:100 parts by weight, was continued for about 2,400 hours at 100 pounds per square inch gage pressure, with hydrogen flushing after every 4 or 5 days. The results show that fairly uniform activity was maintained during the 2,400 hours of operation. Equally good durability at atmospheric pressure of a Co–ThO_2–MgO–kieselguhr catalyst and with higher yield per cubic meter of synthesis gas and higher space-time yield under conditions comparable with those of test 23, was obtained in the "X" series of tests (see tables 39 and 40).

[5] As will be shown in discussion of the "X" series of tests, use of Johns-Manville Hyflo-Cel as a carrier results in catalysts of appreciably lower activity than when Filter-Cel or a similar diatomaceous earth is used. Hyflo Super-Cel is prepared by treating Filter-Cel with a small amount of sodium carbonate and calcining at about 900° C. It was used in the earlier tests before its inferiority to Filter-Cel was determined.

TABLE 33.—*Tests on pelleted cobalt-nickel and nickel catalysts* [1]

[Atmospheric pressure of $1H_2+1CO$ gas.[2] All catalyst compositions in parts by weight]

Catalyst No.	Composition of catalyst	Pretreatment: Reduction	Pretreatment: Induction	Test No.	Duration of test, hours	Average temperature ° C.	Space velocity [3]	Contraction, percent	Hydrocarbon products: C1–C4, g./m.3 (4)	Hydrocarbon products: 0° C. Stabilizer gas: Weight, percent	Hydrocarbon products: Liquids plus solids: g./m.3 (4) (5)	Hydrocarbon products: Liquids plus solids: Weight, percent	Hydrocarbon products: Liquids plus solids: Space time yield [6]	H_2O, g./m.3 (4)
36A	NiO : CoO : MnO : Al_2O_3 : kieselguhr :: 2.5 : 2.5 : 1 : 0.25 : 6.25	Slow	Rapid	26a	34	208	Poor activity							
38A	NiO : MnO : NaO.Al_2O_3.SiO_2 :: 5 : 1 : 6	do	do	24a	9	183	148	27	22.1	51.9	20.5	48.1	3.03	47.8
60A	NiO : CoO : ThO_2 : H. S. C. :: 1 : 1 : 0.2 : 3.8	do	do	32a	42	196	163	33	19.7	30.8	44.2	69.2	4.55	65.9
				b	67	198	166	41	13.7	21.4	57.7	78.6	9.46	100.0
61A	NiO : CoO : ThO_2 : H. S. C. :: 1 : 1 : 0.2 : 2.2	do	do	46a	127	193	166	46	9.9	12.6	68.8	87.4	11.28	107.7
				b	90	190	166	40			28.0		3.45	79.1
62A	NiO : ThO_2 : kieselguhr :: 4.5 : 0.5 : 5	do	Intermediate.	56a	172	181	123	35			28.8		3.54	72.9
				b	48	196	124	40	56.0	60.8	36.1	39.2	4.43	84.9
				c	87	194	123	29	53.4	71.7	21.1	28.3	2.60	32.7
				d	49	188	172	29	30.0	48.8	31.5	51.2	5.42	58.5
64A	NiO : CoO : ThO_2 : H.S.C. :: 1 : 1 : 0.1 : 2.2	do	do	41a	69	203	166	48	38.4	34.1	74.2	65.9	12.31	71.4
				b	74	198	164	42	20.5	23.7	65.9	76.3	10.81	89.4
				c	43	198	139	38	23.9	32.4	49.9	67.6	6.94	84.2
				d	48	199				Poor activity				
65A	NiO : CoO : ThO_2 : Al_2O_3 pellets :: 1 : 1 : 0.2 : 4.9	Rapid	Slow	86a	81	178								

[1] All catalysts listed in this table were prepared by the International Nickel Fellowship at the Mellon Institute and pelleted by the Bureau of Mines, except No. 60A, which was pelleted at the Mellon Institute. Nos. 64A and 65A were impregnated catalysts.
[2] Contains 3 percent N_2, 1 percent CH_4, and 0.2 percent CO_2.
[3] Volumes of feed gas per hour per volume of catalyst.
[4] Grams per cubic meter of feed gas.
[5] Bromine numbers and specific gravity of liquid products ranged from 33 to 58 and 0.691 to 0.737, respectively, the average being 41 and 0.74, respectively.
[6] Kilograms per cubic meter of catalyst per hour.

TABLE 34.—*Test 23, cobalt-thoria-H. S. C.*[1] *catalyst*

[Catalyst 2A[2]; pellets; $2H_2 + 1CO$ [3] at 100 pounds gage pressure; slow reduction; rapid induction at 100 pounds pressure]

Test No.	Duration of test, hours	Temperature, °C.	Space velocity [6]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases (C_1–C_4): Total volume, liters	Molecular weight	Olefin content, volume, percent	Grams per cubic meter [7]	Weight, percent, of total hydrocarbons	Liquids plus solids [4]: Total weight, grams	Grams per cubic meter [7]	Weight, percent, of total hydrocarbons	Space-time yield [8]	Unreacted gases [5]: Total volume, cubic feet	Volume, percent: Hydrogen	Carbon monoxide	Nitrogen
a	51.1	180	154	55	14.5	18.5	0.0	17.8	19.9	19.4	28.9	32.2	4.45	10.67	65.1	34.9	0.0
b	92.9	182	146	50	11.7	25.2	6.3	18.7	24.3	41.0	58.3	75.7	8.52	12.30	60.2	35.8	4.0
c	99.2	186	232	44	13.9	26.4	10.9	14.8	24.2	51.5	46.5	75.8	10.79	21.70			
d	98.7	197	233	53	22.3	28.7	7.8	25.9	36.7	49.3	44.6	63.3	10.40	18.13	70.2	23.1	6.7
e	93.1	195	230	34	21.2	24.3	5.8	22.3	20.7	88.3	85.4	79.8	19.65	23.63	57.1	36.2	6.7
f	124.5	204	240	63	39.9	23.5	8.5	29.2	33.2	84.6	58.8	66.8	14.10	18.66	57.2	38.7	4.1
g	120.9	189	232	53	27.7	23.9	12.6	21.9	27.8	76.8	56.9	72.2	13.20	21.93	62.0	33.5	4.5
h	109.5	194	239	50	23.3	23.7	7.0	19.6	27.8	64.1	50.9	72.2	12.16	21.91	60.6	34.6	4.8
i	101.0	208	235	47	24.1	23.6		22.3	26.8	69.4	60.8	73.2	14.29	21.00	58.7	37.7	3.6
j	103.8	197	237	50	29.7	24.7	10.2	27.7	33.1	66.1	55.9	66.9	13.25	20.42	66.6	31.2	2.2
k	121.5	195	197	52	29.1	26.9	8.7	30.5	36.3	61.4	53.5	63.7	10.53	19.06	54.4	41.9	3.7
l	106.8	186	192	52	12.0	25.8	13.0	14.1	21.2	51.4	52.3	78.8	10.03	16.58	75.0	24.2	0.8
m	107.3	198	192	46	20.6	24.5	11.0	22.8	30.0	52.3	53.1	70.0	10.20	18.34	58.5	39.2	2.3
n	114.0	202	198	46	18.6	24.5	9.8	19.3	23.6	65.9	62.6	76.4	12.40	19.56	55.6	40.0	4.4
o	86.1																
p	115.5	192	192	53	25.5	23.0	10.2	24.5	31.2	57.8	54.1	68.8	10.39	17.79	56.9	37.3	5.8
q	120.5	196	192	53	27.8	25.6	9.9	28.5	32.1	67.1	60.2	67.9	11.55	18.58	56.2	35.9	7.9
r	112.9	198	191	51	24.2	23.6	10.7	24.7	29.9	59.8	57.8	70.1	11.05	17.64	54.3	37.9	7.8
s	106.4	198	192	49	21.3	29.4	9.4	28.6	36.3	49.0	50.1	63.7	9.62	17.68	55.9	36.4	7.7
t	84.9	196	192	55	11.3	27.3	21.3	17.5	25.7	39.7	50.6	74.3	9.72	12.23	58.9	30.9	10.2
u	84.5	193	217	55						28.2	32.2		6.98	13.44	59.2	37.5	3.3
v	119.5	198	90	73	6.8	17.1	23.7	10.0	11.9	38.3	73.8	88.1	6.64	4.84	42.9	52.0	5.1
w	116.3	198	96	71	6.2	23.7	23.3	12.9	15.4	35.9	70.7	84.6	6.79	5.15	43.8	50.6	5.6

[1] Composition of catalyst, Co : ThO_2 : H. S. C. : : 100 : 18 : 100 parts by weight.
[2] Volume of catalyst used was 48 cc.
[3] Contains 0.2 percent CO_2, 1.5 percent CH_4, 2 percent N_2.
[4] Average specific gravity and bromine number of liquid product were 0.73 and 30, respectively.
[5] Calculated on CO_2- and O_2-free basis.
[6] Volume of feed gas per hour per volume of catalyst.
[7] Grams per cubic meter of feed gas.
[8] Kilograms per cubic meter of bulk volume of catalyst per hour.

TABLE 35.—*Atmospheric pressure tests on promoted cobalt catalysts*

[Pellets [1]; rapid reduction; slow induction; $2H_2 + 1CO$ synthesis gas [2]]

Catalyst No.	Test No.	Duration of test, hours	Temperature, ° C.	Space velocity [5]	Contraction, percent	0° C. stabilizer gases (C_1–C_4): Total volume, liters	Molecular weight	Olefin content, volume, percent	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Liquids plus solids [3]: Total weight, grams	Grams per cubic meter [6]	Weight percent of total hydrocarbons	Space-time yield [7]	Unreacted gases [4]: Total volume, cubic feet	Volume, percent: Hydrogen	Carbon monoxide	Nitrogen
12B [8]	75*a*	87.7	176	126	71	6.2		37.0			25.9	58.6		6.88	4.6	55.4	38.8	5.8
	b	120.5	185	122	75	9.9	21.6	32.5	16.2	17.9	43.7	74.4	82.1	9.08	5.1	48.2	47.9	3.9
	c	112.5	180	122	71	6.0	26.9	36.7	13.2	14.0	44.5	81.4	86.0	9.93	5.5	48.2	45.0	6.8
	d	116.8	182	122	73	9.3		30.0			51.3	90.0		10.97	5.5	42.1	46.6	11.3
	e	69.3	185	115	67						30.7	96.8		11.13	3.7			
	f	104.5	192	123	78						56.2	109.0		13.40	3.9	59.5	26.0	14.5
89A [9]	67*a*	41.5	168	103	20			29.1			6.8	31.7		3.26	6.0	57.8	37.0	5.2
	b	88.8	185	101	48	5.1	24.9	8.6	12.6	15.1	31.8	70.6	84.9	7.12	8.3	67.5	27.2	5.3
	68*a*	56.8	173	103	59	3.4	24.5	5.7	15.2	24.6	11.4	46.5	75.4	4.79	3.5	57.0	41.0	2.0
	b	93.3	176	105	75	20.3	21.1	3.1	46.6	34.2	36.8	89.6	65.8	9.40	3.6	85.6	10.0	4.4
	c	57.2	183	86	68						19.1	78.8		8.43	4.5	50.7	38.2	11.1
	d	37.8	187	86	62	.1	26.4	4.2	.7	.6	17.5	109.3	99.4	9.40	1.0	40.3	50.8	8.9
89B [9]	[10] 69*b*	63.0	186	94	56						26.6	89.6		8.43	4.5	44.0	25.5	30.5
	c	118.2	189	93	55						37.1	67.2		6.25	9.7	41.5	30.8	27.7
	d	92.3	193	91	66	1.1	29.9	20.0	7.6	6.7	20.6	106.5	93.3	9.65	2.3	31.7	25.6	42.7
	f	57.0	192	102	65	7.6	23.8	19.5	27.7	23.7	26.0	89.2	76.3	9.10	3.6	54.4	39.7	5.9
	g	93.8	193	94	63	9.3	53.4	45.0	50.4	33.8	43.5	98.8	66.2	9.27	5.7	35.6	25.8	38.6
	[11] 70*b*	63.5	187	129	60						46.2	112.8		14.56	5.7	14.2	11.2	74.6
	c	118.9	188	129	50	.1					58.5	75.8		9.78	13.3	18.6	18.2	63.2
	d	115.0	193	133	58	2.1	33.6	23.3	4.1	4.5	67.3	87.8	95.5	11.69	11.2	14.6	13.4	72.0
	e	103.5	196	130	59	12.5	30.3	23.9	25.1	22.8	57.1	84.9	77.2	11.06	9.6	13.8	13.7	72.5
	g	83.0	188	80	80	33.7		11.4			35.7	108.0		8.64	2.3	54.2	34.8	11.0
	71*a*	105.7	178	82	49						29.2	67.2		5.51	8.1	56.1	23.2	20.7
	b	116.8	193	83	71	11.9	59.0	70.0	64.4	40.8	45.4	93.3	59.2	7.75	4.9	52.9	42.6	4.5
	c	114.0	185	84	69	10.2	26.1	34.3	24.8	18.5	52.2	109.0	81.5	9.15	5.2	50.6	44.5	4.9

[1] Catalyst used in test 67 was unpelleted, in granules 15- to 20-mesh with a bulk density of 0.36 gram per cc.
[2] Run 70*g* was operated at 100 pounds gage pressure.
[3] Specific gravity and bromine number of liquid product were 0.71–0.74 and 30–60, respectively.
[4] On CO_2- and O_2-free basis.
[5] Volume of feed gas per hour per volume of catalyst.
[6] Grams per cubic meter of feed gas.
[7] Kilograms per cubic meter of bulk volume of catalyst per hour.
[8] Catalyst 12B had the following percent composition by weight, calculated from the weights of reagents used in the preparation: CoO 82, ThO_2 18, Hyflo Super-Cel 100. This catalyst was precipitated from the cobalt and thorium nitrates on the carrier, Hyflo Super-Cel, by potassium carbonate, and dried at 153° C. Bulk density of the pellets was 0.98 gram per cc.
[9] Catalysts 89A and 89B had the following composition: Co 100, ThO_2 6, MgO 12, Hyflo Super-Cel 200 percent by weight. This catalyst was precipitated by sodium carbonate from the cobalt and thorium nitrates on the Hyflo Super-Cel mixed with magnesia, and dried at 120° C. Bulk density of the pellets was 0.82 gram per cc.
[10] Synthesis gas was diluted with 16-percent nitrogen in *b*, *c*, *d*, and *g*.
[11] Synthesis gas contained 29 percent nitrogen in *b*, *c*, *d*, and *e*.

Table 35 contains results of tests of 100 to 600 hours' duration on Co : ThO_2 : Hyflo Super-Cel and Co : ThO_2 : MgO : Hyflo Super-Cel catalysts at atmospheric pressure. The yield per cubic meter of synthesis gas was appreciably higher than in test 23 (table 34), but the space-time yield was about the same as in the latter test. Tests 69 and 70 were conducted with 16 and 29 percent, respectively, of nitrogen in the synthesis gas. In tests 69*f* and 70*g*, $2H_2 + 1CO$ without dilution with nitrogen was used to serve as a "blank" test on the effect of nitrogen, and should be compared with 71*b*+*c*, for this purpose. This comparison indicates no apparent decrease in activity. The nitrogen dilution tests showed also that the yield did not decrease as much as would be expected on the assumption that the reaction rate was directly proportional to the partial pressure of $2H_2 + 1CO$. This is shown in table 36, where the data of runs 69, and 71 are summarized for comparison purposes. The observed yield at 29 percent dilution was about 25 percent greater than calculated. The reaction is therefore less than first order.

LATER TESTS ON PROMOTED COBALT CATALYSTS: REPRODUCIBILITY OF CATALYST PREPARATIONS AND TESTS, COMPARISON OF 30-AND 90-CM. CATALYST DEPTHS, EFFECT OF DIFFERENT INDUCTION PROCEDURES, EFFICIENCIES OF DIFFERENT KIESELGUHRS AS CARRIERS, SPACE-TIME YIELD AT DIFFERENT SPACE VELOCITIES, AND VARIATION OF REACTION TEMPERATURE WITH FLOW AT CONSTANT CONTRACTION

Because of changes in the procedures for recovery of products and analysis, later catalyst tests are designated as the "X" series. In most of the tests of this series, Co–ThO_2–MgO–kieselguhr catalysts (89–type) were used. The results are contained in tables 37 to 46 and the details of catalyst preparation in tables 20 and 21.

TABLE 36.—*Diluent effect of nitrogen using Co : ThO_2 : MgO : H. S. C. catalyst*

Run No.	69*b, c, d, g*	69*f*	70*b, c, d, e*	70*g*	71*b, c*
Duration of test, hours	316	57	490	83	168
Temperature, ° C.	190	192	191	188	185
Space velocity [1]	94	102	130	80	84
In-gas analysis, percent:					
Hydrogen	58.2	68.7	44.4	68.7	68.7
Carbon monoxide	24.2	30.0	26.7	30.0	30.0
Nitrogen	16.3	1.0	28.8	1.0	1.0
Exit-gas analysis, percent:					
Hydrogen	36.3	50.0	14.7	35.4	47.9
Carbon monoxide	25.6	36.6	13.5	22.7	40.0
Nitrogen	33.1	5.4	67.7	7.2	4.3
Bromine No. of oil	34	32	53	33	58
Specific gravity of oil	.731	.732	.719	.729	.716
Oil yield, grams per cubic meter:					
Calculated [2]	86.2		72.4		101
Observed [3]	88.6	89.0	90.4	108	101

[1] Volumes of synthesis gas per volume of catalyst per hour.
[2] Calculated using 101 grams per cubic meter as yield with no nitrogen dilution.
[3] Grams per cubic meter of feed gas, including nitrogen.

TABLE 37.—*Test X–17; 16.9 grams of Co : ThO_2 : MgO : Portuguese kieselguhr*

[Catalyst 89K; granules; atmospheric pressure, *a* to *s*; 100 p. s. i., *t* to *z*; $2H_2 + 1CO$; rapid reduction; slow induction with temperature schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products							CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
					0° C. stabilizer gases				Liquids plus solids				
					CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	g./m.³ [b]	Weight, percent	Space-time yield [c]		
a	82	178	101	52	8.4	4.1	8.7	25.8	60.9	74.2	6.15	3.4	101.0
b	105	184	102	73	15.1	1.9	11.4	23.0	95.8	77.0	9.77	7.3	171.5
c	106	183	99	73	21.8	4.0	17.8	38.6	69.3	61.4	6.86	6.9	170.8
d	105	187	103	78	15.8	(d)	(d)	(d)	115.1	(d)	11.85	10.3	188.6
e	106	192	101	76	(d)	(d)	12.5	(d)	96.2	(d)	9.72	9.0	192.7
f	106	184	100	77	16.8	3.8	13.4	25.9	97.2	74.1	9.72	8.7	170.2
g	106	184	99	75	18.2	2.8	13.3	26.0	97.7	74.0	9.67	9.0	181.5
h	103	190	100	74	18.7	3.3	14.1	25.1	107.8	74.9	10.78	13.1	184.5
i	106	187	99	73	20.1	2.8	13.9	25.8	106.1	74.2	10.50	7.0	171.0
j	106	186	97	73	15.0	1.4	10.5	21.7	97.2	78.3	9.43	7.1	156.9
k	96	185	99	72	12.0	2.0	12.2	23.4	87.7	76.6	8.68	4.4	183.2
l	115	190	100	67	19.4	2.8	15.5	30.3	86.6	69.7	8.66	6.8	165.0
m	115	188	101	66	13.8	3.2	7.3	21.0	91.8	79.0	9.27	4.1	163.9
n	116	186	97	68	17.3	.5	6.8	20.2	97.3	79.8	9.44	5.4	151.4
o	116	188	100	69	13.6	1.4	11.4	22.6	90.5	77.4	9.05	5.5	134.8
p	116	176	44	67	20.6	2.0	9.1	30.0	73.7	70.0	3.24	9.5	162.5
q	90	176	44	67	16.6	3.9	22.1	38.0	69.7	62.0	3.07	9.0	163.0
r	90	187	80	68	17.1	2.6	7.1	23.2	91.2	76.8	7.29	8.3	148.2
s	114	184	101	68	11.4	.0	6.8	21.7	65.0	78.3	6.57	5.0	130.1
t [e]	112	180	101	71	6.8	1.0	5.5	26.2	37.5	73.8	3.79	2.3	129.8
u [e]	115	174	105	75	3.5	.8	4.7	22.8	30.5	77.2	3.20	2.0	98.0
v	114	187	101	72	21.2	2.8	7.1	21.4	114.4	78.6	11.56	7.7	189.6
w	114	188	100	71	13.0	1.7	8.3	18.0	105.2	82.0	10.52	7.0	177.4
x	114	188	98	72	18.4	2.7	12.1	22.6	114.2	77.3	11.20	5.0	213.9
y	89	190	100	74	23.2	3.1	11.5	29.1	92.0	70.9	9.20	7.9	164.2
z	114	187	104	72	15.0	1.1	9.1	21.1	97.8	78.9	10.17	3.4	181.6

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
[e] Some leakage occurred during first 200 hours at 100 p. s. i.

The reproducibility of catalyst preparation and testing is illustrated in figure 17, and the detailed data are summarized in tables 39 and 44, tests X19 and X27. Although the space-time yield (kilograms of oil plus wax per cubic meter of catalyst per hour) at about 100 space velocity (volumes of synthesis gas per volume of catalyst per hour) and about 70 percent contraction (in volume of reactant) was reproducible within about 0.5 kilogram in a total of 9.5, the operating temperature differed by about 10° C. This difference in temperature can at least in part be explained by the difference in weight of the catalyst charge—38.8 grams in test X19 and 34.2 grams in test X27. At a constant space velocity the temperature of operation of identical catalysts should vary in an inverse manner with the weight of the charge. In test X22 (table 41) alkali-washed magnesia and acid-extracted Filter-Cel were used in preparing the Co. : ThO_2 : MgO : kieselguhr catalyst identical in composition with those used

for the reproducibility tests, except that Filter-Cel was used in place of Portuguese kieselguhr. The space-time yield of this run was within the limits of reproducibility of tests X19 and X27, and, in general, the space-time yields of oil plus wax of most of the 89-type cobalt catalysts lie within this range. In test X21 (table 40), in which the catalyst was prepared from untreated Filter-Cel and unwashed magnesia, the catalyst was somewhat less active than in X22, as indicated by a slightly higher operating temperature. The impurities in the magnesia or kieselguhr do not appear to be of importance in the reproducibility of the tests. It should be noted that $1H_2 + 1CO$ gas was used in the first 2 weeks of operation of test X21 and that this test was operated at a space velocity of 110 rather than 100. Thus, the space-time yields of test X21 are about 10 percent higher and the temperature about 2° C. higher than for operation at a space velocity of 100. For purposes of comparison, the space-time yield and temperatures of operation of test X21 were corrected to a space velocity of 100 in figures 18, 21, and 22.

TABLE 38.—*Test X–18; 16.0 grams of Co : ThO_2 : MgO : Portuguese kieselguhr*

Catalyst 89K; granules; atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	0° C. stabilizer gases: C_2, g./m.³ [b]	0° C. stabilizer gases: C_3+C_4, g./m.³ [b]	0° C. stabilizer gases: Weight, percent	Liquids plus solids: g./m.³ [b]	Liquids plus solids: Weight, percent	Liquids plus solids: Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	79	177	104	47	9.7	(d)	(d)	27.5	51.6	72.5	5.36	4.4	81.0
b	107	187	98	72	18.3	(d)	(d)	31.1	71.0	68.9	6.96	7.2	190.0
c	106	187	98	73	21.4	0.6	13.1	34.8	65.4	65.2	6.42	7.0	169.5
d	105	186	102	78	17.3	1.4	10.3	21.8	87.7	75.2	8.84	10.3	159.8
e	106	192	101	75	20.2	2.9	11.2	24.9	103.3	75.1	10.43	9.0	186.0
f	106	190	99	77	(d)	(d)	(d)	(d)	105.0	(d)	10.39	8.8	180.0
g	106	188	101	74	15.7	4.7	12.0	23.8	103.9	76.2	10.49	9.0	171.0
h	103	189	99	69	19.5	2.6	11.9	28.0	87.3	71.0	8.64	8.6	188.2
i	106	188	101	74	14.7	.5	3.4	16.3	96.6	83.7	9.70	5.1	179.3
j	106	186	96	71	18.2	.9	11.3	25.5	89.0	74.5	8.54	6.7	171.6
k	91	186	101	73	13.5	2.2	9.8	22.7	86.6	77.3	8.74	8.5	172.8
l	115	196	100	70	45.6	1.9	11.4	37.8	97.0	62.2	9.70	11.0	164.4
m	115	176	100	68	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
n	116	190	99	64	14.3	1.7	8.9	22.3	88.0	77.7	8.71	7.8	132.5
o	116	188	99	67	14.0	2.1	12.9	26.0	82.7	73.0	8.19	4.7	139.5
p	116	178	43	66	(d)	(d)	27.0	(d)	81.1	(d)	3.48	6.1	165.3
q	90	178	43	67	(d)	(d)	13.0	(d)	66.2	(d)	2.85	6.3	153.7
r	90	190	78	66	13.9	6.3	7.6	23.3	91.4	76.7	7.13	6.0	160.0
s	114	186	101	69	(d)	(d)	(d)	(d)	• 94.2	(d)	9.51	5.0	163.3
t	112	188	131	54	25.7	.7	5.3	26.3	89.0	73.7	11.66	5.5	182.8
u	114	206	131	60	25.3	(d)	(d)	(d)	•103.0	(d)	13.50	7.1	189.0
v	114	204	136	59	21.9	1.2	14.0	28.7	92.1	71.3	12.51	8.3	193.3
w	114	194	98	71	14.8	2.6	9.6	24.9	85.6	75.1	8.00	3.6	169.6

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
• Does not include C_5 or higher in gas from charcoal recovery.

TABLE 39.—*Test X–19; 38.8 grams of Co : ThO_2 : MgO : Portuguese kieselguhr*

[Catalyst; 89K; pellets atmospheric pressure; $2H_2 + 1CO$; rapid reduction; slow induction, with contraction schedule]

Test No.	Duration of test, hours	Average temperature, °C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	0° C. stabilizer gases: C_2, g./m.³ [b]	0° C. stabilizer gases: C_3+C_4, g./m.³ [b]	0° C. stabilizer gases: Weight, percent	Liquids plus solids: g./m.³ [b]	Liquids plus solids: Weight, percent	Liquids plus solids: Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	106	165	103	58	2.4	0.5	9.0	18.1	53.4	81.9	5.50	26.5	121.0
b	106	175	101	77	13.3	5.3	13.6	25.6	92.6	74.6	9.36	20.7	198.5
c	106	177	100	77	29.5	2.5	5.1	27.0	100.2	73.0	10.02	17.4	193.2
d	106	174	101	73	23.8	2.7	17.3	33.0	89.0	67.0	9.00	11.8	187.0
e	103	176	100	75	33.2	2.5	15.6	37.0	87.6	63.0	9.76	9.0	190.4
f	107	175	100	74	23.3	1.5	15.8	29.2	98.8	70.8	9.88	7.8	176.7
g	106	174	97	74	18.5	7.4	12.1	27.1	102.4	72.9	9.94	10.3	168.3
h	91	172	102	71	7.6	4.5	11.7	26.5	66.2	73.5	6.76	13.4	172.5
i	115	186	103	73	35.3	3.1	6.6	36.6	78.4	63.4	8.08	20.5	174.7
j	115	176	103	68	15.1	4.5	11.0	24.6	93.2	75.4	9.60	8.8	175.7
k	116	176	100	66	16.8	2.0	9.6	22.2	99.6	77.8	9.96	6.8	170.0
l	116	176	99	67	17.1	3.1	10.6	27.3	81.9	72.7	8.10	6.6	172.1
m	116	178	101	69	15.9	3.1	12.0	27.0	83.8	73.0	8.46	9.8	172.7
n	90	177	102	70	12.4	2.6	10.5	22.6	87.5	77.4	8.93	8.3	176.3
o	90	178	102	70	20.1	1.3	11.3	24.9	98.8	75.1	10.08	4.8	178.8
p	114	177	101	70	15.4	.9	7.3	22.5	91.2	77.5	9.20	7.8	178.6
q	112	184	104	68	20.1	.7	6.2	24.1	95.1	75.9	13.95	7.6	172.3
r	115	189	288	72	38.7	8.0	14.9	38.2	99.8	61.8	28.73	3.4	183.1
s	114	194	308	72	24.2	3.3	16.1	33.3	87.3	66.7	26.88	5.6	175.8
t	114	199	391	70	20.1	3.2	15.1	29.9	90.2	70.1	35.30	9.4	181.6
u	114	201	436	67	19.0	3.2	6.3	26.0	81.0	74.0	35.30	7.2	146.8
v	88	209	599	58	(d)	(d)	(d)	(d)	• 72.9	(d)	43.60	5.0	143.8
w	114	218	690	56	(d)	(d)	(d)	(d)	• 47.5	(d)	32.80	7.0	138.8
x	114	197	175	70	22.2	2.6	19.9	30.9	100.1	69.1	17.68	4.2	180.8
y	Re-reduction												
z	115	182	97	48	(d)	(d)	(d)	(d)	• 45.4	(d)	4.40	2.1	105.4
A	115	194	98	72	30.2	1.6	20.7	39.3	81.2	60.7	7.94	18.0	189.2
B	114	194	103	71	26.4	2.4	19.1	37.4	80.3	62.6	8.27	21.8	180.8

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
• Does not include C_5 or higher in gas from charcoal recovery.

Comparison of operation with 30-centimeter and 90-centimeter depths of the catalyst bed is illustrated in figure 18, and the detailed data are in tables 46 and 40 for tests X30 and X21. The space-time yield of the 90-centimeter catalyst bed was somewhat higher than that of the 30-centimeter bed, and the data from the longer converter do not scatter as much. The temperature of operation of the longer converter was significantly higher than that of the shorter one. Examination of the methane-production data for X30 and X21 shows averages of 15.6 grams per cubic meter of CH_4 for X30 and 21.3 grams per cubic meter for X21 during the first 1,200 hours of operation. Before concluding that more methane is produced in the 30-centimeter than in the 90-centimeter bed, the reproducibility of the methane data must be considered.

TABLE 40.—*Test X–21; 80.5 grams of Co : ThO_2 : MgO : Filter-Cel*

[Catalyst 89J, pellets; atmospheric pressure, *a* to *o*; 100 p. s. i., *p* to *u*; $2H_2+1CO$, except *a* and *b*, where H_2+1CO was used; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: g./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a [d]	105	180	99	53	16.8	17.6	8.7	48.3	46.4	51.7	4.59	2.9	85.6
b [d]	106	197	101	62	13.8	23.5	10.5	33.1	96.8	66.9	9.78	16.6	161.5
c	102	189	113	74	26.0	1.9	14.1	27.4	111.5	72.6	12.60	9.8	204.6
d	106	190	111	75	22.7	.1	6.7	20.0	118.4	80.0	13.14	9.7	192.3
e	106	182	109	74	20.6	4.1	13.8	28.9	94.7	71.1	10.33	8.1	194.4
f	91	184	113	74	24.5	3.3	13.4	29.0	100.0	71.0	11.40	6.8	195.5
g	115	185	112	74	12.6	.1	9.0	16.8	107.9	83.2	12.09	12.3	192.3
h	115	187	114	73	26.8	2.6	15.5	34.3	86.2	65.7	9.82	5.3	195.7
i	116	186	110	70	27.6	1.1	5.3	23.5	110.6	76.5	12.16	9.7	189.5
j	116	184	114	70	15.1	1.6	10.0	20.6	102.9	79.4	11.74	6.7	185.8
k	116	184	111	67	20.5	1.4	9.3	25.8	90.5	74.2	10.05	5.1	176.7
l	90	185	115	69	16.7	.0	13.0	23.3	98.0	76.7	11.26	6.8	182.1
m	90	186	113	71	17.8	2.1	12.2	24.2	100.7	75.8	11.38	5.3	188.1
n	114	186	100	69	14.4	.5	9.7	20.7	94.4	79.3	9.44	8.6	(*e*)
o	112	188	99	69	17.3	.1	12.8	23.3	99.4	76.7	9.87	8.4	208.4
p	115	188	87	70	26.0	1.0	17.3	27.9	114.6	72.1	10.00	7.5	205.5
q	114	191	103	69	(*d*)	(*d*)	20.2	(*e*)	109.9	(*d*)	11.31	8.1	205.9
r	114	197	101	70	34.1	(*d*)	(*d*)	(*e*)	103.0	(*d*)	10.40	12.1	220.1
s	114	194	99	69	30.9	2.2	12.1	27.5	110.3	72.5	11.80	9.6	231.2
t	90	192	98	69	25.4	4.1	14.3	33.3	87.6	66.7	8.59	12.3	199.7
u	114	192	101	72	27.4	3.6	15.4	31.8	109.4	68.2	11.05	7.2	207.5

[a] Volume of feed gas per hour per volume of catalyst. [b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour. [d] $1H_2+1CO$ used.
[e] Sample or part of sample lost. [f] Does not include C_5 or higher in gas from charcoal recovery.

TABLE 41.—*Test X–22; 28.5 grams of Co : ThO_2 : MgO (alkali-washed) : Filter Cel (acid-extracted)*

[Pellet 890 (Oh); atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, °C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: g./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	103	179	94	32	19.8	2.4	13.4	56.2	27.8	43.8	2.01	5.4	74.2
b	107	183	94	74	12.9	2.5	11.5	22.7	87.4	77.3	8.22	3.6	169.0
c	106	182	95	76	17.1	2.0	10.6	22.8	100.5	77.2	9.98	6.2	198.5
d	91	178	94	74	14.9	1.7	7.5	18.6	105.8	81.4	9.05	4.0	195.2
e	115	183	96	68	20.6	2.1	12.9	24.5	109.8	75.5	10.54	9.3	176.0
f	115	177	95	63	19.4	3.0	6.8	23.5	95.4	76.5	9.06	5.1	158.5
g	115	178	97	69	21.5	1.6	10.2	25.6	97.1	74.4	9.42	5.0	180.6
h	116	177	97	70	14.6	2.4	9.6	21.9	95.2	78.1	9.24	4.8	183.6
i	116	178	95	68	7.2	3.2	8.5	16.3	97.0	83.7	9.22	5.1	161.5
j	90	188	97	65	19.6	2.4	9.1	29.0	72.9	70.1	7.07	3.4	166.7
k	90	187	96	67	21.1	.5	13.1	26.3	97.5	73.7	9.36	9.2	165.3
l	114	184	95	68	10.9	1.5	10.6	18.3	100.2	81.7	9.52	9.6	176.0
m	112	192	156	67	13.5	1.0	3.0	14.1	107.1	85.9	16.70	7.1	181.4
n	114	198	208	69	14.0	2.1	3.9	17.5	94.2	82.5	19.55	6.3	102.3
o	114	202	271	67	17.0	2.6	14.6	29.1	83.2	70.9	22.55	5.2	177.8
p	114	206	351	57	18.7	3.0	10.7	26.1	92.0	73.9	32.30	5.1	148.8
q	114	207	296	63	18.2	2.5	15.2	30.8	80.9	69.2	23.70	5.8	164.5
r	89	192	159	69	[d]14.4	(*d*)	(*d*)	(*d*)	79.5	(*d*)	12.64	7.3	183.3

[a] Volume of feed gas per hour per volume of catalyst. [b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour. [d] Sample or part of sample lost.

TABLE 42.—*Test X–23; 38.7 grams of Co : ThO_2 : MgO : Hyflo Super-Cel*

[Catalyst 89I, pellets; atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C^2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: g./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	106	174	111	37	11.6	1.5	4.6	35.1	32.7	64.9	3.63	7.5	72.9
b [d]	102	188	98	70	23.1	2.7	11.8	36.9	64.2	63.1	6.29	6.6	140.0
c	91	191	92	72	17.9	4.6	13.6	31.8	77.4	68.2	7.12	17.7	158.1
d [d]	110	185	97	75	22.6	2.6	10.2	30.8	79.3	69.2	7.69	15.1	124.5
e	115	189	95	67	15.8	4.2	11.6	34.6	59.7	65.4	5.67	6.6	103.5
f	115	192	98	64	17.9	2.7	10.7	24.9	94.5	75.1	9.26	13.0	135.9
g	116	191	97	61	9.6	.9	12.9	21.2	86.9	78.8	8.42	18.6	134.8
h	116	191	97	64	10.3	4.0	13.7	27.0	75.9	73.0	7.36	18.8	130.4
i	90	189	96	66	27.8	3.4	9.5	41.0	58.6	59.0	5.63	8.8	179.0
j	90	196	100	65	33.9	1.6	15.4	37.7	84.1	62.3	8.41	20.3	150.2
k	114	196	101	66	23.9	1.8	12.6	31.9	81.7	68.1	8.25	15.9	165.9

Test X–24; 35.2 grams of Co : ThO_2 : MgO : Hyflo Super-Cel

[Catalyst 89H, pellets; atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

a	106	175	97	45	16.3	3.0	9.3	40.2	42.6	59.8	4.13	7.7	98.5
b	106	190	95	69	20.0	7.5	13.0	32.5	84.1	67.5	7.98	19.6	163.6
c	91	194	95	64	22.6	3.6	13.9	30.9	89.6	69.1	8.50	21.4	178.3
d [d]	109	191	92	58	24.6	.7	13.8	27.5	103.2	72.5	9.49	15.0	151.3
e	115	193	95	63	18.7	.6	14.3	29.6	79.8	70.4	6.68	11.7	141.2
f	116	193	97	62	(*e*)	(*e*)	(*e*)	(*e*)	[b]87.3	(*e*)	8.47	16.7	(*e*)
g	116	194	98	62	18.8	(*e*)	(*e*)	(*e*)	(*e*)	(*e*)	(*e*)	16.0	(*e*)
h	116	191	93	64	18.3	.3	14.0	31.2	72.0	68.8	6.70	21.1	(*e*)
i	90	194	95	61	21.8	4.0	14.1	38.4	63.8	61.6	6.06	13.8	161.9
j	90	203	94	62	25.4	1.0	13.7	29.5	95.9	70.5	9.02	14.6	153.2
k	114	199	94	63	12.5	1.5	12.8	21.9	95.4	78.1	8.97	16.2	172.8

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
[e] Does not include C_5 or higher in gas from charcoal recovery.
[f] Hydrogen reactivation during week.

Averages of methane data with granular catalyst 89K for tests X17 and 18 (tables 37 and 38) for the first 1,200 hours were 17.1 and 17.0 grams per cubic meter, respectively. Thus with the same catalyst the results are fairly reproducible, and therefore the methane production is significantly smaller in the longer converter.

The effect of different induction procedures using $2H_2 + 1CO$ gas is illustrated by figures 19 and 20; the detailed data for the tests are contained in tables 37, 38, and 45. Figure 19 shows that induction at 100 pounds per square inch rather than at atmospheric pressure resulted in a somewhat lower space-time yield during the first 400 hours of operation, but for subsequent operating periods there was no difference in yield or durability. Figure 20 shows that slow induction with a temperature or a contraction schedule resulted in activity that is identical within the limits of reproducibility of the tests.

TABLE 43.—*Test X–26; 11.0 grams of Co : ThO_2 : MgO : Filter-Cel*

[Catalyst 89J, granules; atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, °C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: g./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	106	181	98	29	9.4	2.1	6.0	33.1	35.3	66.9	3.46	4.2	61.4
b	91	196	99	66	15.7	1.1	6.0	24.5	70.5	75.5	6.98	4.0	149.0
c [d]	109	196	97	57	12.7	3.4	16.5	30.8	73.4	69.2	7.12	4.6	135.6
d	115	193	90	63	11.8	4.0	9.9	21.5	93.8	78.5	8.43	4.4	141.3
e	115	194	104	66	22.9	.7	10.0	26.1	95.0	73.9	9.88	4.8	163.8
f	116	191	97	63	13.0	2.6	8.0	20.0	94.5	80.0	9.15	4.4	159.9
g	116	173	37	66	20.6	1.9	10.3	29.8	71.2	70.2	3.63	4.2	155.4
h	90	176	33	61	25.4	3.4	10.7	39.1	61.6	60.9	2.03	4.0	167.3
i	90	191	71	67	14.1	2.2	10.4	21.3	98.6	78.7	6.91	2.6	166.4
j	114	192	70	68	9.8	2.7	10.5	19.4	95.8	80.6	6.71	4.5	175.0
k	112	186	70	66	8.2	1.3	10.5	17.9	91.8	82.1	6.43	4.6	171.8
l	114	202	99	69	16.3	.0	12.1	22.6	97.3	77.4	9.63	5.5	172.2
m	114	202	99	66	14.1	.0	7.1	20.3	83.2	79.7	8.24	5.5	167.5
n	114	204	97	69	16.0	3.2	17.6	26.8	100.8	73.2	9.78	7.4	165.0
o	114	204	100	66	10.1	1.3	12.7	28.7	84.6	71.3	8.46	8.2	163.6

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Reactivation with hydrogen during this period.

TABLE 44.—*Test X–27; 34.2 grams of Co : ThO_2 : MgO : Portuguese kieselguhr*

[Catalyst 89Q, pellets; atmospheric pressure; $2H_2+1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: g./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	115	176	102	59	7.7	1.3	11.5	22.2	71.9	77.8	7.33	14.8	142.7
b	115	179	101	68	12.1	2.5	10.7	23.8	80.2	76.2	8.20	5.0	178.8
c	116	181	100	66	40.8	1.8	10.7	36.3	93.6	63.7	9.36	7.6	156.5
d	116	179	101	66	22.2	2.4	14.2	30.1	90.3	69.9	9.12	4.6	168.1
e	116	179	100	71	18.5	3.4	7.9	30.0	69.5	70.0	6.95	8.7	155.7
f	90	182	102	67	12.4	.7	19.7	25.3	97.6	74.7	9.88	5.2	175.4
g	90	182	101	70	20.2	2.9	12.3	26.1	100.5	73.9	10.15	3.5	189.1
h	114	183	99	69	23.5	.0	17.4	31.4	89.4	68.6	8.85	7.0	180.8
i	112	185	100	68	14.3	.7	9.6	20.0	95.1	79.4	9.51	10.7	180.2
j	114	187	96	71	15.9	.4	12.3	21.8	102.7	78.2	9.86	2.0	190.4
k	114	186	104	72	14.9	1.5	13.0	23.0	98.2	77.0	10.21	6.6	178.9
l	86	192	165	70	10.7	.7	9.1	19.9	82.3	80.1	13.58	10.6	156.9
m	114	192	146	72	13.6	1.6	10.1	19.8	102.6	80.2	14.98	7.1	188.0

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.

TABLE 45.—*Test X–29; 38.8 grams of Co : ThO_2 : Filter-Cel*

[Catalyst 108B, pellets; atmospheric pressure in tests *a* to *g*; 100 p. s. i. in tests *h* to *o*; $2H_2 + 1CO$; slow reduction; slow induction with temperature schedule]

Test No.	Duration of test, hours	Average temperature, °C.	Space velocity [a]	Contraction, percent	Hydrocarbon products: 0° C. stabilizer gases: CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	Liquids plus solids: G./m.³ [b]	Weight, percent	Space-time yield [c]	CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
a	90	178	100	70	17.5	0.0	6.9	26.5	67.6	73.5	6.76	8.9	166.2
b	90	182	100	68	[d]	[d]	[d]	[d]	[e] 85.1	[d]	8.51	3.7	104.2
c	114	185	100	69	20.3	4.9	12.3	28.9	92.3	71.1	9.23	10.9	186.7
d	112	184	101	69	9.6	.5	10.8	20.1	83.0	79.9	8.38	8.0	161.1
e	114	185	107	74	9.4	1.5	9.5	21.7	74.0	78.3	7.92	4.6	144.7
f	114	189	100	72	15.2	3.5	11.9	24.2	95.8	75.8	9.58	6.1	194.0
g	114	184	100	73	13.0	3.5	11.2	26.4	77.0	73.6	7.70	4.4	166.4
h	114	186	80	70	23.3	1.4	2.4	26.1	77.2	73.9	6.18	5.9	191.4
i	89	186	101	73	21.3	6.1	12.4	32.2	83.7	67.8	8.45	7.3	173.2
j	114	187	100	71	23.1	7.9	11.9	33.3	85.9	66.7	8.59	7.2	166.5
k	114	190	97	71	19.0	3.7	13.2	26.9	97.8	73.1	9.49	2.4	168.4
l	115	192	101	72	27.4	4.0	15.4	34.7	87.9	65.3	8.88	6.2	193.5
m	115	188	103	70	23.5	5.0	16.4	35.9	80.1	64.1	8.25	7.3	172.6
n	115	190	105	70	25.3	4.0	13.7	35.0	79.9	65.0	8.39	7.6	175.4
o	114	190	102	72	24.2	4.0	14.2	35.0	78.8	65.0	8.04	9.4	171.4

Test X–31, 36.0 grams of Co : ThO_2 : Filter-Cel

[Catalyst 108B; 100 p. s. i. pressure, $2H_2 + 1CO$; slow reduction; slow induction at 100 p. s. i. pressure with contraction schedule]

a	114	174	101	54	11.7	4.2	12.2	34.7	52.9	65.3	5.34	7.3	174.6
b	110	183	104	69	[d]	[d]	13.6	[d]	69.7	[d]	7.25	4.4	163.7
c	114	182	96	73	13.3	4.0	12.2	21.9	85.4	78.1	8.20	2.2	136.4
d	89	180	99	73	25.8	5.0	12.9	36.7	75.3	63.3	7.46	6.3	140.3
e	114	188	108	68	26.8	3.9	12.8	30.4	99.6	69.6	10.76	8.3	167.2
f	114	189	95	72	15.9	4.4	14.6	24.3	109.0	75.7	10.35	2.2	175.4
g	115	195	99	71	24.0	4.1	14.2	37.1	71.9	62.9	7.12	2.9	165.0
h	115	190	103	73	[d] 26.2	[d]	[d]	[d]	[e] 87.1	[d]	8.97	8.6	169.1
i	115	190	94	74	34.2	4.6	11.5	35.1	93.1	64.9	8.75	13.0	179.5
j	114	190	99	73	7.5	4.7	14.9	24.0	85.7	76.0	8.48	14.7	170.3

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
[e] Does not include C_3 or higher in gas from charcoal recovery.

The relative efficiency of Hyflo Super-Cel, Filter-Cel, and Portuguese kieselguhr as carriers is shown in figures 21 and 22, tables 39, 40, and 42. Hyflo Super-Cel is definitely inferior to Filter-Cel and Portuguese kieselguhr, the space-time yield being about 2 kilograms lower than for the latter materials. The catalyst made with Filter-Cel kieselguhr gave slightly higher space-time yields but also operated at a higher temperature than catalysts prepared with Portuguese kieselguhr. This difference in operating temperature is in part due to the greater weight of catalyst in tests X19 and X27. The catalysts produced with Hyflo Super-Cel gave lower space-time yields and operated at significantly higher temperatures than catalysts prepared with Portuguese or Filter-Cel kieselguhrs. In figure 22, for test X21, the operating pressure was increased from atmospheric to 100 pounds per square inch after 1,500 hours of operation. At the higher operating pressure the space-time yield was about the same as at atmospheric pressure.

TABLE 46.—*Test X–30; 85.7 grams of Co : ThO_2 : MgO : Filter-Cel*

[Catalyst 89J; pellets; atmospheric pressure; $2H_2 + 1CO$; rapid reduction; slow induction with contraction schedule]

Test No.	Duration of test, hours	Average temperature, ° C.	Space velocity [a]	Contraction, percent	Hydrocarbon products							CO_2, g./m.³ [b]	H_2O, g./m.³ [b]
					0° C. stabilizer gases				Liquids plus solids				
					CH_4, g./m.³ [b]	C_2, g./m.³ [b]	C_3+C_4, g./m.³ [b]	Weight, percent	g./m.³ [b]	Weight, percent	Space-time yield [c]		
a	111	176	86	52	6.6	4.3	6.6	18.8	75.8	71.2	6.52	4.8	136.2
b	115	184	90	74	14.2	.7	8.2	15.9	121.3	84.1	10.93	2.8	194.2
c	114	190	80	73	21.5	4.9	18.7	23.8	144.2	76.2	11.53	12.4	(d)
d	114	200	90	67	(d)	(d)	(d)	(d)	136.4	(d)	12.27	11.9	(d)
e	114	194	111	70	12.4	1.7	11.2	18.2	113.6	81.8	12.60	8.9	210.3
f	89	189	100	71	14.8	0	18.5	21.5	121.5	78.5	12.15	7.6	208.1
g	114	188	106	71	17.1	3.5	13.6	22.8	105.5	77.2	11.17	9.3	188.3
h	114	192	95	72	17.1	1.9	17.0	25.2	107.1	74.8	10.17	10.1	203.2
i	115	192	105	72	17.2	2.7	14.4	24.7	104.8	75.3	11.00	4.5	188.6
j	115	190	103	76	8.0	.6	15.7	20.9	92.0	79.1	9.48	5.8	173.0
k	115	194	102	73	14.4	1.5	13.7	22.2	103.9	77.8	10.60	14.0	193.7
l	114	192	101	74	13.7	.7	18.4	24.7	99.8	75.3	10.08	13.1	186.5

[a] Volume of feed gas per hour per volume of catalyst.
[b] Grams per cubic meter of feed gas.
[c] Kilograms per cubic meter of bulk volume of catalyst per hour.
[d] Sample or part of sample lost.
[e] Does not include C_5 or higher in gas from charcoal recovery.

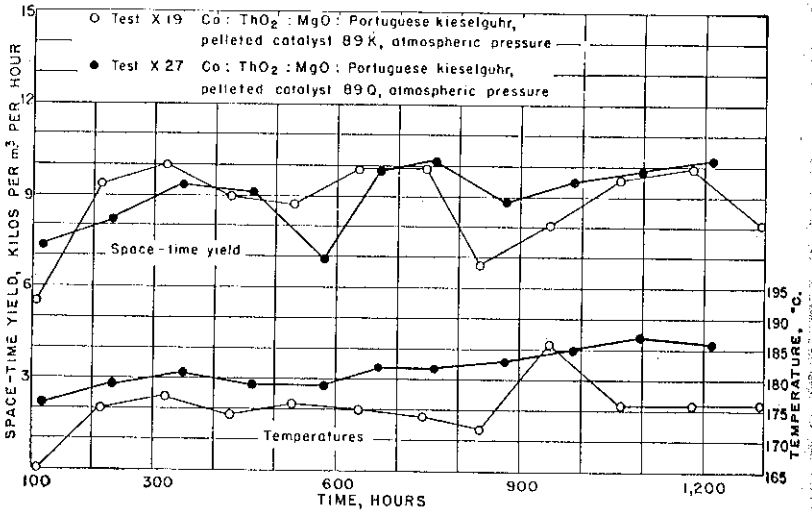

FIGURE 17.—Reproducibility of catalyst preparations and tests.

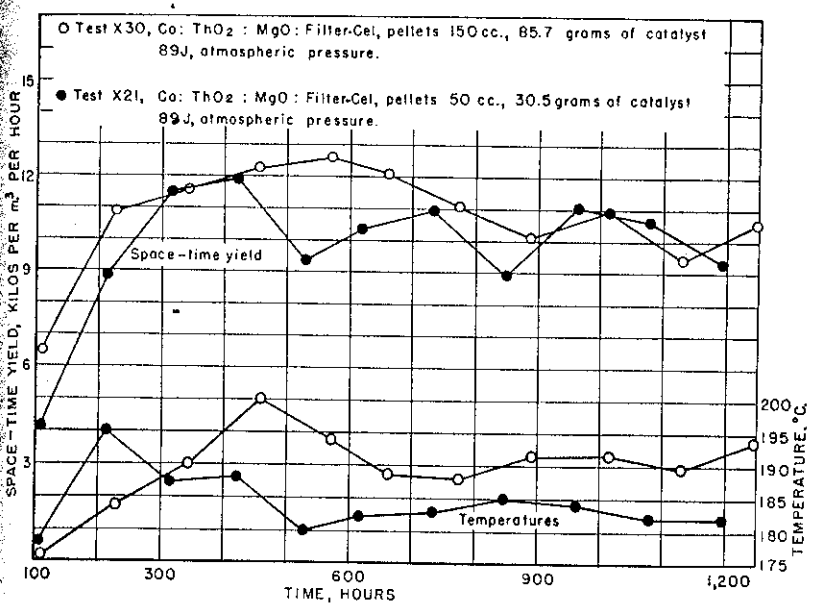

FIGURE 18.—Comparison of operation with 30-cm. and 90-cm. depths of catalyst.

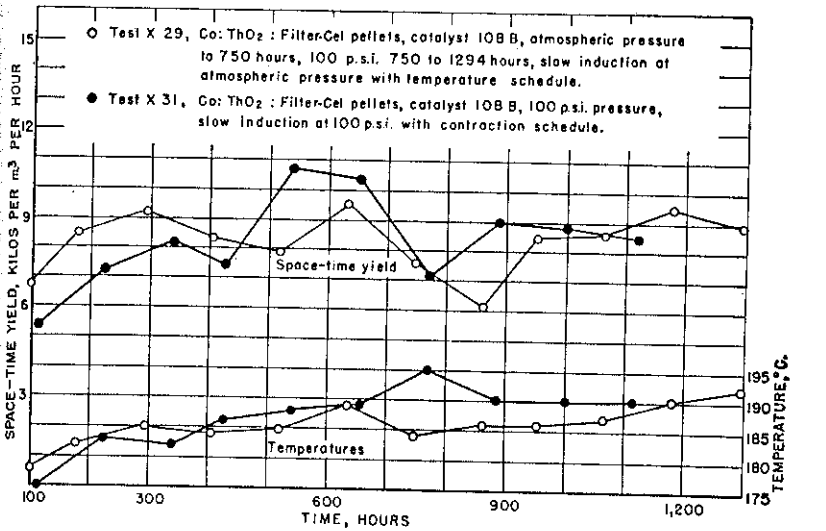

FIGURE 19.—Comparison of induction at atmospheric pressure with that at 100 p. s. i.

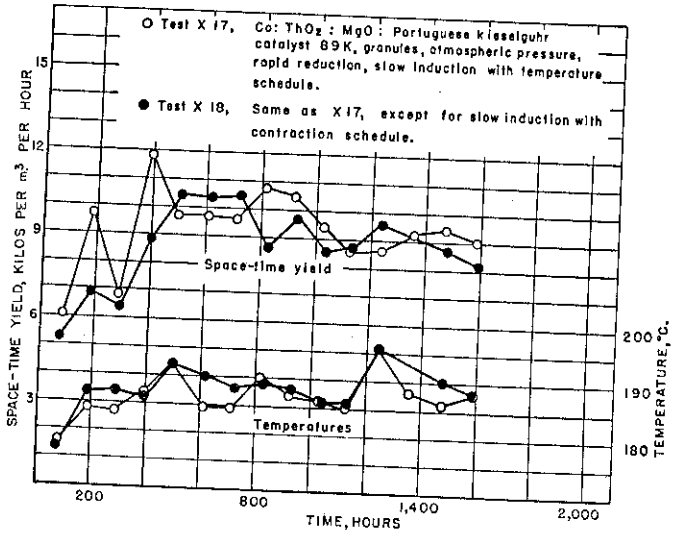

FIGURE 20.—Comparison of two induction procedures.

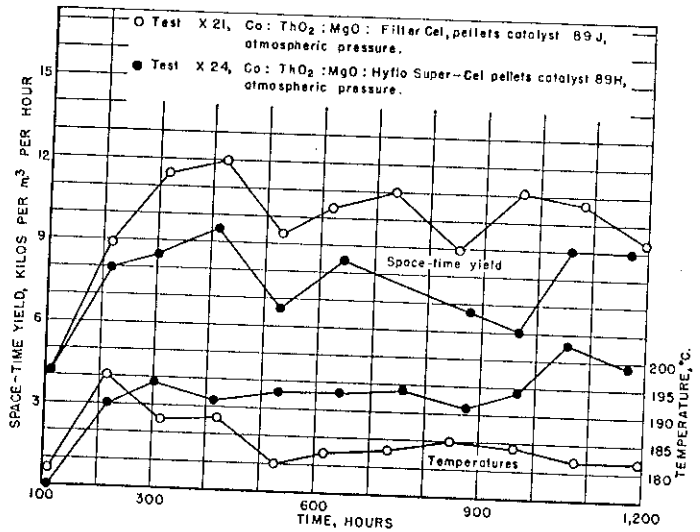

FIGURE 21.—Relative efficiency of Filter-Cel and Celite (Johns-Manville Co. H. S. G.).

The activity of the cobalt–thoria–magnesia–Portuguese kieselguhr catalyst in the form of pellets and of granules is illustrated in figure 23. The space-time yield is about the same for the two forms, but the operating temperature of the granular catalyst is about 12° C. higher than for the pelleted catalyst. This difference in temperature was not unexpected because the weight of catalyst used in test X18 was 16.0 grams, as compared with 38.8 grams in test X19. When compared at equal flows per gram of catalyst, both pellets and granules operated at about the same temperature (see table 47 and figure 26).

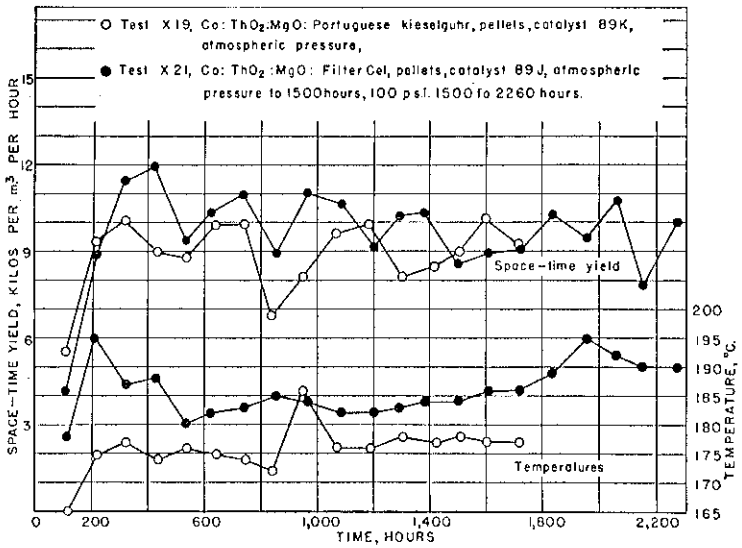

FIGURE 22.—Relative efficiency of Portuguese kieselguhr and Filter-Cel.

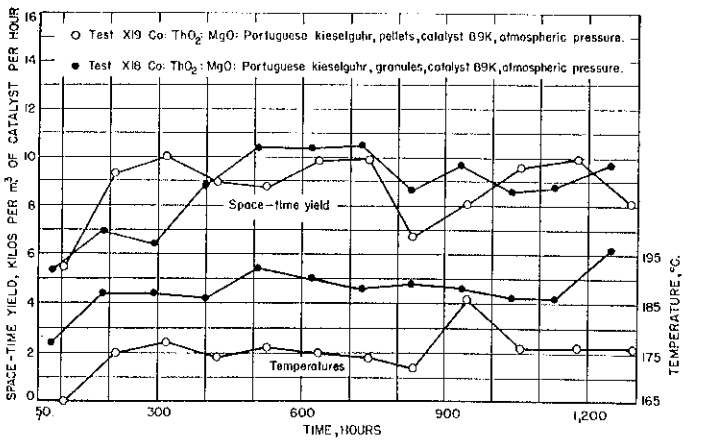

FIGURE 23.—Relative activity of pellets (about 0.8 bulk density) and granules (about 0.3 bulk density).

TABLE 47.—*Summary of statistical analysis of catalyst data*

Test No.	Reference to—		Catalyst and form [1]	Weight of catalyst, g.	Surface area, m.² cc. [2]	Micropore volume, cc./g. [2]	Means of catalyst testing data					
	Fig.	Table					Contraction, percent	Temperature, ° C.	Grams per cubic meter			
									CH_4	C_1–C_4	CO_2	Wax plus oil
X-19	13	24	89K–P	38.8	68.1	0.47	72.7	[3] 176	[4] 21.6	[4] 37.0	[3] 12.7	90.8
X-27	13	29	89Q–P	34.2	58.6	.54	68.8	[3] 182	[4] 17.1	[4] 31.7	[3] 6.1	91.8
X-21 [5]	14	25	89J–P	30.5	54.1	.67	72.0	[3] 186	[3] 21.3	33.9	8.0	[3] 102.2
X-30 [6]	14	31	89J–P	[6] 85.7	50.7	.67	71.7	[3] 191	[3] 15.6	31.6	8.7	[3] 115.0
X-29 [7]	15	30	108B–P	38.8	55.6	.56	70.9	[4] 185	[3] 13.5	[3] 27.4	6.4	84.5
X-29 [8]	15	30	108B–P	38.8	55.6	.56	71.3	[4] 189	[3] 24.4	[3] 43.1	7.0	84.6
X-29 [8]	15	30	108B–P	38.8	55.6	.56	71.3	189	24.4	43.2	7.0	84.6
X-31 [9]	15	30	108B–P	36.0	51.6	.56	71.8	187	23.7	40.7	7.0	86.3
X-21 [5]	-------	25	89J–P	30.5	54.1	.67	72.0	[3] 186	[3] 21.3	[3] 33.9	[4] 8.0	102.2
X-21 [10]	-------	25	89J–P	30.5	54.1	.67	69.5	[3] 192	[3] 26.9	[3] 42.0	[4] 9.3	105.6
X-17	16	22	89K–G	16.9	34.1	1.28	74.4	[4] 186	17.1	33.4	8.3	[4] 97.0
X-18	16	23	89K–G	16.0	32.3	1.28	73.5	[4] 188	17.6	30.2	8.0	[4] 89.5
X-21 [5]	17	25	89J–P	30.5	54.1	.67	72.0	[3] 186	21.3	33.9	8.0	[3] 102.2
X-24	17	27	89H–P	35.2	50.0	.47	62.7	[3] 194	20.3	35.9	[3] 16.6	[3] 85.7
X-19	18	24	89K–P	38.8	68.1	.47	72.7	[3] 176	21.6	[4] 37.0	[3] 12.7	[3] 90.8
X-21 [5]	18	25	89J–P	30.5	54.1	.67	72.0	[3] 186	21.3	[4] 33.9	[3] 8.0	[3] 102.2
X-18	19	23	89K–G	16.0	32.3	1.28	73.5	[3] 188	[4] 17.6	[4] 30.2	[3] 8.0	89.5
X-19	19	24	89K–P	38.8	68.1	.47	72.7	[3] 176	[4] 21.6	[3] 37.0	[3] 12.7	90.8
X-21 [5]	-------	25	89J–P	30.5	54.1	.67	72.0	[3] 186	[3] 21.3	[4] 33.9	[3] 8.0	102.2
X-26 [11]	-------	28	89J–G	11.0	22.9	1.97	63.0	[3] 194	[3] 15.4	[4] 27.7	[3] 4.4	85.4
X-21 [5]	-------	25	89J–P	30.5	54.1	.67	72.0	[3] 186	[4] 21.3	[4] 33.9	[3] 8.0	[3] 102.2
X-22	-------	26	89O–P	28.5	73.7	.69	69.6	[3] 181	[4] 16.9	[4] 29.0	[3] 5.6	[3] 95.9
X-18	-------	23	89K–G	16.0	32.3	1.28	73.5	[3] 188	[4] 17.6	30.2	[3] 8.0	89.5
X-26 [11]	-------	28	89J–G	11.0	22.9	1.97	63.0	[3] 194	[4] 15.4	27.7	[3] 4.4	85.4
X-23	-------	27	89I–P	38.7	58.2	.43	66.8	[3] 190	20.3	35.3	[4] 14.1	[4] 76.2
X-24	-------	27	89H–P	35.2	50.0	.47	62.7	[3] 194	20.3	35.9	[4] 16.6	[4] 85.7

[1] G=granules; P=pellets.
[2] Areas and pore volumes of unreduced catalysts.
[3] Probably significant.
[4] Possibly significant.
[5] 105 to 1500th hours at atmospheric pressure.
[6] Long converter, which holds 3 times the volume of small converters.
[7] 105 to 750th hours at atmospheric pressure.
[8] 750 to 1294th hours at 100 lb. per square inch.
[9] Entire experiment at 100 lb. per square inch.
[10] 1,500 to 2,260th hours at 100 lb. per square inch.
[11] Averaged over period of operation at space velocity of 100.

Because the data of the catalyst testing show considerable variation from week to week as shown for temperatures and space-time yields in figures 17 and 22, it was desirable to test the significance of the differences of the means by statistical methods as developed by Student [6] for small samples. With this method the probability that two groups of data may be samples of the same "parent group" may be estimated. The probability of finding differences of means greater than observed, on the basis of two samples taken from the same parent group was computed. If this probability is less than 8 percent, the samples were probably from different parent groups, and the difference

[6] Student [On the Probable Error of the Mean]: Biometrika, vol. 6, 1908, p. 1.
Yule, G. U., and Kendall, M. G., An Introduction to the Theory of Statistics: London, 1937, p. 442.

was probably significant. For probabilities from 8 to 25 percent the differences were regarded as possibly significant, and for probabilities greater than 25 percent, differences were not considered significant.

In addition to the temperatures and space-time yields, which are compared graphically in figures 17 to 22, the temperature and the yields of methane, C_1 to C_4 hydrocarbons, carbon dioxide, and oil plus wax, per cubic meter of synthesis gas were compared statistically in table 47. In all tests the means of the data for the first 1,000 hours following the induction week were compared, except where the periods of comparison are indicated. Pertinent data about the catalysts—the weight of catalyst, surface area of unreduced catalyst in square meters per cubic centimeter of catalyst, and micropore volume in cubic centimeters per gram—are included in the table. It should be noted that the space-time yields as used in the previous figures at a space velocity of 100, equal the yield of liquids plus solids per cubic meter multiplied by a constant; hence, any significant difference for the liquids plus solids is also a significant difference in the space-time yield.

The conclusions from the table are the same as those from the figures, and several additional observations can be made regarding the yields of CH_4, C_1–C_4 hydrocarbons, and CO_2. When significant differences in average temperatures occur, the catalyst operating at the lower temperature usually has a greater surface area per cubic centimeter and a greater weight per charge. This will be discussed in the section on surface areas. If significant differences in CH_4, C_1–C_4 hydrocarbons, or CO_2 occur under similar operating conditions, the catalyst producing smaller amounts of these products usually has a higher micropore volume; that is, catalysts with a lower density produce less of these undesirable products.

In X19 and X27 significant differences occur in the yields of CO_2 and possibly significant differences in the yields of CH_4 and C_1–C_4 hydrocarbons, in addition to the difference in temperature shown in figure 14. The differences in the product distribution reflect the difference in pore volumes. Comparison of tests X21 and X30 with pelleted catalyst 89J in the 30-centimeter and 90-centimeter converters, respectively, indicate that the catalyst in the longer converter produced less CH_4 and more liquids plus solids, and operated at a higher temperature than in the short converter. The difference in the yields of liquids plus solids, however, may be due to the relatively smaller losses in recovering the larger amounts of products from the longer converter.

Comparison of the periods of atmospheric and 100-pound-per-square-inch operation of test X29 indicates that more methane and C_1–C_4 hydrocarbons were formed in the pressure operation. The temperatures may not be comparable because the catalyst was operated for 750 hours before the pressure operation was begun. Comparison of the pressure operation of test X29 and test X31 shows that the yields of CH_4 and C_1–C_4 hydrocarbons were about the same, indicating that the atmospheric operation of test X29 resulted in the same distribution of products as in X31, which was operated under pressure from the beginning. The distribution of products of the atmospheric and pressure operation of test X21 is similar to that in

run 29, in that the pressure operation produced more CH_4 and C_1–C_4 hydrocarbons than atmospheric operation.

Differences of the means of tests X17 and X18 for temperature and wax plus oil are possibly significant. The difference in temperature may be explained by the slightly greater weight of catalyst in test X17.

In tests X21 and X24 with pelleted catalysts 89J and H, prepared with Filter-Cel and Hyflo Super-Cel kieselguhrs, respectively, the temperature of operation in test X24 was significantly higher. The means of CH_4 and C_1C_4 hydrocarbon yields were about the same, but if the catalysts ware compared at equal contractions the yields of CH_4 and C_1–C_4 hydrocarbons probably would be significantly higher for test X24. The catalyst in X24 produced significantly more CO_2 than that in test X21, which is consistent with the larger pore volume of catalyst 89J.

The temperature and space-time yields of liquids plus solids in tests X19 and X21 have been discussed previously (fig. 22). Significant differences are found in the means of C_1–C_4 hydrocarbons, the catalyst in text X19 with the smaller pore volumes producing larger amounts of these products.

The differences in temperature in tests X18 and X19 with granular and pelleted catalyst 89K have been discussed in connection with figure 23. The catalyst in granular form produced significantly less CH_4, C_1–C_4 hydrocarbons, and CO_2 than the corresponding pelleted

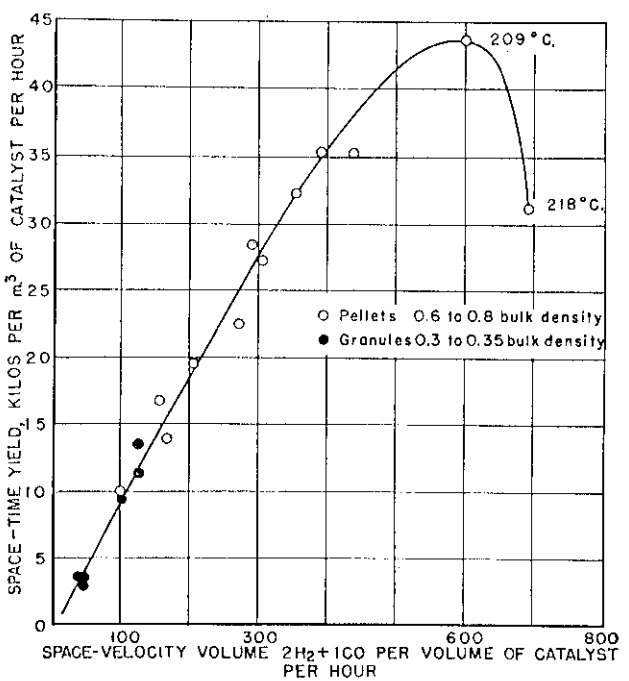

FIGURE 24.—Space-time yield at different space velocities for Co : ThO_2 : MgO : kieselguhr at 185°–200° C.

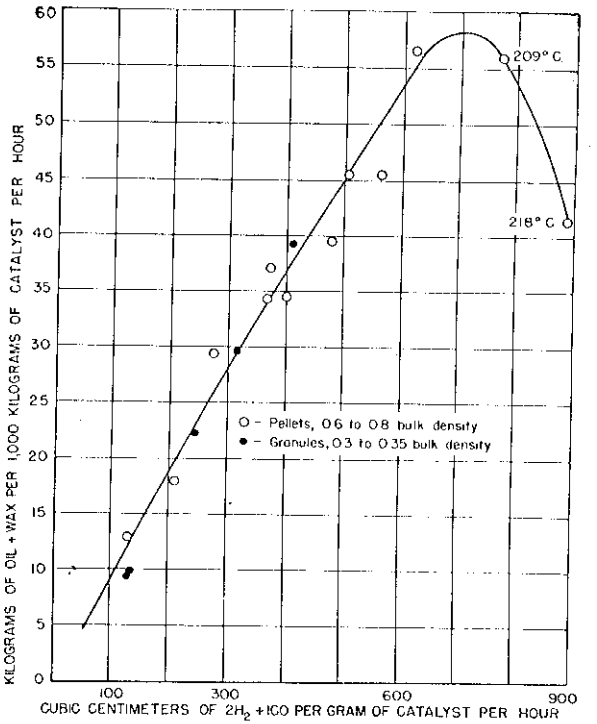

FIGURE 25.—Yield of oil per unit weight of catalyst per hour at different gas throughputs for Co : ThO MgO : kieselguhr at 185°–200° C.

catalyst, although the yield of liquids plus solids was about the same for the two forms. Tests X21 and X26 with pelleted and granular catalyst 89J are similar to tests X18 and X19, in that the granular catalyst produced less CH_4, C_1–C_4 hydrocarbons, and CO_2 than the corresponding pellets. In a comparison of granular catalysts 89K and J in tests X18 and X26, the difference in the averages of CH_4 is possibly significant, but this difference would disappear if the catalysts were compared at equal contraction.

Tests X21 and X22 show that catalyst 89J produced more CH_4, C_1–C_4 hydrocarbons, and CO_2 than 89O, even though the pore volumes were about equal.

Tests X23 and X24 with catalysts 89I and H, both of which contained Hyflo Super-Cel as a carrier, were similar, except that the yield of liquids plus solids for test X23 was lower.

In figures 24 and 25 the space-time yield for all tests at 185° to 200° C. with the cobalt–thoria–magnesia–kieselguhr catalysts was plotted againstthe space velocity. Figure 24 shows the variables calculated on a catalyst-volume basis and figure 25 on a weight basis. The data for the granules are in table 38, test X18, and table 43, test X26, and for the pellets in table 39, test X19, and table 41, test X22. For both figures 24 and 25 the data for the granules were consistent with those for the pellets. Both curves have a maximum beyond

which it was necessary to increase the reaction temperature a greater amount per unit change in space velocity to maintain a desired contraction. The decrease in space-time yield beyond this point may be due to two causes: (1) Overheating of the catalyst owing to the large amount of heat produced per unit volume of catalyst may cause changes in the catalyst and in the reaction mechanism; (2) at these high flows, diffusion may be the controlling step in the synthesis. At lower flows, diffusion is probably not important, as indicated by the rather high apparent activation energy of 25 kilocalories per mole (figs. 26 and 27 and accompanying text). Factor 1 could be eliminated or decreased by making the distance between catalyst and cooling surface shorter.

In test X19 the catalyst activity decreased when the operating temperature was 207° C. or higher. Operation at 218° C. caused some permanent loss of activity, as indicated by the increased temperature of operation at a given space velocity and contraction before (X19q) and after (X19x) operation at 218° C.

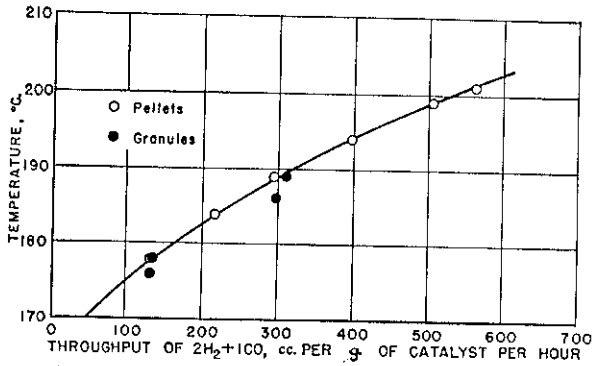

FIGURE 26.—Variation of temperature with flow of $2H_2 + 1CO$ at constant contraction.

In figure 26 the data given in table 48 for variation of reaction temperature with throughput of synthesis gas at 65.4 to 71.6 percent contraction are presented. A correction can be calculated assuming that the synthesis reaction rate is directly proportional to the partial pressure of $2H_2 + 1CO$, so as to provide comparisons at a given contraction, for example, at 70 percent. The reproducibility of the tests

TABLE 48.—*Temperature coefficient of synthesis rate on cobalt catalysts*

Test No.	Temperature		Throughput of $2H_2+1CO$ cc./g. of catalyst/hour	Contraction
	°C.	°K.		
X19	178	451	130	70.0
	184	457	216	67.8
	189	462	294	71.5
	194	467	397	71.6
	199	472	504	70.4
	201	474	562	66.9
X18	189	462	309	65.4
X17	178	451	134.5	66.7
	176	449	130	67.2
	186.5	459.5	296	67.2

is not good enough, however, to justify such a correction. In figure 27 from the slope of the line obtained by plotting the logarithm of the throughput of $2H_2 + 1CO$ against the reciprocal of the temperature (in degrees absolute), the activation energy of the reaction was calculated. It is 24 ± 2 kilogram-calories per mole.

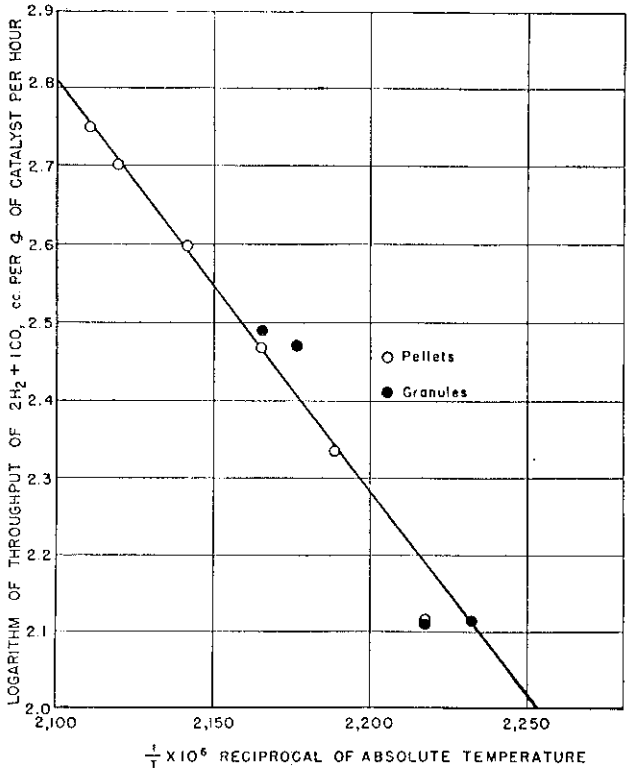

FIGURE 27.—Temperature coefficient of synthesis on cobalt.

CHARACTERISTICS OF PRODUCTS FROM COBALT CATALYSTS

Bromine numbers are given in table 49 for liquid products from tests X17 to X24, and X26 and X27, in all of which 89-type cobalt–thoria–magnesia–kieselguhr catalysts were tested at atmospheric pressure. The bromine numbers varied from 6 to 15 for catalysts operating below 195° C. and at low flows of synthesis gas. Operation at higher flows and at correspondingly higher temperatures (to maintain constant contraction) produced liquids with bromine numbers up to 33, this number increasing with increasing flows and temperatures.