Table II-1. SUMMARY OF KINETIC STUDIES OF THE FISCHER-TROPSCH SYNTHESIS ON COBALT-BASED CATALYSTS

REFERENCE	CATALYST	REACTOR TYPE	OPERATING CONDITIONS T [°C]	P [MPa]	H_2/CO_{in} [molar]	INTRINSIC KINETIC EXPRESSION [a]	EQ
Brötz[1]	$Co/MgO/ThO_2/$ kies.	Fixed-bed	185-200	0.1	2	$-R_{H_2+CO} = \frac{aP_{H_2}^2}{P_{CO}}$	(3)
Anderson[2]	$Co/ThO_2/$kies.	Fixed-bed	186-207	0.1	0.9-3.5	$-R_{H_2+CO} = \frac{aP_{H_2}^2 P_{CO}}{(1+bP_{H_2}^2 P_{CO})}$	(4)
Yang et al.[3]	$Co/CuO/Al_2O_3$	Fixed-bed	235-270	0.17-5.5	1.0-3.0	$-R_{H_2+CO} = aP_{H_2}P_{CO}^{-0.5}$	(5)
Pannell et al.[4]	$Co/La_2O_3/Al_2O_3$	Berty (low conversion)	215	0.49-0.8	2	$-R_{H_2+CO} = aP_{H_2}^{0.55}P_{CO}^{-0.33}$	(6)
Rautavuoma and van der Baan[5]	Co/Al_2O_3	Fixed-bed (low coversion)	250	0.1	0.2-4.0	$-R_{CO} = \frac{aP_{H_2}P_{CO}^{1/2}}{(1 + bP_{CO}^{1/2})^3}$	(7)
Wang[6]	$Co/B/Al_2O_3$	Fixed-bed (low conversion)	181	0.1-0.2	0.25-4.0	$-R_{CO} = aP_{H_2}^{0.68}P_{CO}^{-0.5}$	(8)
Sarup and Wojiechowski[7]	Co/kies.	Berty	190	0.2-1.5 [b]	0.5-8.3 [b]	$-R_{CO} = \frac{aP_{CO}^{1/2}P_{H_2}^{1/2}}{(1+bP_{CO}^{1/2}+cP_{H_2}^{1/2}+dP_{CO})^2}$	(9)
and Wojiechowski[8]						$-R_{CO} = \frac{aP_{CO}P_{H_2}^{1/2}}{(1+bP_{CO}+cP_{H_2}^{1/2})^2}$	(10)

[a] a, b, c, and d in these equations are temperature-dependent constants.

[b] These ranges of operating conditions are estimated from their experimental data.

Table II-2.

ACTIVITY FOR REPEATED CONDITIONS OF 240°C, 0.79 MPa, $H_2/CO=2$, AND SYNTHESIS GAS FEED RATE OF 0.067 Nl/min/g of catalyst†

Time-On-Stream [h]	Oxygen Closure [% molar]	$-R_{H_2+CO}$ [mmol/min/gcat]	P_{H_2} [MPa]	P_{CO} [MPa]
257.5	97.06	0.678	0.48	0.25
617.0	101.23	0.680	0.48	0.24
1073.0‡	100.21	0.594	0.45	0.25
2176.5	99.89	0.694	0.47	0.24

† Flow is calculated at standard conditions; grams of catalyst are on an unreduced basis.

‡ H_2/CO and feed rate were slightly lower for this material balance at 1.95 and 0.066 standard l/min/gcat, respectively.

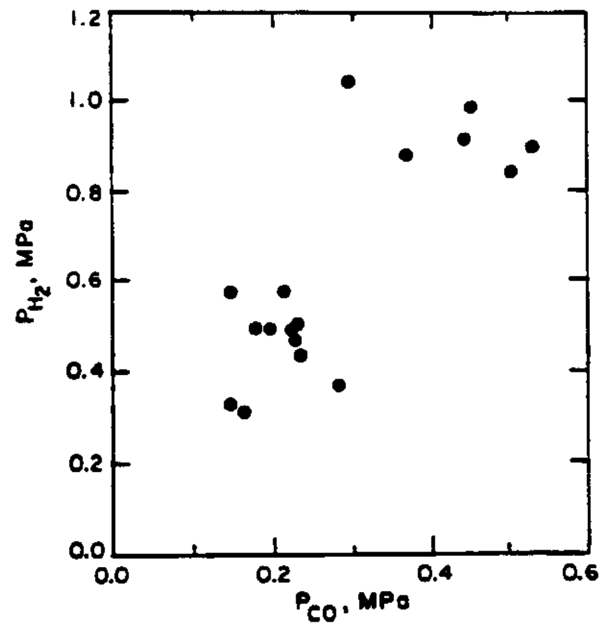

Fig. II-1 Plot showing lack of covariance between P_{H_2} and P_{CO} at 220°C.

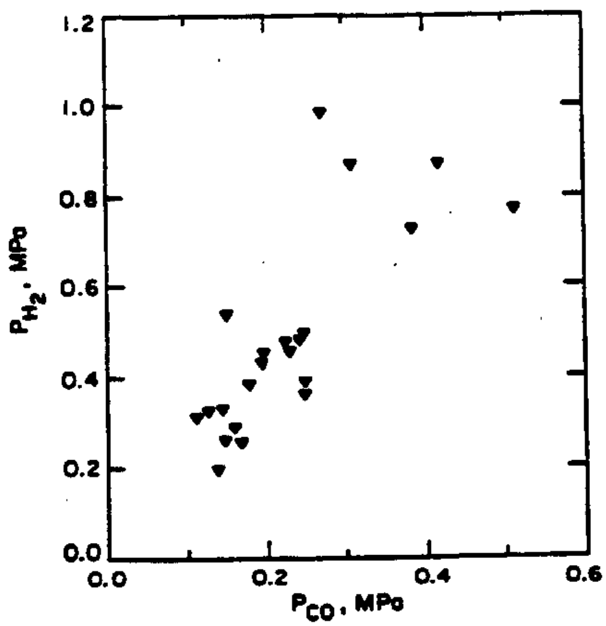

Fig. II-2 Plot showing lack of covariance between P_{H_2} and P_{CO} at 240°C.

Table II-3. R^2 for Linearized Expressions

eq	T, °C	R^2	eq	T, °C	R^2
17	220	0.954	20	220	0.970
	240	0.909		240	0.886
18	220	0.938	21	220	0.968
	240	0.945		240	0.984
19	220	0.927			
	240	0.590			

Table II-4. Nonlinear Regression Statistical Analyses

eq	residuals [sum of squared errors]	F ratio	R^2
4	0.340	42.06	0.663
7	0.072	303.27	0.929
14	0.245	85.82	0.758
15	0.214	101.61	0.788
16	0.062	361.22	0.938

Table II-5. Results of Nonlinear Fit of Data from This Study at 220 and 240 °C to Eq 16

reactor temp, °C	a[a]	std error of a[a]	t value[b] of a	b[c]	std error of b[b]	t value[b] of b
240	75.76	9.20	8.23	11.61	0.97	12.02
220	53.11	1.38	38.63	22.26	3.63	6.62

[a] In mmol/(min·g of catalyst·MPa^2). [b] There were 23 data points collected at 240 °C and 17 at 220 °C. Critical t values for 99% confidence that the parameters are statistically significant are $t_{0.995,21}$ = 2.831 for 240 °C; $t_{0.995,15}$ = 2.947 for 220 °C. t values above these critical values indicate that one can be 99% confident that the parameters are significant. [c] In 1/MPa.

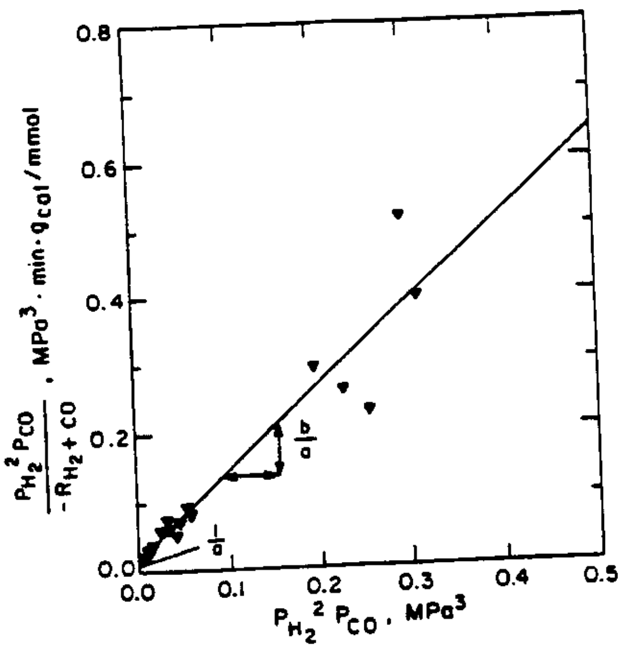

Fig. II-3 Test of eq 17 with experimental results at 240°C. Solid line is best fit linear regression line.

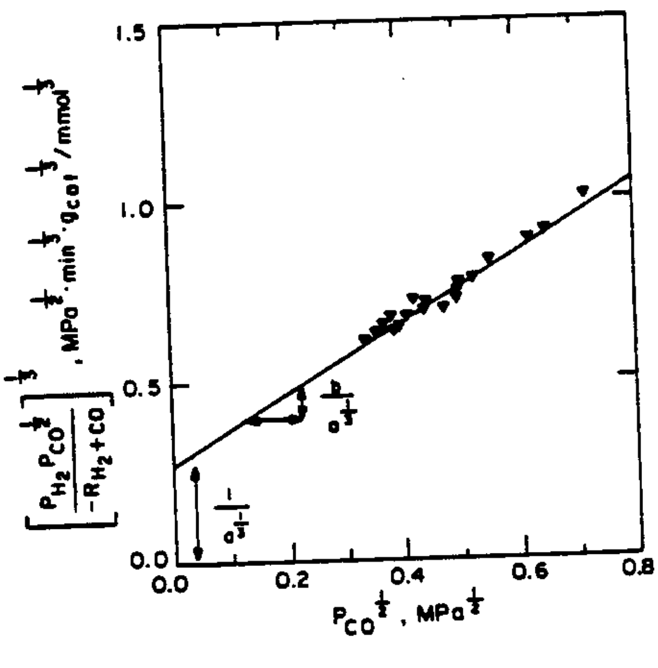

Fig. II-4 Test of eq 18 with experimental results at 240°C. Solid line is best fit linear regression line.

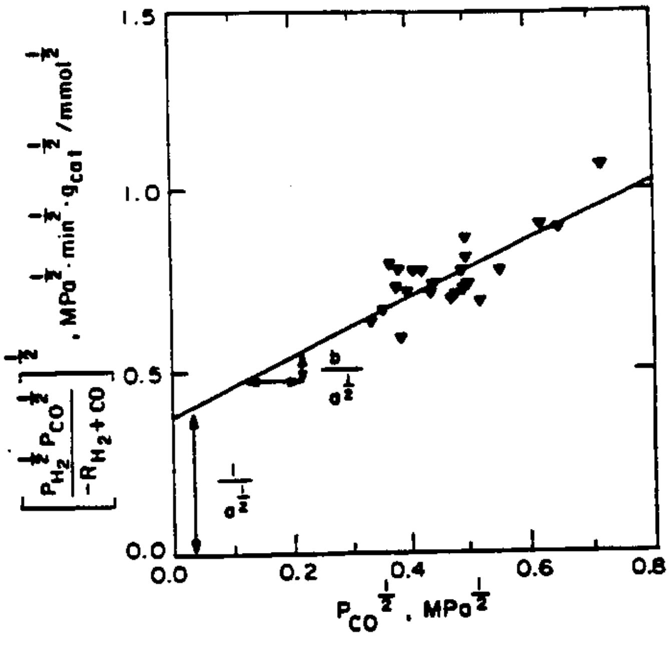

Fig. II-5 Test of eq 19 with experimental results at 240° C. Solid line is best fit linear regression line.

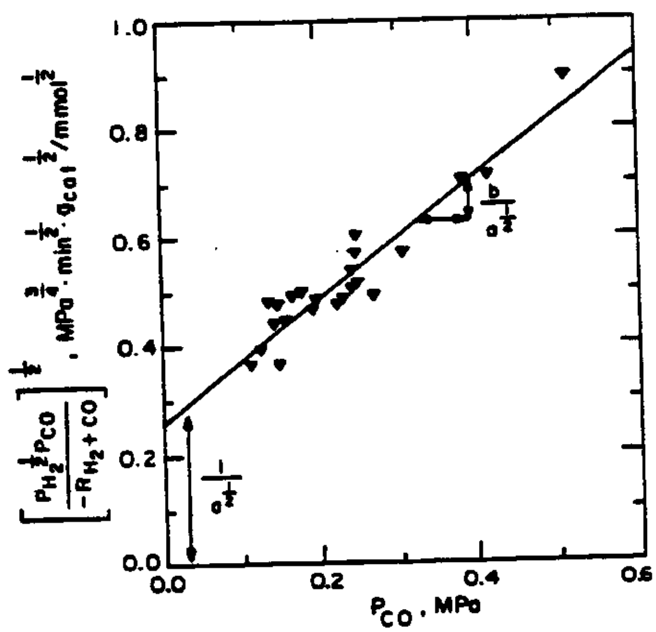

Fig. II-6 Test of eq 20 with experimental results at 240° C. Solid line is best fit linear regression line.

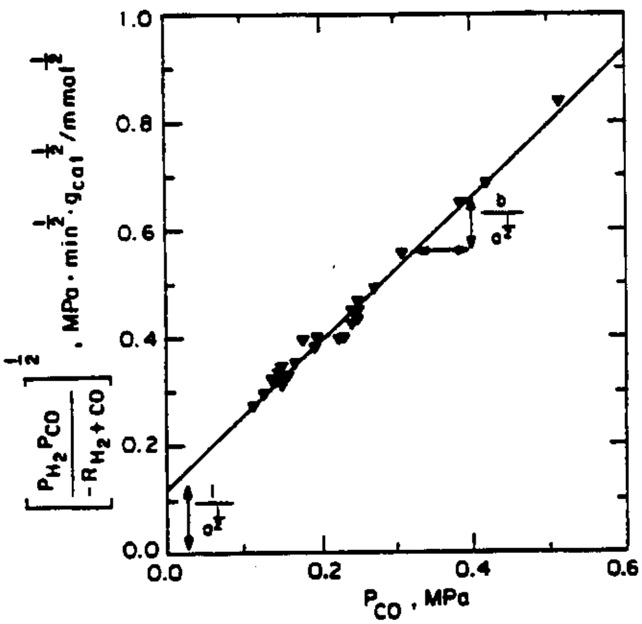

Fig. II-7 Test of eq 21 with experimental results at 240°C. Solid line is best fit linear regression line.

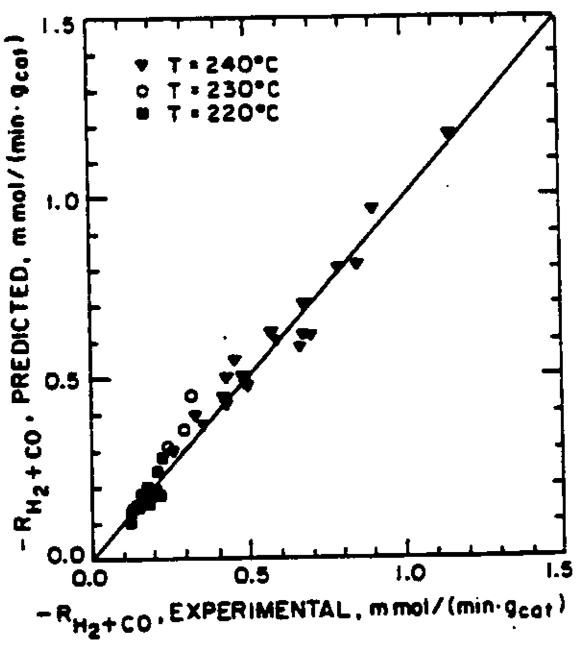

Fig. II-8 Parity plot comparison of data with prediction from eq. 16. Solid line gives predicted values.

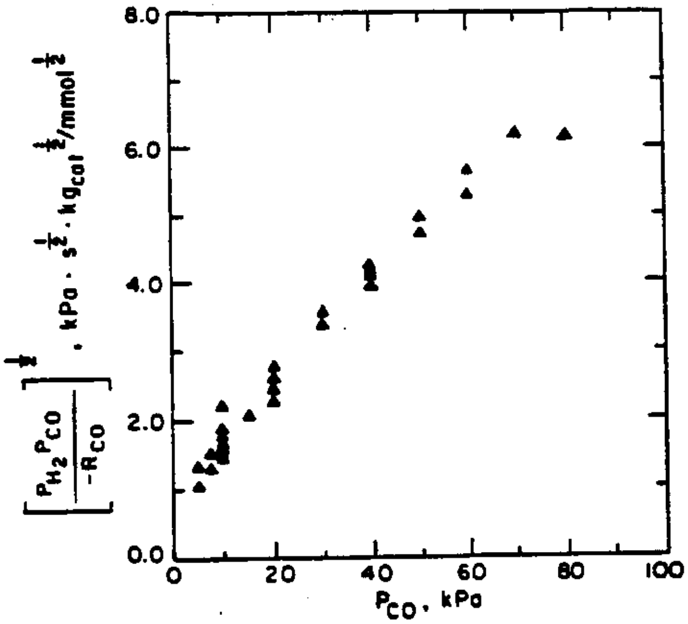

Fig. II-9 Test of eq 21 with data from Rautavuoma and van der Baan.[5]

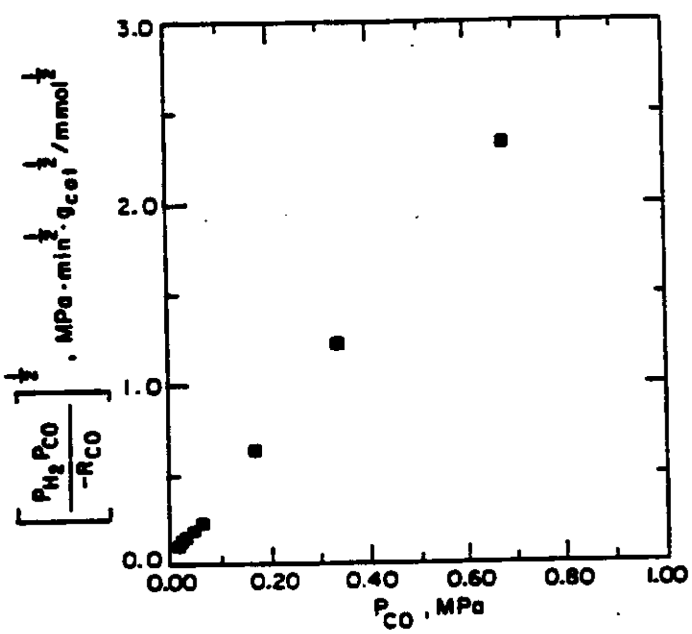

Fig. II-10 Test of eq 21 with data from Wang[6] (pp 100-101).

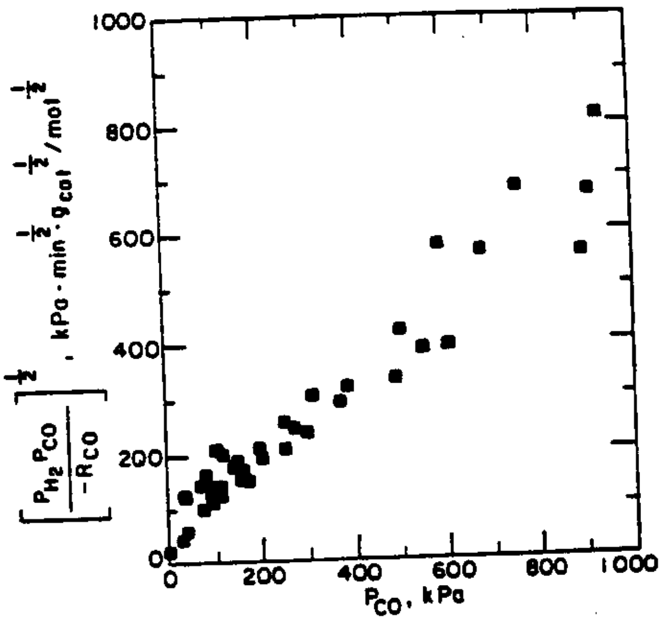

Fig. II-11 Test of eq 21 with data from Sarup and Wojciechowski.[7]