CATALYSIS OF COAL GASIFICATION AT ELEVATED PRESSURE

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INTRODUCTION

The gasification of coal with steam and oxygen under elevated pressure is an essential step in the Bureau of Mines Synthane process for converting coal to synthetic pipeline gas. Use of a suitable catalyst or additive in the gasification step could conceivably improve the gasification of coal. Earlier investigators have catalyzed the gasification of coke and carbon with various additives and have demonstrated that some benefits would result from the catalysis of gasification at atmospheric pressure. Vignon (1), for example, showed that the percentage of methane in water gas made from coke can be increased significantly by addition of lime to the coke. Neumann, Kroger, and Fingas (2) demonstrated the feasibility of improving the gasification of graphite at 450° to 1,000° C through addition of K_2O, CuO, and other salts. Continuation of the studies by Kroger and Melhorn (3) indicated that addition of either 8 pct Li_2O or (8 pct K_2O + 3 pct Co_3O_4) to low-temperature coke increased steam decomposition at temperatures of 500° to 700° C. More recently, Kislykh and Shishakov (4) studied the effect of $Fe(CO)_5$, (Fe_2O_3 + $CuCl_2$), K_2CO_3, and NaCl upon fluid-bed gasification of wood charcoal at 750° C and atmospheric pressure. They found that sodium chloride was the most effective additive, accelerating gasification by 62 pct and increasing steam decomposition 2.5-fold.

The work on catalysis reviewed thus far does not include gasification at elevated pressures nor the use of volatile coals. The bench-scale work now reported compares the catalytic activity of various additives in the gasification of volatile coals with steam under pressure and studies other process parameters of interest such as gasification temperature, type of contact with the catalyst, degree of gasification, and repeated use of a catalyst. Results of pilot plant gasification tests using additives are also reported.

Bench-Scale Studies

The gasification tests were conducted in two bench-scale reactor units, units A and B. The units were essentially the same; each unit contained an electrically heated reactor constructed of a 21-in-long section of 3/4-in, schedule 160 pipe of type 321 stainless steel. The coal-additive charge was contained in the middle 6 in of the reactor to minimize the spread of bed temperatures. Alumina cylinders filled the void space at each end of the reactor. Three thermocouples were located in the 6-in reactor zone, 1/2 in, 3 in, and 5-1/2 in from the top of the zone. The maximum temperature occurred at the middle thermocouple and was considered the nominal temperature of the reaction. The top and bottom bed temperatures were generally within 35° C of the maximum temperature.

During a gasification test, the coal charge was gasified by steam, which was introduced by saturation of the nitrogen carrier gas.

Figure 1 shows a schematic flowsheet of a reactor unit and its auxiliary equipment: high-pressure gas supply, silica gel and charcoal purifiers, calibrated capillary meter as feed gas flow indicator, gas saturator to humidify the feed gas, condenser and trap for liquid product collection, and gasometer for metering and collecting of total product gas. Reactor pressure was controlled by a back-pressure regulator. Temperature of the gas saturation was controlled within $\pm$ 0.6° C by a chromel-alumel thermocouple control system.

Analyses of dry product gases were done by mass spectrometer as well as gas chromatography. The liquid product about 95 pct water, was drained and weighed.

Coal Used

The coal charged in all the tests discussed in this report was a single batch of high-volatile bituminous coal (Bruceton, Pa.) that had been pretreated at 450° C with a steam-air mixture to destroy its caking quality. The pretreated coal was crushed and sieved to a particle size of 20 to 60 mesh. Proximate and ultimate analyses of the pretreated coal are shown in table 1 below, in weight percent:

TABLE 1. - Analyses of pretreated coal used for feedstock

Proximate		Ultimate	
Moisture	1.5	Hydrogen	3.9
Volatile	22.4	Carbon	74.3
Fixed carbon	65.5	Nitrogen	1.5
Ash	10.6	Oxygen	8.7
		Sulfur	1.0
		Ash	10.6

Standard Gasification Tests for Screening Additives

Standard gasification tests were conducted in units A and B to determine the effect of various additives upon rate of carbon gasification, rate of gas production, and other gasification parameters.

In unit A, the standard gasification tests using various catalysts were made at the selected operating conditions of 850° C, 300 psig, and 5.8 g/hr steam feed carried by 2,000 cm^3 N_2/hr. The coal charge was 10 g plus 0.5 g of catalyst. All catalysts were either powders or crystals that were admixed with the coal except in the case of experiment 203. In experiment 203, a metal tubular insert was flame-spray coated with about 10 g of unactivated Raney nickel, then inserted in the coal bed. In experiment 200, the Raney nickel catalyst powder was activated or approximately 65 pct reduced by treatment with 2 pct sodium hydroxide solution. In the reduced activated state, the catalyst was dried, mixed with coal, and charged into the unit under an inert atmosphere of nitrogen.

Reaction time, at the desired reaction temperature, was held constant at 4 hrs. An additional heat-up time of about 40 min was needed to reach the desired reaction temperature. Steam flow was not started until bed temperature exceeded 200° C. Conditions in unit B were the same as in unit A except that the steam rate was slightly lower at 5.0 g/hr.

Generally, tests were conducted in triplicate or higher replication. The average deviations in carbon gasification rate determinations generally ranged from 1 to 5 pct.

The experimental results of the screening tests conducted in unit A are presented in tables 2a and 2b; and for unit B, are presented in tables 3a and 3b. The specific gas production rates and gasification rates presented are based on the approximate 4-hr reaction time at 850° C. The results indicate that methane production rates as well as carbon gasification rates can be increased significantly by admixing certain compounds with the coal feed.

The rate of carbon gasification for the uncatalyzed coal was about 10 pct higher in unit A than in unit B (experiment 167 vs 300). The slightly higher steam rate in unit A is suspected as the cause of the higher reaction rate. Because of this difference in absolute rates, the percent increases achieved in gasification rates and gas production rates due to additives were related only to rates obtained in the gasification of the uncatalyzed coal in the same unit. Shown in table 4 are the relative effects of 40 additives upon the production of methane and hydrogen; and shown in table 5 are their relative effects upon the production of carbon monoxide and the gasification of carbon. The additives are listed in decreasing order of percent increased production. The corresponding reactor unit used (either A or B) is also listed.

Table 4 shows that at standard test conditions, all the additives listed except $ZnBr_2$ increased methane production and that all the tested additives increased hydrogen production significantly. The sprayed Raney nickel catalyst increased methane production by 24 pct and was the most effective material for promoting methane production. The next three materials ranking highest in promoting methane production were $LiCO_3$, Pb_3O_4, and Fe_3O_4 with respective methane increases of 21, 20, and 18 pct.

A comparison of the methanation activity of zinc oxide with that of zinc bromide indicates that the anion group of a catalyst can exert significant influence on the activity.

As shown in table 4, the alkali metal compounds proved to be among the best promoters of hydrogen production. The percent increase in hydrogen produced was 105, 83, 55, and 53 pct, respectively, with the addition of KCl, K_2CO_3, $LiCO_3$, and NaCl. The sprayed Raney nickel was the third most effective promoter of hydrogen production yielding a hydrogen increase of 63 pct.

Table 5 shows that the alkali metal compounds K_2CO_3, KCl, and $LiCO_3$ gave the greatest increase in carbon monoxide production as well as in carbon gasification; the increases ranged from 40 to 91 pct. The compound NaCl provided a significant increase of 31 pct in carbon gasification but was much less effective in increasing the production of carbon monoxide (7-pct increase).

As shown in tables 2b and 3b, the unit heating values of the total product gases generally decreased as a result of mixing additives with the coal but, since the total gas make was increased, the total amount of fuel value produced as product gas increased.

Two methods of applying catalyst--by admixing with the coal or by coating the surface of an insert or carrier--may be compared in the case of unactivated Raney nickel catalyst (experiments 203 and 197).

TABLE 2a. - Specific rate of gas production when using various catalysts (Series A)

Test conditions - Unit A: Charge, 10 g pretreated Bruceton coal, 0.5 g catalyst; feed, 5.8 g H_2O/hr + 2000 std cc N_2/hr; approximately 4-hr duration; 300 psig; 850° C

Catalyst	Expt. No.	No. of test	Total dry gas production rate, N_2-free bases, std cc/hr/g coal charged	Specific production rate of constituent gases, std cc/hr/g coal charged							
				H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_8	C_3H_6
No catalyst	166	6	331	166	49.7	70.2	43.7	0.06	0.93	0.24	0.12
Raney nickel, unactivated:											
Sprayed	203	6	453	271	53.7	72.3	54.2	.12	.80	.22	.05
Mixed	197	3	414	216	52.1	95.5	49.1	--	1.19	.18	--
Raney nickel, activated											
Mixed	200	3	442	243	47.9	104.5	45.31	.10	0.84	.13	--
NaCl	209	3	471	254	53.0	115.5	47.6	.33	.55		
KCl	212	3	615	340	90.1	137.3	46.7	.07	.64	.33	.03
ZnO	215	3	440	232	52.2	104.4	50.0	.05	.92	.13	.13
$NiCl_2.6H_2O$	216	3	442	237	51.7	103.6	48.4	.14	.82	.18	.16
$NiSO_4.6H_2O$	217	3	420	220	48.0	102.9	48.0	.21	.78	.23	.05
K_2CO_3	218	3	578	309	95.0	126.4	46.2	.31	.72	.22	.06
$ZnBr_2$	219	3	418	224	53.9	96.2	42.6	.18	.79	.10	.08
SnO_2	224	3	395	213	37.7	98.1	44.0	.15	.65	.33	.28
Fe	225	3	367	193	39.1	88.3	45.4	.09	.95	.38	.24

TABLE 2b. - Specific rate of liquid production, carbon gasification, and gaseous heating value production when using various catalysts (Series A)

Test conditions - Unit A: Charge, 10 g pretreated Bruceton coal, 0.5 g catalyst; feed, 5.8 g H_2O/hr + 2000 std cc N_2/hr; approximately 4-hr duration; 300 psig; 850° C

Catalyst	Expt. No.	Product liquid, g/hr/g coal charged	Carbon gasification rates, g/hr/g coal charged	Unit heating value N_2-free product gas, Btu/SCF	Gaseous heating value produced, Btu/hr/cu ft coal charged
No catalyst	167	0.478	89×10^{-3}	353	57,700
Raney nickel, unactivated:					
Sprayed	203	.472	98×10^{-3}	359	80,254
Mixed	197	.501	106×10^{-3}	336	68,712
Raney nickel, activated:					
Mixed	200	.489	107×10^{-3}	322	70,258
NaCl	209	.506	117×10^{-3}	318	74,032
KCl	212	.480	148×10^{-3}	307	93,250
ZnO	215	.490	112×10^{-3}	330	71,718
$NiCl_2.6H_2O$	216	.493	110×10^{-3}	328	71,716
$NiSO_4.6H_2O$	217	.498	108×10^{-3}	328	68,163
K_2CO_3	218	.494	144×10^{-3}	312	89,011
$ZnBr_2$	219	.454	104×10^{-3}	324	66,783
SnO_2	224	.507	98×10^{-3}	326	63,700
Fe	225	.517	94×10^{-3}	339	61,500

TABLE 3a. - Specific rate of gas production when using various catalysts (Series B)

Test conditions - Unit B: Charge, 10 g pretreated Bruceton coal, 0.5 g catalyst; feed, 5.0 g H_2O/hr plus 2000 std cc N_2/hr; approximately 4-hr duration; 300 psig; 850° C

Catalyst	Expt. No.	No. of tests	Total dry gas production rate, N_2-free bases, std cc/hr/g coal charged	Specific production rate of constituent gases, std cc/hr/g coal charged							
				H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_8	C_3H_6
No catalyst	300	3	297	147	37.7	69.9	40.8	0.18	0.72	0.20	0.24
$Ca(OH)_2$	301	3	345	180	32.0	86.2	45.4	.09	.63	.12	.19
Ni_2O_3	302	3	359	189	43.9	80.9	42.8	.07	.74	.73	.50
NiO	303	3	373	194	52.0	82.0	43.9	--	.94	.22	.29
Ni	304	3	366	189	53.6	76.6	46.2	.17	.46	.29	.27
Fe_3O_4	305	3	380	195	60.3	78.0	45.6	.15	.49	.27	.22
CuO	306	3	385	201	56.3	79.9	46.8	.12	.52	.17	.07
MnO_2	307	3	375	193	45.7	90.2	44.9	.10	.79	.10	.15
BaO	308	3	395	202	48.9	97.1	45.5	.13	.73	.15	.13
ZrO_2	309	3	377	192	57.8	80.0	46.2	.12	.88	.05	.12
SrO	310	3	392	203	48.2	91.3	47.6	.15	.76	.15	.15
Bi_2O_3	311	2	390	200	63.9	80.4	44.4	.19	.72	.15	.04
Sb_2O_5	312	2	391	201	63.6	79.7	45.9	.19	.45	.15	.15
MgO	313	3	384	199	48.4	87.7	47.7	.18	.72	.30	.23
PbO_2	314	3	400	210	52.7	89.1	47.7	.08	1.00	.18	.23
MoO_3	315	3	380	202	45.0	86.6	45.5	.03	1.09	.30	.13
TiO_2	316	3	380	197	48.9	85.7	47.2	.33	0.68	.13	.23
CrO_3	317	3	378	194	52.5	84.4	46.1	.07	.79	.07	.15
$LiCO_3$	318	3	439	228	64.9	95.9	49.2	.19	.57	.27	--
V_2O_5	319	3	367	188	47.7	83.5	45.9	.12	.71	.20	.12
Cr_2O_3	320	3	374	184	58.6	83.0	47.4	.57	.57	.10	.12
Pb_3O_4	321	3	400	205	57.2	87.3	49.1	.13	.72	.15	.13
B_2O_3	322	3	394	203	61.0	79.0	47.4	.05	1.59	1.32	.08
Al_2O_3	323	3	380	196	54.6	82.2	46.7	.15	0.61	0.13	.09
CoO	324	4	383	201	48.6	87.0	45.4	.25	.43	.17	.7
Cu_2O	325	6	385	203	53.1	84.4	44.1	.28	.42	.14	.13

TABLE 3b. - Specific rate of liquid production, carbon gasification, and gaseous heating value production when using various catalysts (Series B)

Test conditions - Unit B: Charge, 10 g pretreated Bruceton coal, 0.5 g catalyst; feed, 5.0 g H_2O/hr plus 2000 std cc N_2/hr; approximately 4-hr duration; 300 psig; 850° C

Catalyst	Expt. No.	Product liquid, g/hr/g coal charged	Carbon gasification rates, g/hr/g coal charged	Unit heating value N_2-free product gas, Btu/SCF	Gaseous heating value produced, Btu/hr/cu ft coal charged
No catalyst	300	0.464	81×10^{-3}	350	51,300
$Ca(OH)_2$	301	.447	88×10^{-3}	339	57,700
Ni_2O_3	302	.439	92×10^{-3}	344	60,960
NiO	303	.422	97×10^{-3}	340	62,700
Ni	304	.413	96×10^{-3}	349	63,100
Fe_3O_4	305	.396	100×10^{-3}	345	64,800
CuO	306	.418	99×10^{-3}	344	65,500
MnO_2	307	.406	98×10^{-3}	333	61,700
BaO	308	.417	104×10^{-3}	328	64,050
ZrO_2	309	.405	99×10^{-3}	344	64,200
SrO	310	.417	101×10^{-3}	337	65,200
Bi_2O_3	311	.415	102×10^{-3}	340	65,500
Sb_2O_5	312	.414	102×10^{-3}	343	66,200
MgO	313	.391	100×10^{-3}	342	64,900
PbO_2	314	.397	103×10^{-3}	339	67,000
MoO_3	315	.438	96×10^{-3}	339	63,800
TiO_2	316	.364	99×10^{-3}	342	64,200
CrO_3	317	.398	99×10^{-3}	340	63,400
$LiCO_3$	318	.364	113×10^{-3}	334	72,400
V_2O_5	319	.402	96×10^{-3}	341	61,900
Cr_2O_3	320	.394	102×10^{-3}	345	63,700
Pb_3O_4	321	.410	105×10^{-3}	342	67,600
B_2O_3	322	.399	104×10^{-3}	355	69,200
Al_2O_3	323	.424	99×10^{-3}	342	64,300
CoO	324	.355	98×10^{-3}	336	63,800
Cu_2O	325	.363	98×10^{-3}	336	63,900

TABLE 4. - Increase in the production of methane and hydrogen

Catalyst	Unit	Increase in CH_4, pct	Catalyst	Unit	Increase in H_2 produced, pct
Raney nickel, unactivated spray	A	24	KCl	A	105
$LiCO_3$	B	21	K_2CO_3	A	83
Pb_3O_4	B	20	Raney nickel unactivated spray	A	63
Fe_3O_4	B	18	$LiCO_3$	B	55
MgO	B	17	NaCl	A	53
PbO_2	B	17	Raney nickel activated mix	A	46
SrO	B	17	$NiCl_2 \cdot 6H_2O$	A	43
TiO_2	B	16	PbO_2	B	43
Cr_2O_3	B	16	ZnO	A	40
B_2O_3	B	16	Pb_3O_4	B	39
CuO	B	15	SrO	B	38
ZnO	A	14	B_2O_3	B	38
Al_2O_3	B	14	Cu_2O	B	38
Ni	B	13	CuO	B	37
ZrO_2	B	13	BaO	B	37
Sb_2O_5	B	13	Sb_2O_5	B	37
CrO_3	B	13	MoO_3	B	37
V_2O_5	B	13	CoO	B	37
Raney nickel unactivated mix	A	12	Bi_2O_3	B	36
BaO	B	12	$ZnBr_2$	A	35
MoO_3	B	12	MgO	B	35
$NiCl_2 \cdot 6H_2O$	A	11	TiO_2	B	34
$Ca(OH)_2$	B	11	$NiSO_4 \cdot 6H_2O$	A	33
CoO	B	11	Fe_3O_4	B	33
$NiSO_4 \cdot 6H_2O$	A	10	Al_2O_3	B	33
MnO_2	B	10	NiO	B	32
NaCl	A	9	CrO_3	B	32
Bi_2O_3	B	9	MnO_2	B	31
NiO	B	8	ZrO_2	B	31
Cu_2O	B	8	Raney nickel unactivated mix	A	30
KCl	A	7	Ni_2O_3	B	29
K_2CO_3	A	6	Ni	B	29
Ni_2O_3	B	5	SnO_2	A	28
Raney nickel activated mix	A	4	V_2O_5	B	28
Fe	A	4	Cr_2O_3	B	25
SnO_2	A	1	$Ca(OH)_2$	B	22
$ZnBr_2$	A	-3	Fe	A	16

TABLE 5. - Increase in production of carbon monoxide and gasification of carbon.

Catalyst	Unit	Increase in CO produced, pct	Catalyst	Unit	Increase in carbon gasified, pct
K_2CO_3	A	91	KCl	A	66
KCl	A	81	K_2CO_3	A	62
$LiCO_3$	B	72	$LiCO_3$	B	40
Bi_2O_3	B	69	NaCl	A	31
Sb_2O_5	B	69	Pb_3O_4	B	30
B_2O_3	B	62	BaO	B	28
Fe_3O_4	B	60	B_2O_3	B	28
Cr_2O_3	B	55	PbO_2	B	27
ZrO_2	B	53	Bi_2O_3	B	26
Pb_3O_4	B	52	Cr_2O_3	B	26
CuO	B	49	Sb_2O_5	B	26
Al_2O_3	B	45	ZnO	A	26
Ni	B	42	SrO	B	25
Cu_2O	B	41	$NiCl_2 \cdot 6H_2O$	A	24
PbO_2	B	40	MgO	B	23
CrO_3	B	39	Fe_3O_4	B	23
NiO	B	38	CuO	B	22
BaO	B	30	ZrO_2	B	22
TiO_2	B	30	TiO_2	B	22
CoO	B	29	CrO_3	B	22
MgO	B	28	Al_2O_3	B	22
V_2O_5	B	27	$NiSO_4 \cdot 6H_2O$	A	21
MnO_2	B	21	MnO_2	B	21
MoO_3	B	19	CoO	B	21
Ni_2O_3	B	16	Cu_2O	B	21
SrO	B	15	Raney nickel activated mix	A	20
Raney nickel, unactivated spray	A	8	NiO	B	20
$ZnBr_2$	A	8	Raney nickel unactivated mix	A	19
NaCl	A	7	Ni	B	19
Raney nickel, unactivated mix	A	5	MoO_3	B	19
ZnO	A	5	V_2O_5	B	19
$NiCl_2 \cdot 6H_2O$	A	4	$ZnBr_2$	A	17
$NiSO_4 \cdot 6H_2O$	A	-3	Ni_2O_3	B	14
Raney nickel activated mix	A	-4	Raney nickel, unactivated spray	A	10
$Ca(OH)_2$	B	-15	SnO_2	A	10
Fe	A	-21	$Ca(OH)_2$	B	9
SnO_2	A	-24	Fe	A	6

Admixing of the catalyst with the coal provides better contact between coal and catalyst than does the insertion of catalyzed surfaces into the bed of coal. The superior contact achieved by admixing the catalyst and coal is proven by the higher specific rate of carbon gasification obtained by the admixed Raney nickel (unactivated) in experiment 197 over that of sprayed Raney nickel (unactivated) in experiment 203 (tables 2a and 2b). This is further confirmed analytically by the larger amount of carbon left in the residue in the case of the sprayed Raney nickel catalyst.

Table 2a indicates that the Raney nickel (unactivated) catalyst was more effective in promoting methane production when sprayed on a surface than when it was admixed with the coal charge. Apparently, the process of methane synthesis from CO and H_2 was more effectively promoted by the sprayed Raney nickel (unactivated) catalyst. Another possible reason for the greater production of methane in the case of the sprayed Raney nickel (unactivated) catalyst is that the poorer contact between coal and catalyst resulted in less reforming of methane and other hydrocarbons. Hydrogen production was also greater when the sprayed Raney nickel (unactivated) catalyst was used than when Raney nickel (unactivated) was admixed with the coal.

Effect of Temperature and Steam Rate

Gasification experiments similar to the standard tests were conducted in unit A, except that the reaction temperatures were varied from 650° to 950° C and steam rates used were 1.16 and 5.8 g/hr. The catalyst used was flame-sprayed Raney nickel 65 pct activated. Also, tests were conducted at 750° C and 1.16 g/hr steam rate with sprayed Raney nickel activated and charged wet and at 850° C, and 5.8 g/hr steam rate with sprayed Raney nickel unactivated.

Results of these experiments are presented in figures 2, 3, 4, 5, and 6, where rates of production of methane, hydrogen, carbon monoxide, carbon gasification, and production of total dry gas, respectively, are shown. At the temperatures and steam rates shown in these figures, the presence of the sprayed Raney nickel insert has resulted in a higher production of nearly all the major gases and in a higher carbon gasification than that achieved without catalysts. One exception is in the case of methane production with the activated sprayed Raney nickel at 850° and 950° C for 5.8 g/hr steam rate (fig. 2), when methane production was greater for the uncatalyzed reaction than for the catalyzed reaction. However, a 6-pct increase in methane production was achieved at 850° C and 5.8 g/hr steam rate when the unactivated sprayed Raney nickel was used as compared to when no catalyst was used (fig. 2). The other exception is in the production of carbon monoxide at 950° C and 1.16 g/hr steam rate (fig. 4). In this case, carbon monoxide production was 5 pct lower for the catalyzed reaction than for the uncatalyzed reaction.

In general, effectiveness of the catalyst decreases as temperature is increased. For example, the increases achieved in carbon gasification and in total gas production due to the use of catalyst became smaller as the reaction temperature increased from 750° to 950° C (Figs. 5 and 6). In the 5.8 g/hr steam rate tests, the carbon gasification rate at 750° C was increased by 0.017 g/hr/g coal charged for a 33-pct increase, whereas at 950° C the increase in carbon gasification was negligible at an increment of 0.001 g/hr/g coal charged. Similarly, total gas production was increased 43 pct at 750° C and 10 pct at 950° C.

As shown by the gas production and carbon gasification rates presented in figures 2 through 6, for reaction temperatures of 750° C and higher, the higher steam feed rate of 5.8 g/hr resulted in significantly higher production rates over that achieved at the lower steam rate of 1.16 g/hr.

Repeated Use of Sprayed Raney Nickel Catalyst

To determine the stability of sprayed Raney nickel catalyst, a single insert flame-sprayed with Raney nickel catalyst was subjected to four gasification tests at 750° C, 300 psig, and a steam rate of 1.16 g/hr. The resulting gas production rates are shown in fig. 7; also shown is the base case, with no catalyst inserted in the bed.

Gas production rates presented in figure 7 indicate that the activity of the sprayed Raney nickel catalyst insert decreased rapidly with use. The gas production of the fourth test (17.8 hr service), was only about 10 pct greater than that obtained when no catalyst was used. An extrapolation of the total gas production rate as a function of accumulated service time on one catalyst insert indicates that the catalyst insert would be completely ineffective after about 20 hrs of operation. Considerable flaking-off of the catalyst is apparent; thus the need is indicated for an effective bonding agent or alloying substance that will increase the physical durability of the catalyst. Sulfur compounds gasified from the coal are also suspected of poisoning the nickel catalyst and resulting in the decline in activity with time.

Effect of Extent of Gasification Time

A series of tests were conducted to determine whether catalysts remain effective as the extent of gasification increases. Sprayed Raney nickel inserts and CaO powder were subjected to the standard test conditions of 850° C, 300 psig, 5.8 g/hr steam rate but with gasification times varying from 2 to 8 hrs. The abridged results presented in table 6 show that although the overall rate of gasification decreases with extent of gasification or with the length of time of gasification, the catalysts tested still generally increased the rate of carbon gasification, and the rate of gas production, as indicated by CH_4 production, over that achieved with no catalyst.

TABLE 6. - Effect of extent of gasification time upon overall effectiveness of catalyst

Unit A. - Temperature, 850° C, N_2 flow, 2000 std cc/hr; steam rate, 5.8 g/hr

	CH_4 production		Carbon gasification	
Gasification time, hr	2	6	2	6
Rates with no catalyst	53.3 cc/hr/g	28.6 cc/hr/g	0.087 g/hr/g	0.062 g/hr/g
Rates with CaO	56.9 cc/hr/g	30.7 cc/hr/g	.090 g/hr/g	.062 g/hr/g
Increase due to CaO	7 pct	7 pct	3 pct	0 pct
Rates with sprayed Raney nickel catalyst	70.9 cc/hr/g	38.3 cc/hr/g	.093 g/hr/g	.063 g/hr/g
Increase due to Raney nickel	33 pct	34 pct	7 pct	2 pct

Effect of Residues from Catalytic Gasification

The catalytic effectiveness of ash residues (some contain either residual KCl or K_2CO_3) from total gasification operations were tested and compared with the effectiveness of the fresh additive, K_2CO_3 and KCl.

The gasification residues were prepared by nominally complete steam-gasification of coal in a 1-in diameter electrically heated, vertically mounted stainless-steel reactor. The coal charge consisted of 70 g of pretreated Bruceton coal plus 3.5 g of admixed catalyst; the charge was gasified at 950° to 970° C and atmospheric pressure using a steam feed rate of 45 g/hr. The preparatory gasification step was stopped whenever the flow of dry product gas appeared to cease. Carbon and ash content of the pretreated coal and of residues after total gasification and residue analyses are presented in table 7. The ash analyses show that ash from the catalyzed coals contained significantly larger amounts of potassium than did the ash of uncatalyzed coal.

In the standard screening tests conducted in unit A, the amount of residue admixed with the 10-g coal charge was one-seventh of the residue from the total gasification. Thus, a theoretical equivalent of 0.5 g of the original 3.5 g of catalyst was charged with the coal in the standard screening test. Production rates obtained in the standard screening tests are presented in table 8 for the case of plain pretreated coal, for the cases of addition of catalyst-free residue, pure K_2CO_3 and KCl, and for the addition of residues from the total gasification of the coals admixed with K_2CO_3 and KCl.

The results of the tests on residues from total gasification of coal indicate that potassium compounds, K_2CO_3 and KCL, in the residues retained most of their activity in increasing the production of methane, lost part of their capability of increasing hydrogen production, and inhibited carbon monoxide production. The addition of 1.14 g of catalyst-free residue had very little effect on either methane or total gas production (experiment 220 vs 167).

Pilot-Plant Tests

Tests using additives mixed in the coal feed were conducted in the Bureau's 4-in diameter Synthane gasifier system. In this system, coal is first decaked in a fluidized-bed pretreater and then dropped into the fluidized-bed gasifier for steam-oxygen gasification. The general operation has been described by Forney and others (5).

Ranges of pretreater and gasifier conditions used in this series of tests were as follows:

		Pretreater	Gasifier
Coal rate,	lb/hr	17.8 - 21.2	----- ----
O_2 feed,	scf/lb coal	.31 - .37	2.12 - 3.4
N_2 feed,	scf/lb coal	5.4 - 6.2	----- ----
Steam feed,	scf/lb coal	----- -----	19.6 - 25.4
Av. temp.,	° C	388 515	907 - 945

Pretreater and gasifier pressure was 40 atm.

TABLE 7. - Carbon, ash content, and ash analysis of pretreated Bruceton coal and of residues from total gasification

Gasification conditions: Charge, 70 g pretreated Bruceton coal, 3.5 g of catalyst; water rate, 45 cc/hr 950-970° C, atmospheric pressure

	Expt. No.	Carbon and ash content, pct		Mineral analysis of ash, pct									
		Carbon	Ash	Al_2O_3	CaO	Fe_2O_3	Mgo	P_2O_5	K_2O	SiO_2	Na_2O	SO_3	TiO_2
Charge coal	C-1	74.3	10.6	25.9	1.7	10.8	0.9	<0.01	1.7	54.8	1.6	1.6	1.0
Residues:													
No catalyst	D-1	1.67	98.9	25.1	1.6	14.4	.8	----	1.9	54.7	1.5	---	---
K_2CO_3	D-2	0.47	99.9	19.7	1.1	10.8	.8	----	24.3	41.7	1.6	---	---
KCl	D-3	4.7	95.1	22.2	1.3	12.4	.7	----	13.1	48.5	1.4	0.4	---

TABLE 8. - Specific production and gasification rates resulting from addition of potassium compounds and various gasification residues

Standard test conditions: Unit A: 10 g pretreated Bruceton coal, 0.5 g catalyst (residue charge as indicated); feed 5.8 g H_2O/hr + 2000 std cc N_2/hr; approximately 4-hr duration; 300 psig; 850° C

	Expt. No.	No. of tests	Residue charged		Total dry gas production rate, N_2-free basis, std cc/hr/g coal charged	Specific production rate of constituent gases, std cc/hr/g coal charged							
			No.	Amt., g		H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_8	C_3H_6
No catalyst	167	6			331	166	49.7	70.2	43.7	0.06	0.93	0.24	0.12
Catalyst-free residue	220	3	D-1	1.12	344	180	39.2	79.3	43.9	.07	.81	.33	.21
K_2CO_3	218	3			578	309	95.0	126.4	46.2	.31	.72	.22	.06
K_2CO_3 residue	221	3	D-2	1.41	398	205	45.8	98.1	47.6	.27	.72	.12	.30
KCl	212	3			615	340	90.1	137.3	46.7	.07	.64	.33	.03
KCl residue	222	3	D-3	1.26	370	175	47.8	94.7	48.6	.22	.72	.19	.24

	Expt. No.	Product liquid, g/hr/g coal charged	Carbon gasification rates, g/hr/g coal charged	Unit heating value N_2-free product gas, Btu/SCF	Gaseous heating value produced, Btu/hr/cu ft coal charged
No catalyst	167	0.478	89×10^{-3}	353	57,700
Catalyst-free residue	220	.449	88×10^{-3}	344	58,500
K_2CO_3	218	.494	144×10^{-3}	312	89,000
K_2CO_3 residue	221	.487	104×10^{-3}	332	65,300
KCl	212	.480	148×10^{-3}	307	93,300
KCl residue	222	.469	104×10^{-3}	336	61,300

To alleviate operating difficulties in the pretreater due to unwanted steam condensation, a nitrogen gas feed was substituted for the steam feed of the pretreater.

The coal feed was Illinois No. 6, River King Mine, 20 x 0 mesh size. Additives used were hydrated lime and dolomite, and additive concentrations used in the coal feed mixtures were 5 and 2 pct by weight, respectively. The analyses and sizes of the additives were as follows:

Hydrated lime: minimum CaO, 72 wt pct
minimum MgO, .05 wt pct
95 pct less than 325 mesh, and

Dolomite : $CaCO_3$, 55 wt pct
$MgCO_3$, 44 wt pct
85 pct less than 100 mesh

Results

The effect of the additives upon the percent carbon gasified and percent steam decomposed can be seen in figure 8 for gasification temperature in the 900° to 950° C range. Addition of 5 pct of either hydrated lime or dolomite to the coal resulted in significant increases in carbon gasified. The 5-pct hydrated lime addition resulted in an increase in carbon gasified of about 29 pct at an average gasification temperature of 914° C. Addition of 5 pct dolomite gave a 20-pct increase in carbon gasified at 945° C. These increases compare favorably with the 9-pct increase obtained in the 850° C bench-scale test list using 5-pct addition of hydrated lime.

The 2-pct addition of dolomite did not significantly increase the percent carbon gasification.

Steam decomposition was not significantly increased by either dolomite or hydrated lime at the 2- and 5-pct levels, respectively.

The effect of the additive upon yield of hydrogen and methane in the pilot-plant unit is shown in figure 9. At an average gasification temperature of 914° C, addition of 5 pct hydrated lime in the coal feed increased the hydrogen yield approximately 30 pct from 6.25 to 8.1 scf/lb of moisture-and-ash-free coal feed. A similar increase of 17 pct was obtained by the use of 5 pct dolomite in the coal feed at 945° C average gasification temperature. Such significant increases in hydrogen production were also observed in the bench-scale tests.

The yield of methane was increased significantly by 25 pct at 914° C average gasification temperature through the addition of 5 pct hydrated lime. The use of 5 pct dolomite at 945° C gasification temperature brought no significant increase in methane yield. Failure of catalytic action to increase the yield of methane at the higher gasification temperature (945° C) agrees with the general trend observed on bench-scale tests--that the increase in gas yield due to catalyses decreases with increase in temperature.

The effect of additives upon the yield of carbon monoxide is shown in figure 10. Addition of hydrated lime and dolomite at the 5-pct concentration levels brought respective increases of 23 and 26 pct in yield of carbon monoxide. Figure 11 shows similar increases in product gas yield ($CO + H_2 + CH_4$), for the same additions.

Addition of dolomite at the 2-pct level failed to bring any significant increase in yields of methane, hydrogen, or carbon monoxide.

Other results in pilot-plant operation due to the use of dolomite and hydrated lime at the 2- and 5-pct concentration levels, respectively, are that higher peak temperatures could be tolerated in the gasifier without incurring excessive sintering. With no additive in the coal, if a local temperature in the gasifier exceeded 1000° C, the operation generally would terminate because of excessive sintering or slagging of the char ash. With the additives in the coal, local temperatures as high as 1045° C were encountered with no adverse effect on operations. A similar elevation in sintering temperature induced by the addition of limestone to the feed coal is reported to be a key feature of the high-temperature Winkler process (6).

SUMMARY AND CONCLUSIONS

The overall results of the bench-scale investigation suggest that the use of suitable additives would improve the coal gasification reaction at elevated pressures. In connection with possible benefits to the Synthane process for making high-Btu gas, it appears that appropriate additives could significantly increase production of methane and hydrogen in the gasification step.

The bench-scale study thus far has shown the following:

1. Alkali metal compounds and many other materials such as oxides of iron, calcium, magnesium, and zinc significantly increase the rate of carbon gasification and the production of desirable gases such as methane, hydrogen, and generally carbon monoxide during steam-coal gasification at 850° C and 300 psig.

2. The greatest yield of methane occurred with the use of an insert flame-sprayed Raney nickel catalyst (unactivated), which has a limited life of activity. Significant methane increase resulted from the addition of 5 pct by weight of $LiCO_3$, Pb_3O_4, Fe_3O_4, MgO, and many other materials.

3. The increased gasification resulted whether the extent of coal gasification was small or great.

4. At temperatures above 750° C, catalytic effectiveness decreased with further increase in temperature.

5. Residue from total gasification of coal mixed with potassium compounds still contained a significant concentration of potassium (over 10 pct) and was effective as an additive in increasing production of hydrogen and methane.

Operation of the 4-in diameter Synthane pilot-plant gasifier at 40 atm pressure and average temperature of up to 945° C with dolomite and hydrated lime additives at 5-pct concentration has increased product gas ($CO + H_2 + CH_4$) yield significantly and has increased allowable operating temperatures.

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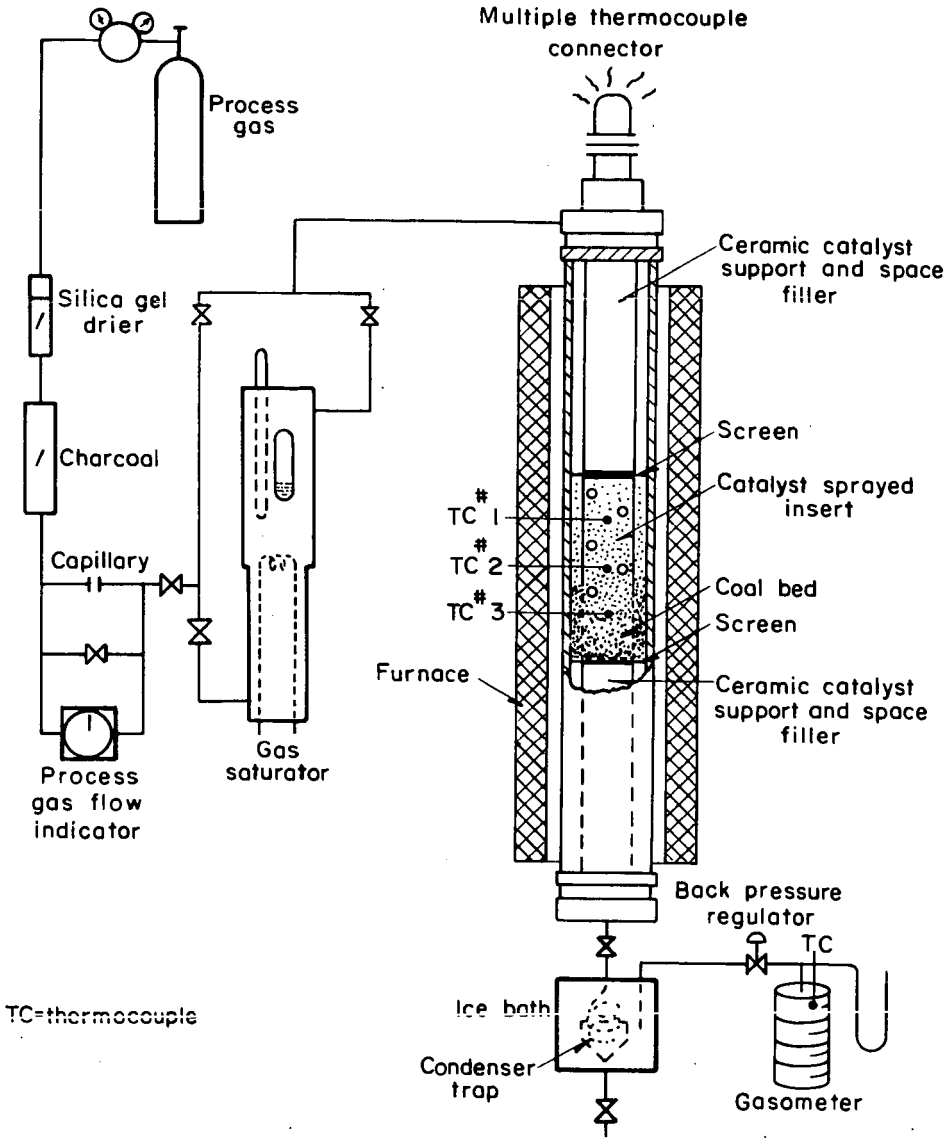

Figure 1.—Apparatus for the catalytic gasification of coal.

L-10298

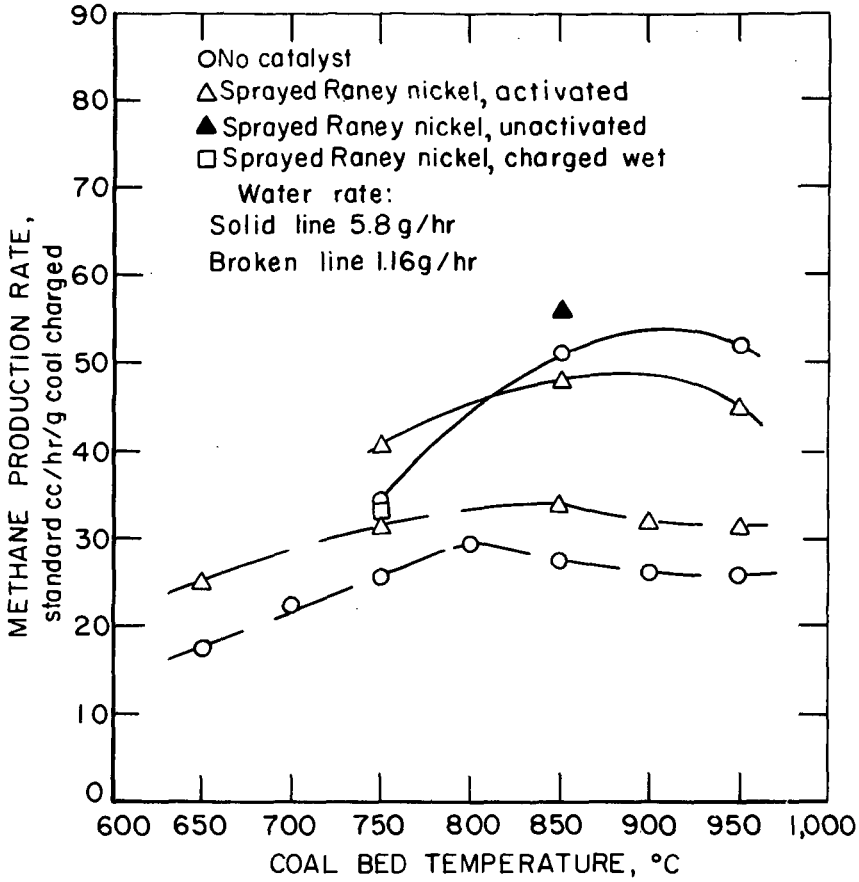

Figure 2-Effect of temperature upon methane production rate using sprayed Raney nickel. Test conditions: pressure, 300 psig; flow, 2,000 standard cc/hour N_2; water, 5.8 and 1.16 g/hour.

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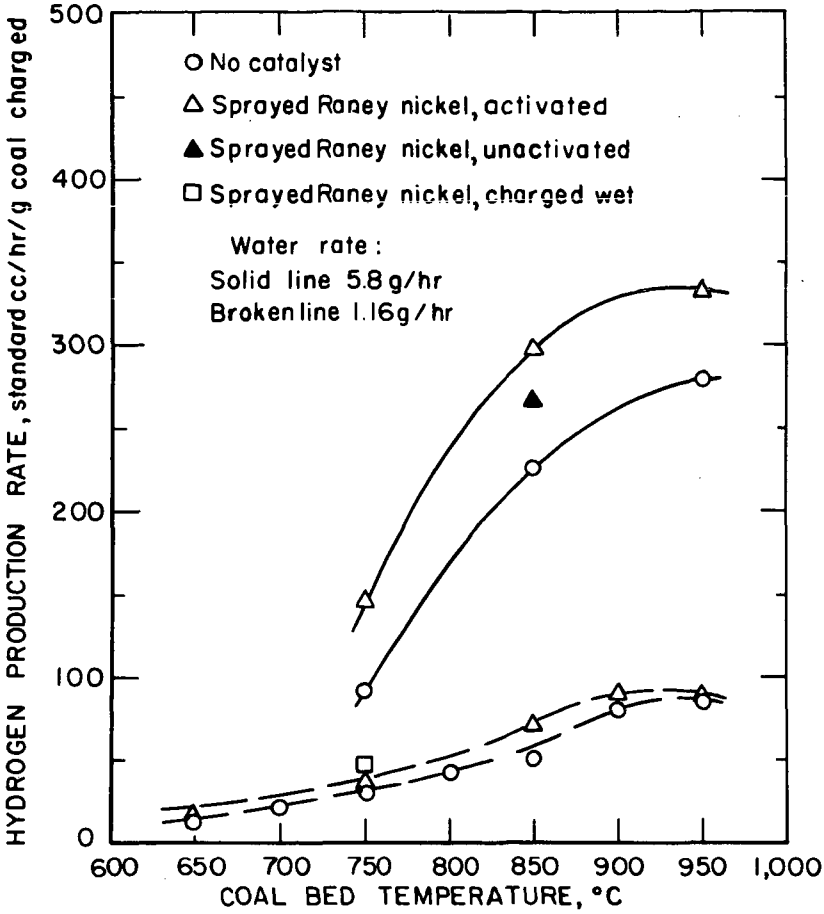

Figure 3. – Effect of temperature upon specific production of hydrogen, using sprayed Raney nickel. Test conditions: pressure, 300 psig, flow, 2,000 standard cc/hour N_2; water, 5.8 and 1.16 g/hour.

4-26-68 L-10551

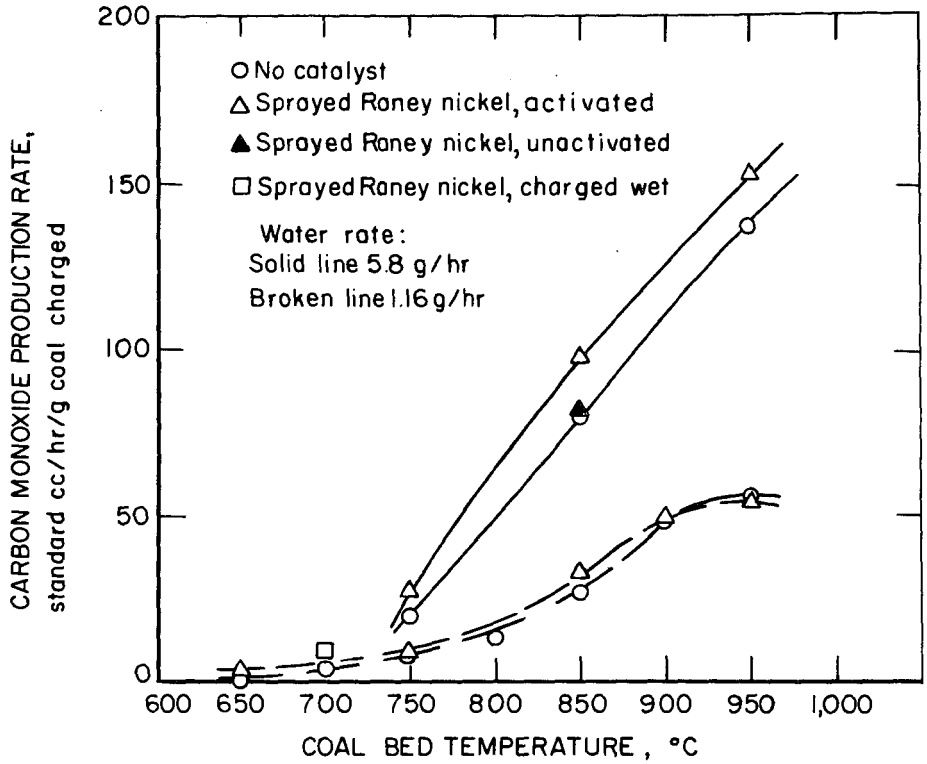

Figure 4.-Effect of temperature upon carbon monoxide production rate using sprayed Raney nickel. Test conditions: pressure, 300 psig; flow 2,000 standard cc/hour N_2; water, 5.8 and 1.16 g/hr.

4-29-68 L-10552

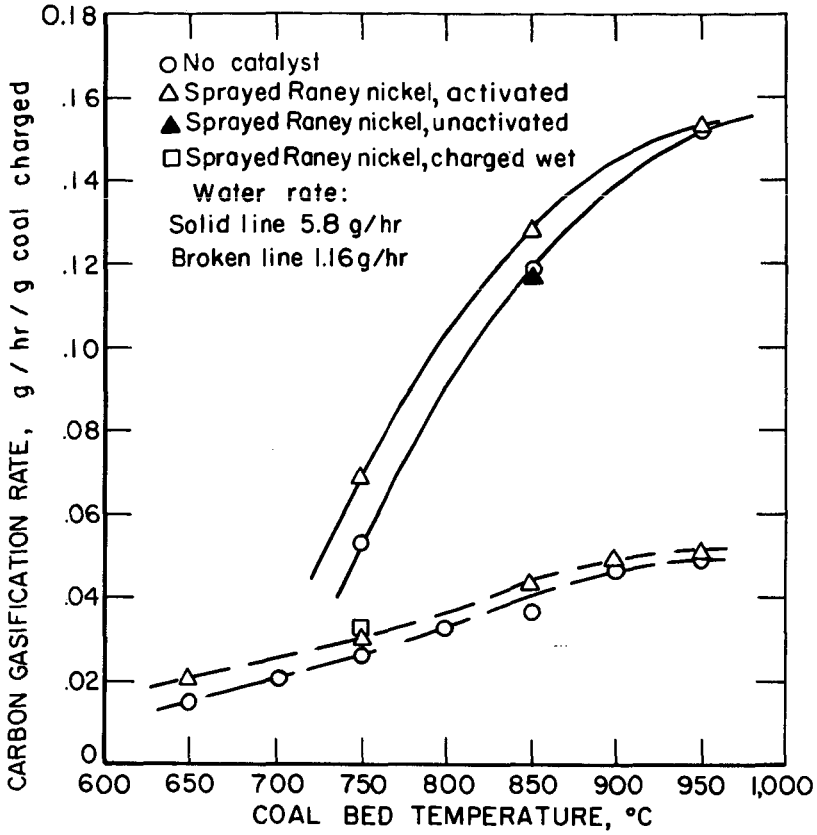

Figure 5.-Effect of temperature upon carbon gasification rate using sprayed Raney nickel. Test conditions: pressure, 300 psig; flow, 2,000 standard cc/hr N_2; water, 5.8 and 1.16 g/hr.

4-30-68 L-10555

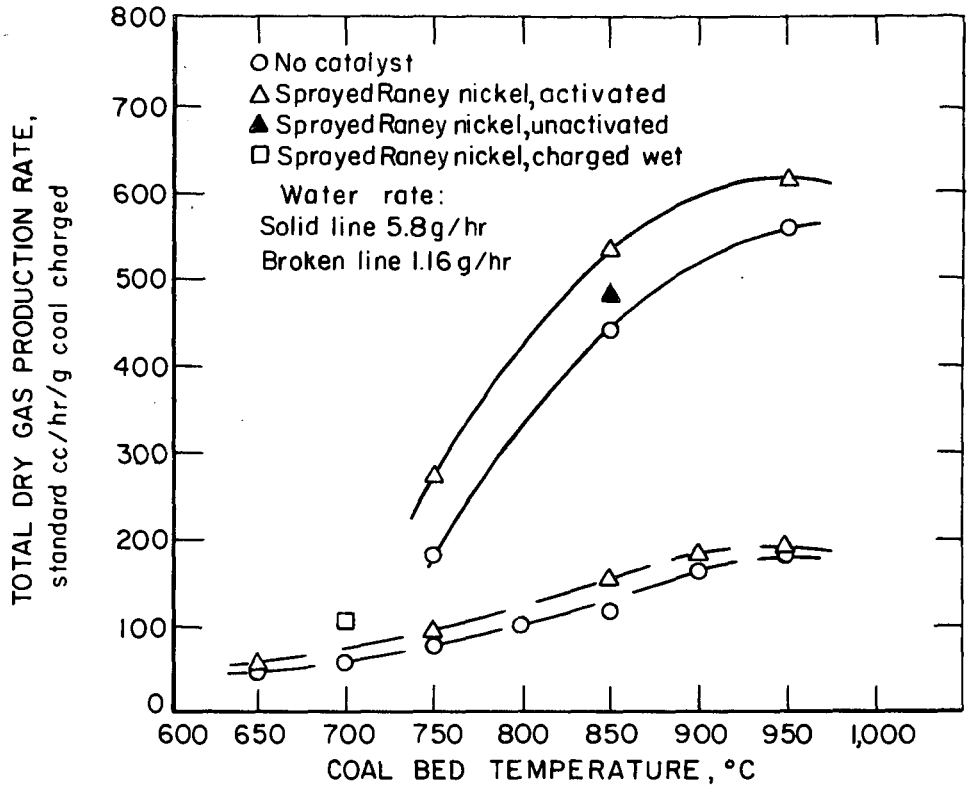

Figure 6.–Effect of temperature upon total dry gas production rate using sprayed Raney nickel. Test conditions: pressure, 300 psig; flow 2,000 standard cc/hour N_2; water, 5.8 and 1.16 g/hour.

4-29-68 L-10553

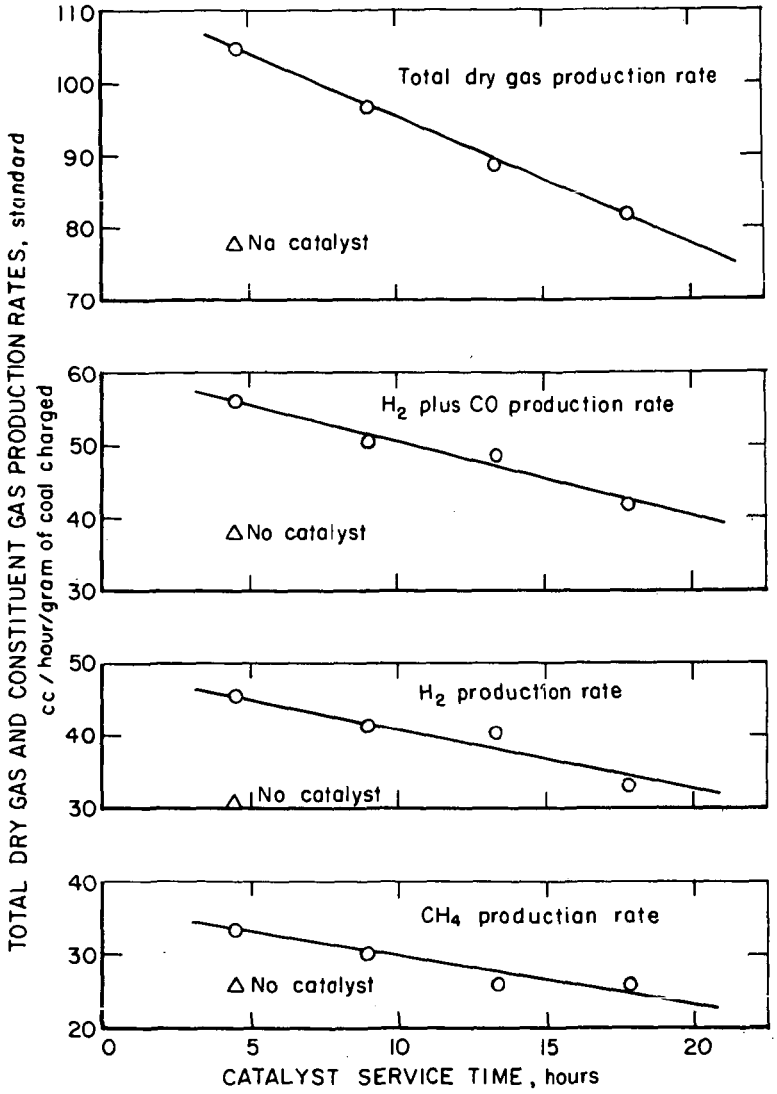

Figure 7.—Effect of catalyst service time upon gas production rates. Test conditions: temperature, 750°C; flow, 2,000 standard cc/hour N_2 and 1.16 g/hour water.

2-17-71 4-25-68 L-10545

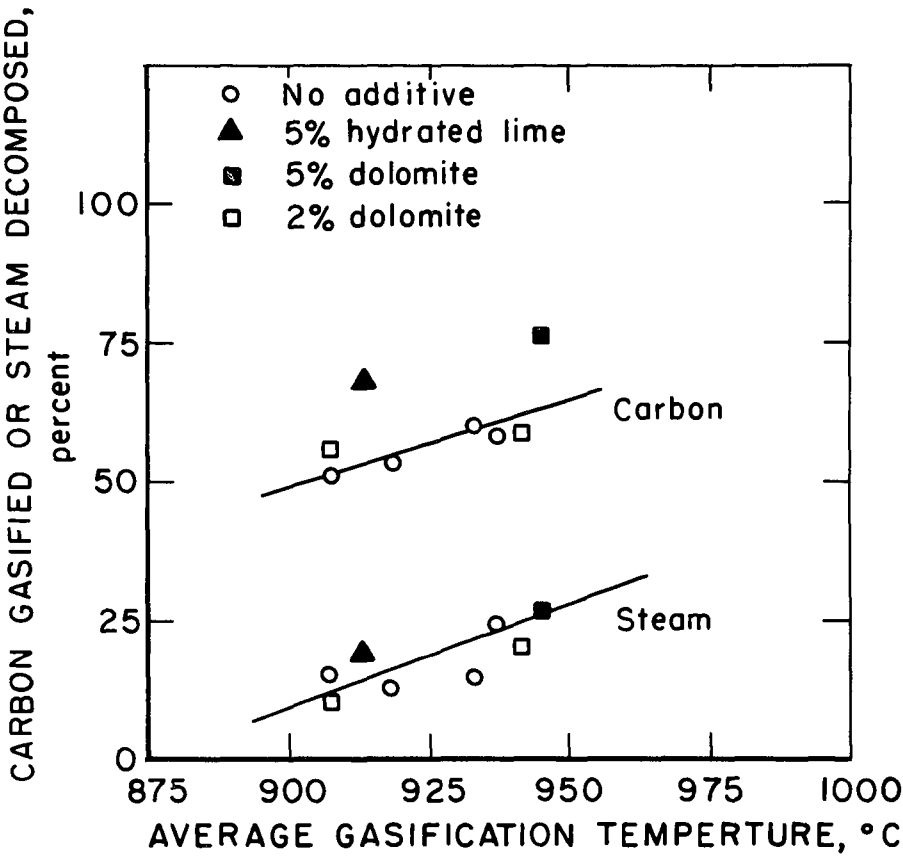

Figure 8– Effect of additives on percent carbon gasified and percent steam decomposition in 4" synthane gasifier operating at 40 atm.

L-13094

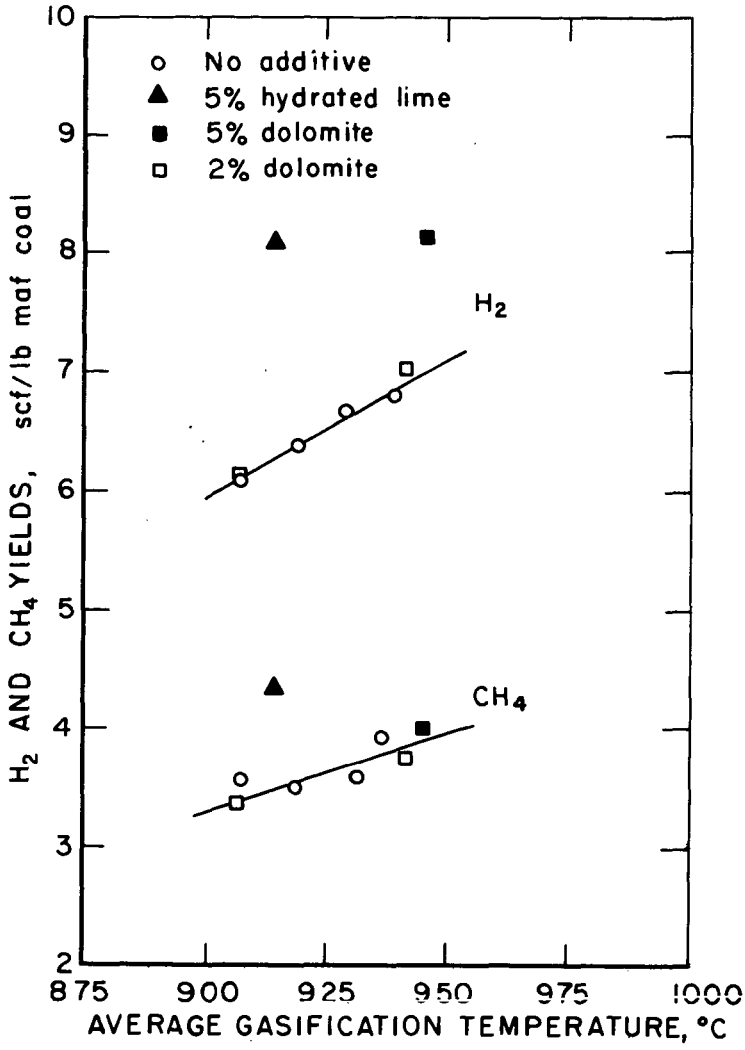

Figure 9 – Effect of additives on yield of hydrogen and methane in 4" synthane gasifier operating at 40 atm.

L-13095

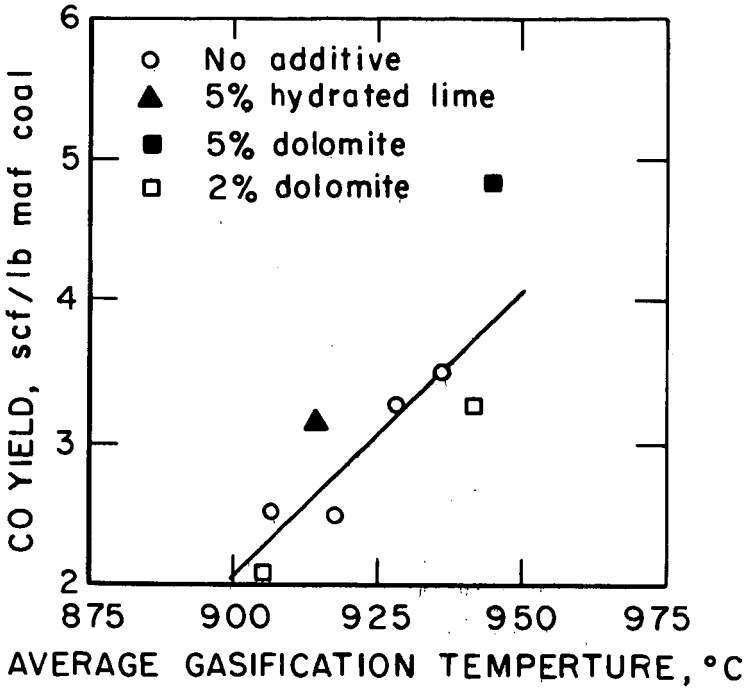

Figure 10- Effect of additives on yield of carbon monoxide in 4" synthane gasifier operating at 40 atm.

L-13096

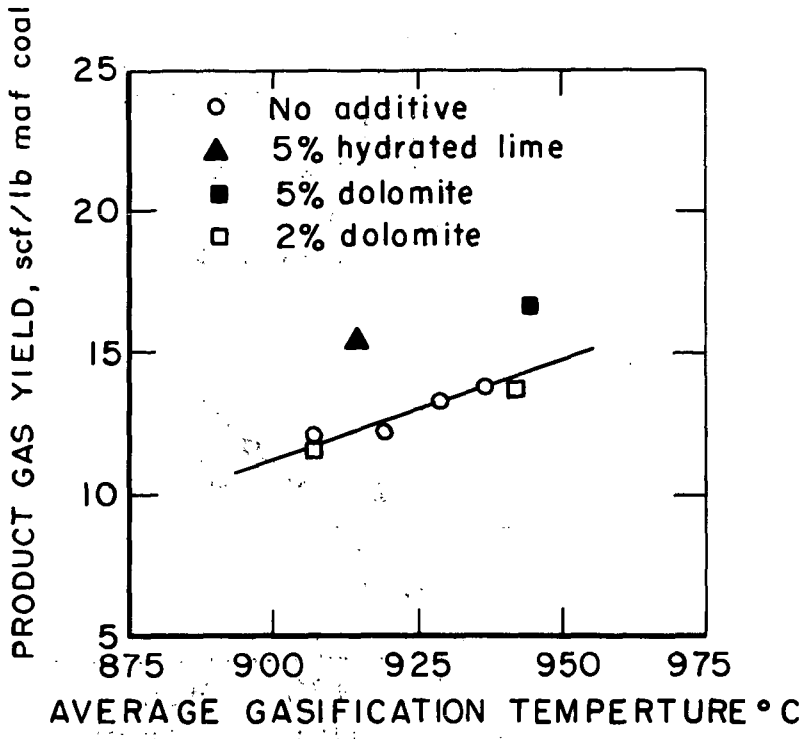

Figure 11 — Effect of additives on yield of product gas ($CO + H_2 + CH_4$) in 4" synthane gasifier operating at 40 atm.

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