CATALYTIC GASIFICATION OF GRAPHITE AND CHARS

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LBL--27175

DE89 014907

INTRODUCTION

In earlier papers [1-5] we have reported on the low temperature catalytic gasification of carbonaceous materials with steam. The use of catalysts is necessary if the process is to be carried out at temperatures below 1000 K. While alkaline or alkaline-earth hydroxides and carbonates have been studied by many investigators, they show catalytic activity only at temperatures above 1000 K. Transition metals, in particular nickel and iron, are able to catalyze the process at temperatures as low as 750 K but they deactivate very fast. These transition metal catalysts are active only if the reaction conditions permit their presence in the metallic state.

In our earlier work we have described catalysts which are mixtures of potassium hydroxide and nickel oxide and have demonstrated that they showed the highest activity of all the systems previously studied at below 1000K. We also showed that this catalyst mixture formed a relatively low melting eutectic that can wet the surface of the carbon substrates forming a liquid film which attacks the carbonaceous material by edge recession mode rather than by a channeling mode which prevails for potassium hydroxide alone and nickel alone.

A disadvantage found with the potassium-nickel catalysts is that they have a tendency to deactivate over a period of time when used on chars due to an interference or poisoning by ash components in the char. The present paper presents information on the role of ash components on catalytic gasification and describes another type of catalyst, namely a mixture of alkali and earth alkali oxides such as K_2O-CaO, which is almost as active and is less sensitive to poisoning than the potassium-nickel composition.

EXPERIMENTAL

Four chars ranging from lignite to bituminous coal char have been gasified along with graphite in the presence of various catalysts. The chars and their composition are summarized in Table 1.

The graphite used was spectroscopic grade graphite (Ultra Carbon Corp., type UCP-2, 325 mesh) having a BET surface area of $47 m^2/g$.

The carbonaceous samples were impregnated by incipient wetness methods with solutions of KOH, KNO_3, $Ca(NO_3)_2$, or $Ni(NO_3)_2$ respectively. The atomic ratio of K/M^{2+} was equal to 1 and the ratio of K/C = 0.01. The samples were dried at 920 K for one hour and the nitrates were decomposed. In some experiments with char the catalyst was prepared first by mixing aqueous solutions of KNO_3 and $Ni(NO_3)_2$ or $Mg(NO_3)_2$ and drying. The solid catalyst was then finely ground with the char in the correct proportions.

The experimental setup of the flow reactor is shown in Fig. 1. The reactor is a 3.7 mm ID 316 stainless steel tube. Between 0.5 and 1.0 g of sample is deposited between two alumina wool plugs. Passing steam through the system in the absence of a sample does not give any reaction. The reaction temperature can be adjusted to $\pm 1^{\circ}C$ of the desired value. Steam is produced by pumping water with a Harvard Compact Infusion pump, Model 975, through heated lines with an inlet temperature to the reactor of 450 K. At water flows of less than 0.1cc/min total pressure in the reactor is 15 psig ±1 psig. A liquid rate of .06cc/min was selected as a standard flow, equivalent to 270 cc/min of steam at 850 K. Steam leaving the reactor is condensed by volume expansion. Gas produced is measured and analyzed by gas chromatography and liquid water is measured to permit a mass balance.

A thermal detector with a column of 100/120 carbosieve S-II, 10' x 1/8", supplied by SUPELCO is used for the analysis of H_2, CO, CO_2, and CH_4. Water is eluted from the column at a flow rate of 30 ml/min He carrier gas, a column temperature of 425 K for 9 min, followed by a rise to 500 K achieved at a rate of 25°/min and maintained at 500 K for 12 min.

The flow reactor test is standardized as follows: The reactor containing the carbon plus catalyst mixture is heated to 725 K at a rate of 125°/hr in a 5cc/min helium flow. The temperature of 725 K is maintained for 2 hours to assure complete decomposition of the catalyst nitrates and their conversion to oxides. Water flow is then started and the temperature is raised at a rate of about 10°/min to the desired reaction temperature, usually 900 K.

RESULTS

Potassium-nickel catalysts which show high activity at gasification temperatures in the 600-900K range deactivate as a function of time, apparently due to interaction with ash components of chars.

In a search for catalysts which would be likely to show less deactivation by ash components and which would also be less expensive than nickel, it was found that alkali-earth alkali combinations are of considerable interest. Potassium-calcium oxide mixtures were only slightly less active than potassium-nickel.

Activation energies for the potassium-nickel and potassium-calcium catalysts were determined on graphite and are not appreciably different on various chars (Table 2).

In general graphite and chars exhibit the same gasification mechanism as evidenced by similar activation energies: kinetic rate = $p^n(H_2O)p^n(H_2)$, $0<n<1$ and $\Delta E = \sim 63$ Kcal.

The ease of gasification increases in the order: graphite < bituminous < subbituminous < lignite chars. Table 3 illustrates this behavior. While K-Ca is more active for lignite and subbituminous chars than K-Ni, the reverse is true for bituminous chars.

No difference in gasification was observed between catalyst prepared by impregnation of char or by physical mixing of catalyst and char.

In kinetic studies of steam gasification of a number of chars impregnated with 1% of equimolar potassium and nickel oxides or of K-Ca oxides, it was found that the predominant gas composition is H_2 and CO_2. It was observed that the CO/CO_2 ratio of gases produced varies with different chars. Thus, the ratio is .8 for Illinois #6 char and .08 for North Dakota lignite char, which has a much higher ash content. It was also found that impregnation with potassium hydroxide alone results in much higher CO/CO_2 ratios than K/Ni and therefore, in less hydrogen. Thus, Illinois #6 char with potassium alone produces a 3.5 CO/CO_2 ratio compared to .8 for K/Ni. Essentially no CH_4 was found.

The rate of hydrogen production as a function of catalyst loading increases rapidly in the case of the North Dakota char. This is shown in Table 4. Gasification at 890 K resulted in an almost 5-fold increase in the hydrogen production rate when the loading was 2.5% rather than 1% with an additional increase of 20% when the loading was 3.2%.

Catalytic activity of ash components in the char was observed in a number of cases and particularly for the North Dakota char. In the absence of a catalyst, initial gasification was observed (Fig. 2) until a total of about 30% of the char was gasified. The rate of hydrogen production per minute declined rapidly and eventually died. When the remaining 70% of the char was impregnated with 1% Ni/K, gasification resumed at a good rate and with only a slight decline in hydrogen production (Fig. 3). The North Dakota char was demineralized by HF/HCl treatment to an ash content of less than 2%. The demineralized char showed no activity in the absence of added catalysts. This proves that the previously observed gasification activity of the native char was due to a catalytic action of the ash.

After impregnation of the demineralized char with Ni/K rapid gasification occurs as shown in Fig. 4. The rate of gasification of the demineralized char promoted by Ni/K is almost an order of magnitude higher than that observed for the steam deactivated char with the same catalyst (Fig. 3). The gas product distribution is the same, namely mostly CO_2 and hydrogen with small amounts of CO and with almost negligible CH_4 production. The decline in hydrogen production shown in Fig. 4 at the end of gasification is due to the relatively small amounts of char remaining in the reactor after about 75% carbon conversion.

A comparison of the rate of char conversion for alkali-alkali earth (K-Ca) catalysts and for alkali-transition metal catalysts (K-Ni) is shown in Fig. 5 for a subbituminous char (Rosebud). The superiority of the K-Ca catalyst over the K-Ni catalyst is apparent. When the char is first demineralized, the K-Ni catalyst shows better gasification than the raw char, while the K-Ca catalyst looses some activity when used in the demineralized char. This indicates that ash components poison the K-Ni catalyst but enhance the activity of the K-Ca catalyst.

An important finding toward proposing a reaction mechanism is the fact that the catalysts used in this work can dissociate water at reaction conditions in the absence of carbon. With a K-Mg catalyst the activation energy for H_2 production from water was 132 Kcal/mol. It has also been noted that while the stoichiometric ratio of H_2/CO_2 in carbon gasification should be 2, it is slightly higher than 2 during the first 50% of gasification and lower than 2 during the second half. This indicates sorption of CO or CO_2 on the char in early stages of gasification and desorption in the later states. Breaking of C-C bonds is probably the rate controlling step. Figure 6 shows the ratios of H_2/CO_2 produced at various stages of gasification.

CONCLUSION

Graphite and chars can be gasified at 800-900°K by treatment with steam in the presence of catalysts comprising mixtures of potassium and nickel salts or potassium and calcium salts. The ease of gasification increases graphite < bituminous < subbituminous < lignite. The catalysts must be wetting the carbonaceous material and gasification proceeds by edge recession. Potassium-nickel catalysts, while slightly more active, are more subject to poisoning by ash components than potasssium-calcium catalyts. An important first step in the gasification mechanism appears to be water dissociation that is catalyzed by all the active catalysts.

ACKNOWLEDGEMENT

This work was supported by the Assistant Secretary for Fossil Energy, Office of Management and Technical Coordination, Technical Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF760098, through the Morgantown Energy Technology Center, Morgantown, WV 26505.

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Table 1..PROXIMATE, ULTIMATE, AND INORGANIC CHEMICAL ANALYSES OF COALS USED IN GASIFICATION TESTS

Seam 8 Mine 125 KY No. 13	N.Dakota Lignite	Rosebud	OH Pitt No. Franklin	
Proximate Analysis, wt%				
Moisture	3.4	23.1	2.5	9.8
Volatile Matter	71.6	28.5	38.6	32.2
Ash	25.0	11.3	7.5	7.3
Fixed Carbon	-.	37.1	51.4	50.7
Total	100.0	100.0	100.0	100.0
Ultimate Analysis, wt% (dry basis)				
Ash		14.66	7.68	8.08
Carbon		62.78	74.47	73.74
Hydrogen		4.40	5.24	4.82
Sulfur		1.29	3.21	1.40
Nitrogen		0.99	1.50	1.85
Oxygen (by difference)		15.88	7.90	10.11
Total		100.00	100.00	100.00
Ash Composition, wt%				
SiO_2	26.1	48.8	41.6	58.5
Al_2O_3	13.7	23.55	20.9	26.9
Fe_2O_3	6.6	7.02	31.7	8.1
TiO_2	0.6	0.12	1.02	0.87
P_2O_5	0.2	0.25	0.07	0.16
CaO	22.4	7.16	1.14	0.90
MgO	8.1	2.57	0.36	1.21
Na_2O	1.8	0.09	0.35	0.24
K_2O	.6	0.36	0.98	2.94
SO_3	18.1	9.91	1.00	0.80
Total	98.2	99.78	99.2	100.62
Ash Content (as ashed for analysis of ash, dry basis)			7.7	8.2
Basic Ash Constituents, wt%		19.22	35.2	13.4
Dolomite Ratio, wt%		56.6	4.3	15.8
SiO_2/Al_2O_3 Ratio		2.1	2.0	2.2
Forms of Sulfur, wt% (dry basis)				
Pyritic		0.76	2.37	0.40
Sulfate		0.015	0.21	0.10
Organic		0.52	0.97	1.03
Total		1.28	3.56	1.53

Forms of Iron (dry basis)	wt%	% of Fe	wt%	% of Fe	wt%	% of Fe
Pyritic	1.32	62*	2.07	96	0.35	70
HCl-Soluble	0.12	6	0.08	4	0.15	30
Total of HCl Sol + Pyritic	2.13*	100	2.15	100	0.50	100
Acid-Insoluble	0.69	--	<0.10	--	<0.1	
Pyritic, % of total Fe**	--		97		54	

*Based on total iron including 0.69 wt% HCl-insoluble

**Of 1/4-inch-top-size coal after storage

Table 2: Arrhenius Analysis for Gasification

Catalyst and Char	Activation Energy Kcal/mol
K-Ni Graphite	~61.0
K-Ca Rosebud Char	58.8
K/Ca Franklyn Char	64.4
K-Ca Franklyn Char demineralized	63.1
K-Ni Franklyn Char	54.1

Table 3: Relative Gasification Conversion of Chars

Catalyst Activity	Char Class	% Conversion at 900K After 1000 Min
K-Ca > K-Ni	Lignite	100
K-Ca > K-Ni	Subbituminous	90-100
K-Ni > K-Ca	Bituminous	45-50

Table 4. Rate of H_2 Production as Function of Catalyst Loading Ni/K = 1.0.

Ni/C	H_2 rate ml/min	m mol/H_2/mol Ni/min
1.0×10^{-2}	0.5	49
2.5×10^{-2}	2.48	97
3.2×10^{-2}	2.90	89

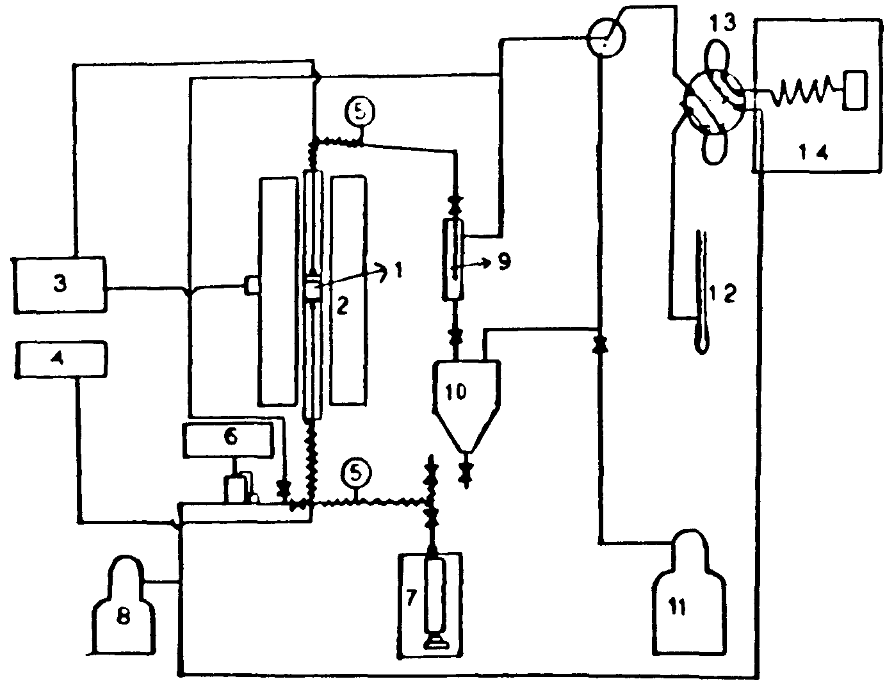


Figure 1. Experimental Setup

1. Sample
2. Oven
3. Temperature control
4. Temperature indicator
5. Pressure gauges
6. Mass flow controller
7. Syringe pump
8. He 99.99% bottle
9. Expander
10. Water recipient
11. Callibrating mixture for G.C.
12. Bubble flowmeter
13. Gas sample valve
14. Gas chromatograph

⋈ : Valve
∿∿∿ : Wire heater

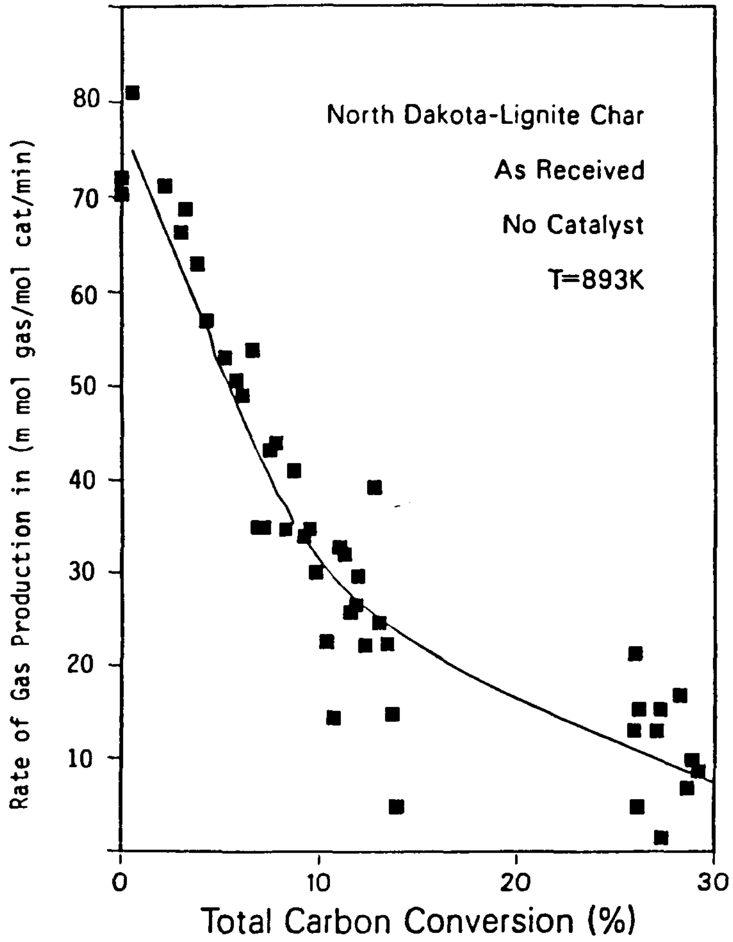


Fig. 2.: Variations of the rate of carbon gasification by steam at 893 K, with total carbon conversion, for North Dakota-lignite char, as received, without addition of any catalyst.

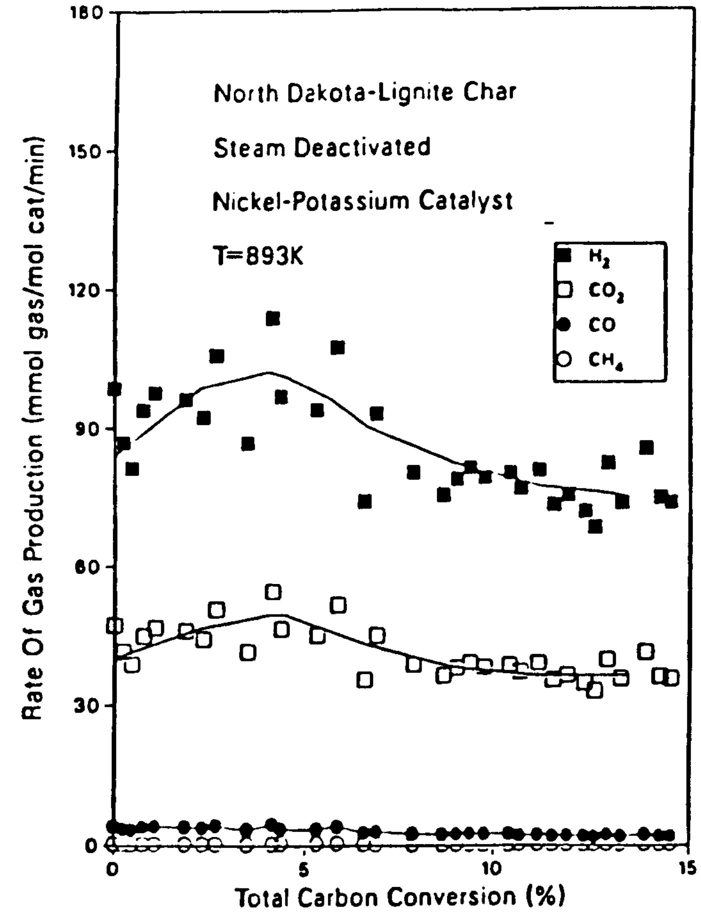


Figure 3. Rate of gas production, as a function of carbon conversion, for all the gases formed on the steam gasification of deactivated char at 893 K, catalyzed by the nickel-potassium mixture. The molar ratio of nickel to potassium was equal to 0.9, and the catalyst loading was equal to 2.0 mmol cat/g char. The initial weight of char was 0.6 g.

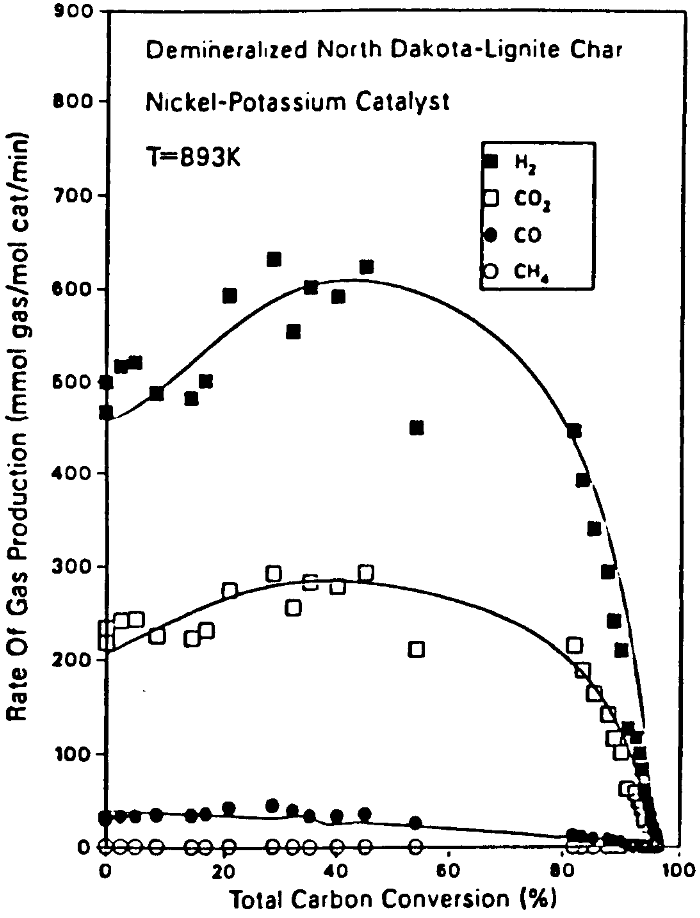
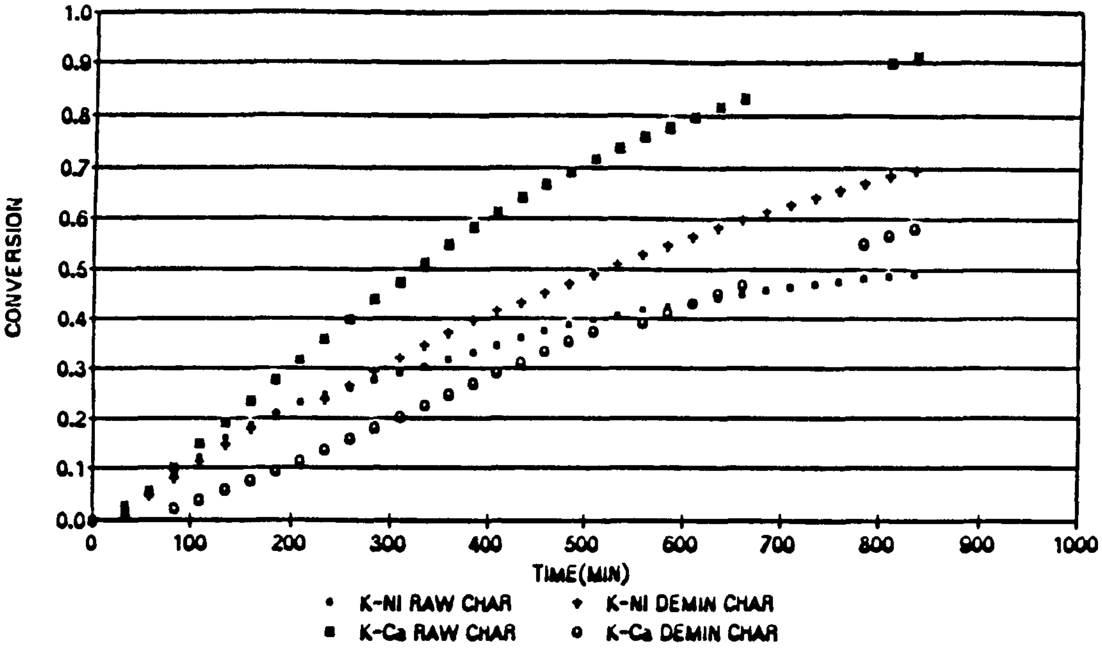


Figure 4. Rate of gas production as a function of carbon conversion, for all the gases formed from the steam gasification of demineralized char at 893 K, catalyzed by the nickel-potassium mixture. The molar ratio of nickel to potassium was equal to 0.9, and the catalyst loading was equal to 2.0 mmol cat/g char. The initial weight of char was 0.5g.

Fig. 5. Rosebud Char Steam Gasification
K-Ca and K-Ni Compared



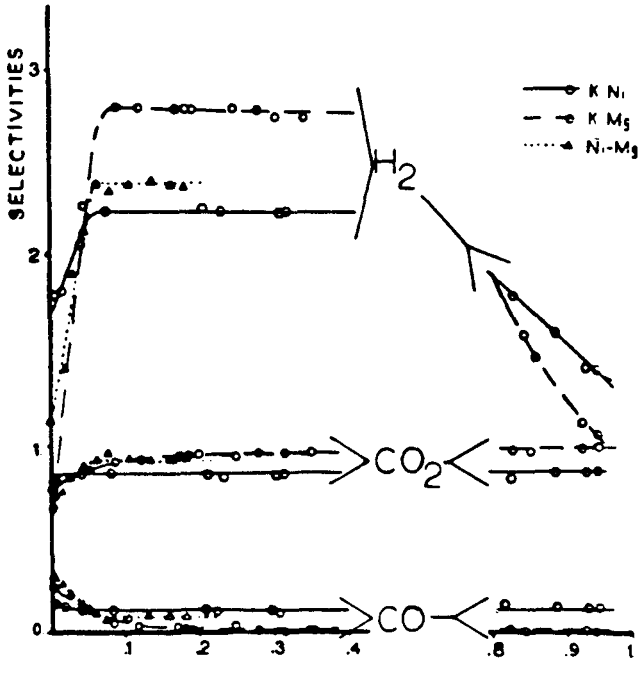


Fig. 6. Selectivity vs. Conversion for Steam Gasification of North Dakota Char Demineralized.