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### Fundamental Studies of Catalytic Gasification: Annual Report, October 1, 1987–September 30, 1988

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October 1988

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ANNUAL REPORT

October 1, 1987 - September 30, 1988

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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## I. Task Description for FY 1988

In the past this program has investigated the role of catalysts in relatively low temperature steam gasification. New mechanisms have been demonstrated and it has been shown that combinations of alkali hydroxide with transition metal oxides form compounds which act as the true catalyst to produce mostly hydrogen and carbon dioxide. This has further been confirmed by surface science studies and by transmission electron microscopy. At the lower temperatures (~800 K) used, hydrogen and CO<sub>2</sub> are the products formed, but the effect of temperature and of the exact composition of the NiO/KOH catalyst that has been studied in the greatest detail on the CO<sub>2</sub>/CO ratio remains to be defined. Similarly, a clear definition of the advantages of different alkali-transition metal oxide compositions is required. It appears possible that with the right catalyst and conditions, either syn-gas or H<sub>2</sub> + CO<sub>2</sub> can be produced. Inexpensive transition metal oxide-alkali catalysts will be evaluated as will be the effect of mineral matter in chars and coke and the role of different partial pressures of H<sub>2</sub>, CO and H<sub>2</sub>S.

## II. Introduction

The "Highlight" section of this report summarizes the accomplishments of work during fiscal year 1988 and partially repeats findings reported in the quarterly reports of December 1987 (LBL-24531), March 1988 (LBL-25041) and June 1988 (LBL-25416) along with new information obtained during the last quarter. The "Progress of Studies" section reports the results obtained during the June-September period of 1988.

## III. Highlights

- Catalysts used in the steam gasification of chars must be able to dissociate water at operating temperature and should form low melting eutectica to permit an edge recession type attack on the char.

- Catalysts used in this work dissociate water  $>550^{\circ}\text{C}$  and there is evidence that a mechanism prevails which involves carbon oxidation by the oxygen from water dissociation and simultaneous generation of hydrogen.
- Some chars give activity in the absence of catalysts during early stages of gasification, but this activity dies before 20% of the char is gasified. If extraneous catalysts are added after this initial gasification has died, the gasification resumes at steady rates.
- Nickel-potassium catalysts which have been used in our work in the past gradually deactivate when used on chars, apparently because of interaction of ash components with the nickel constituent. Demineralized chars can be catalytically gasified without deactivation.
- Mixtures of alkali and earth alkali, particularly potassium-calcium oxides are almost as active as K-Ni and do not deactivate during gasification of chars.
- K-Ca as well as K-Ni catalysts produce  $\text{H}_2$  and  $\text{CO}_2$  at temperatures in the  $580\text{--}720^{\circ}\text{C}$  range. At temperatures  $>700^{\circ}\text{C}$   $\text{H}_2$  and  $\text{CO}$  are produced.
- Different chars vary in their ease of gasification:  
lignite  $>$  subbituminous  $>$  bituminous  $>$  graphite.
- Graphite and chars exhibit similar gasification mechanisms as evidenced by similar activation energies.  
Kinetic rate  $\approx p^{1/2}(\text{H}_2\text{O})/p^{1/2}(\text{H}_2)$   
 $\Delta E = 250 \text{ KJ/mole } (\sim 63 \text{ Kcal/mole}).$
- There is no evidence for either water gas shift occurring or for  $\text{CO}$  being an intermediate during gasification.

- A series of controlled atmosphere electron microscopies (CAEM) was taken of graphite gasification with K-Ca catalysts. This showed edge recession attack similar to that observed with K-Ni and in contrast to the channeling attack observed with potassium salts alone and nickel alone. Edge recession is clearly faster than channeling. Activation energies calculated from CAEM data check those obtained in a flow reactor.
- Surface area determinations show a decrease in the area of the raw char in the same order as their resistance to gasification. Impregnated catalysts have very low surface area, probably due to pore plugging. After partial gasification of catalyst containing char, the surface area increases by more than an order of magnitude.

#### IV. Progress of Studies

##### a) Steam Gasification of Chars

In addition to the previously reported gasification results of a lignite (N. Dakota), a subbituminous (Rosebud) and a bituminous (Ohio Pitt #8) char, an additional bituminous char (Kentucky No. 13) has been evaluated for steam gasification after impregnation with either K-Ca or K-Ni oxides. An analysis of this char is presented in Table 1 in comparison with two of the other chars.

Figures 1 and 2 show the conversion vs. time curves and the rate of gasification for K-Ca impregnated KY No. 13 char (Fig. 1) and the demineralized K-Ca impregnated char (Fig. 2). Figure 3 shows conversion and rate of gasification when the KY No. 13 char was impregnated with K-Ni, while Fig. 4 gives the same information for the demineralized K-Ni impregnated char.

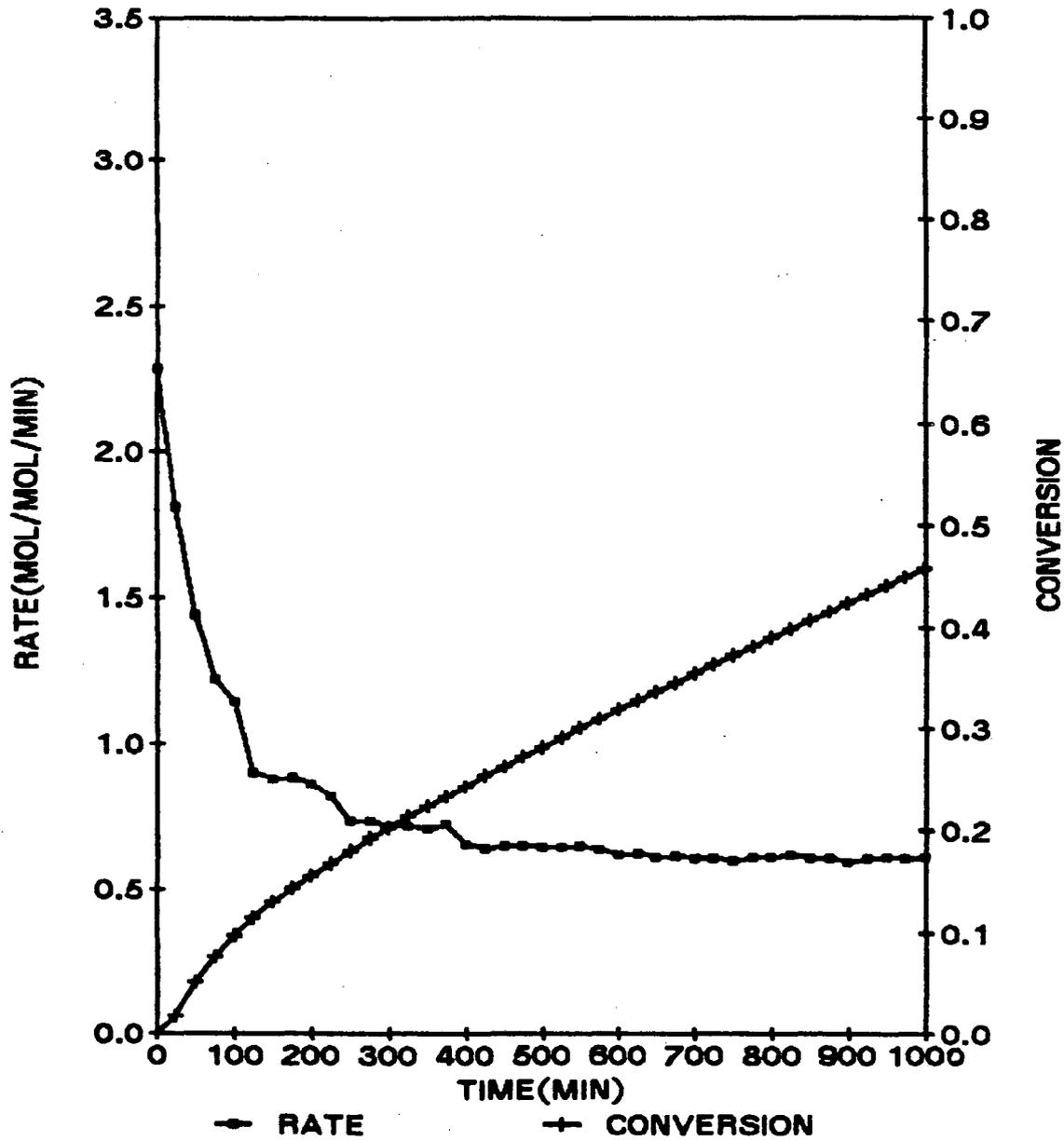
Table 1..PROXIMATE, ULTIMATE, AND INORGANIC CHEMICAL ANALYSES OF COALS USED IN GASIFICATION TESTS

Seam Mine	Rosebud	OH Pitt No. 8 Franklin 125	KY No. 13			
<b>Proximate Analysis, wt%</b>						
Moisture	23.1	2.5	9.8			
Volatile Matter	28.5	38.6	32.2			
Ash	11.3	7.5	7.3			
Fixed Carbon	37.1	51.4	50.7			
Total	100.0	100.0	100.0			
<b>Ultimate Analysis, wt% (dry basis)</b>						
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			
<b>Ash Composition, wt%</b>						
SiO <sub>2</sub>	48.8	41.6	58.5			
Al <sub>2</sub> O <sub>3</sub>	23.55	20.9	26.9			
Fe <sub>2</sub> O <sub>3</sub>	7.02	31.7	8.1			
TiO <sub>2</sub>	0.12	1.02	0.87			
P <sub>2</sub> O <sub>5</sub>	0.25	0.07	0.16			
CaO	7.16	1.14	0.90			
MgO	2.57	0.36	1.21			
Na <sub>2</sub> O	0.09	0.35	0.24			
K <sub>2</sub> O	0.36	0.98	2.94			
SO <sub>3</sub>	9.91	1.00	0.80			
Total	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 <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Ratio	2.1	2.0	2.2			
<b>Forms of Sulfur, wt% (dry basis)</b>						
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			
<b>Forms of Iron (dry basis)</b>						
	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

K-Ca KYNo13 CHAR. STD.COND.  
RATE & CONVERSION VS TIME



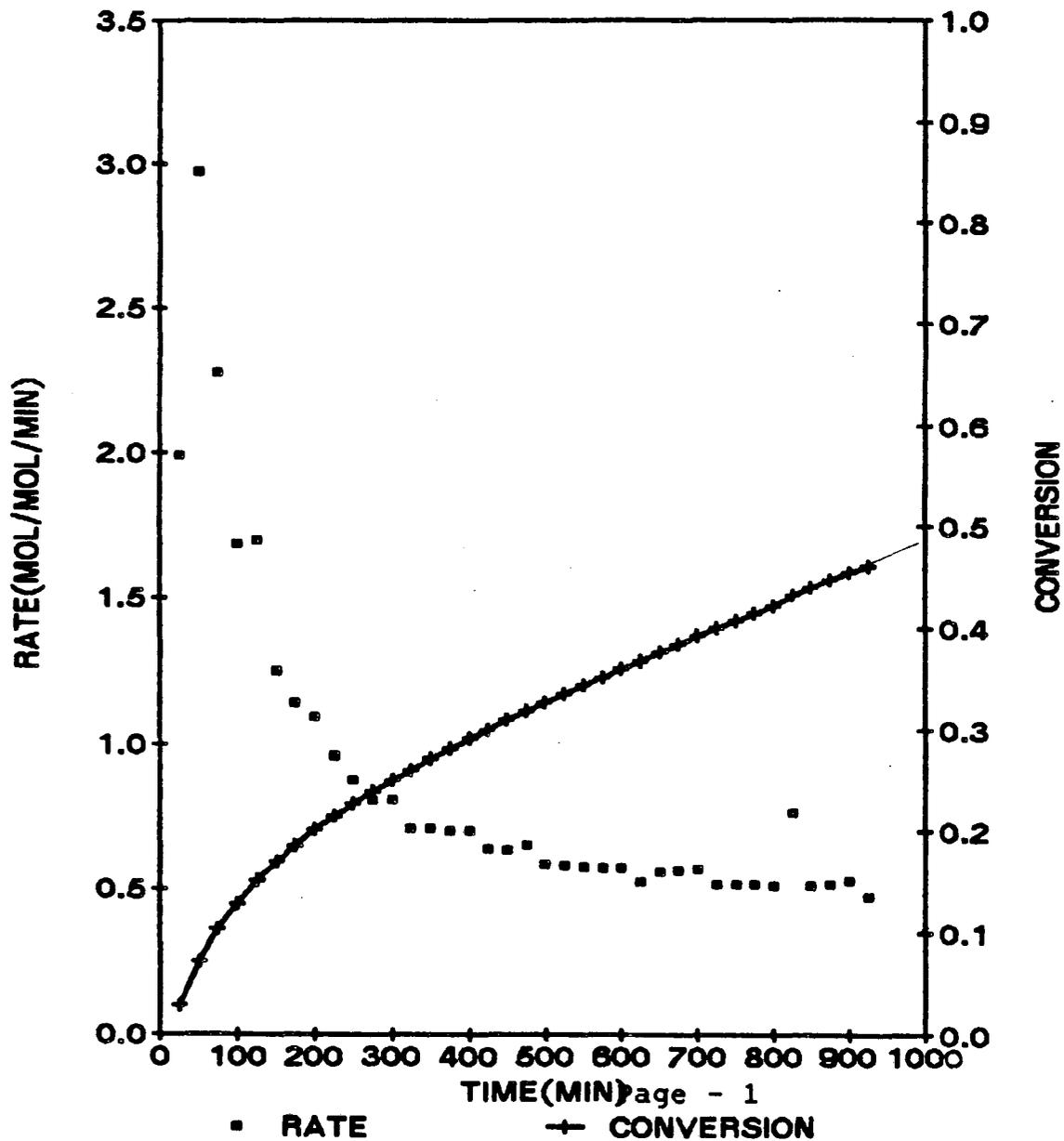
K-Ca KY13 STANDARD  
RAW

CONDITIONS

Ea=41.93Kc  
Ko=1.175 E  
r=0.997  
Ea=262.3KJ

Fig. 1

K-Ca KYN<sub>o</sub>13 DEMINERALIZED.STD.COND.  
RATE & CONVERSION VS TIME



K-Ca KY13 STANDARD CONDITIONS  
DEMINERALIZED

Ea=42.80Kcal  
r=0.995  
Ko=1.423 E10  
Ea=267.7Kj/m

Fig. 2

K-Ni KYNo13

Ea=33.98 Kcal/mol

RAW

standard conditions

Ko=1.434 E8

r=0.989

Ea=212.5KJ/MOL

K-NI KY No13 CHAR STD. COND.  
RATE & CONVERSION VS TIME

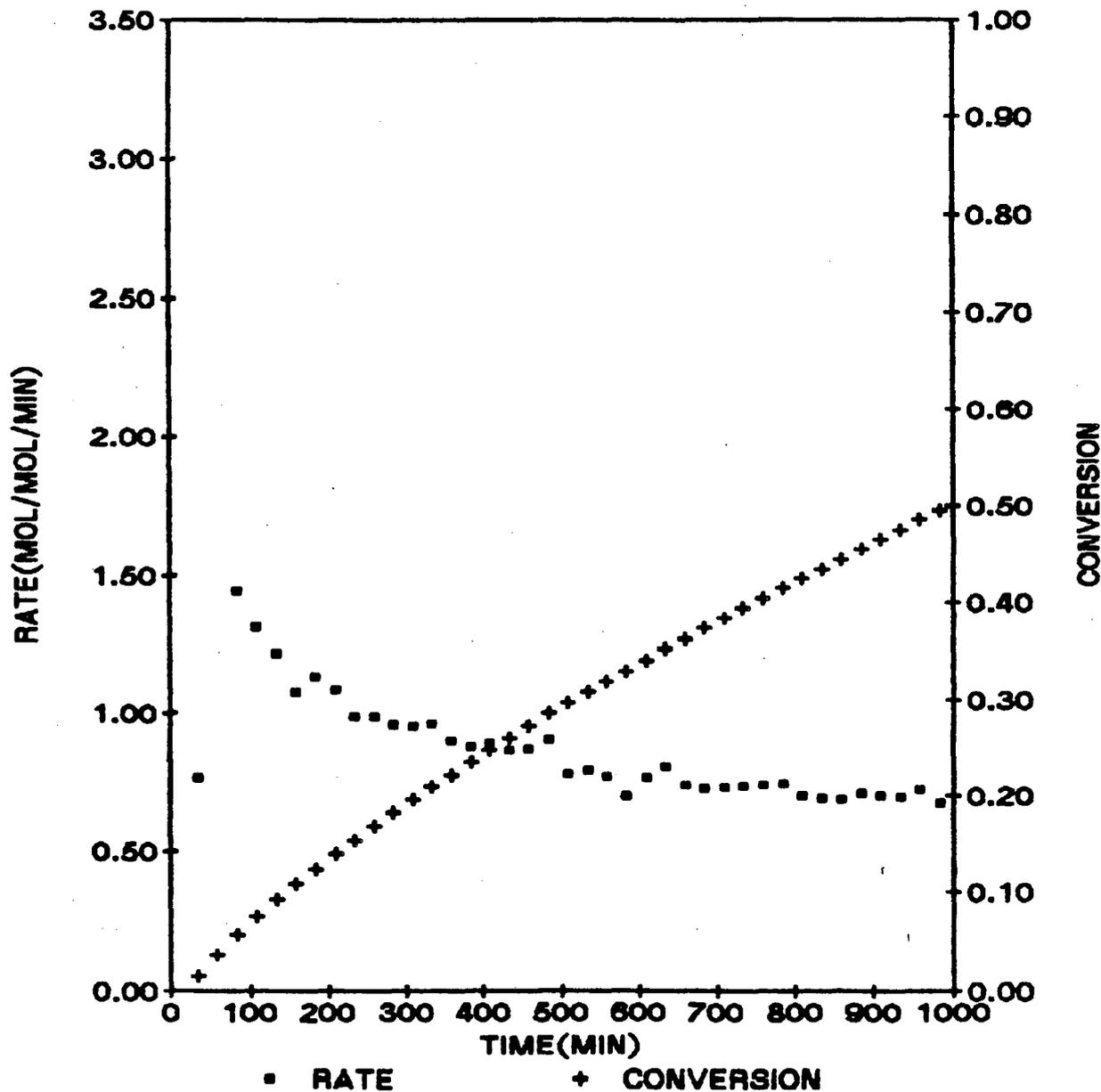


Fig. 3

### K-NI KY13 DEMINERALIZED RATE & CONVERSION VS TIME

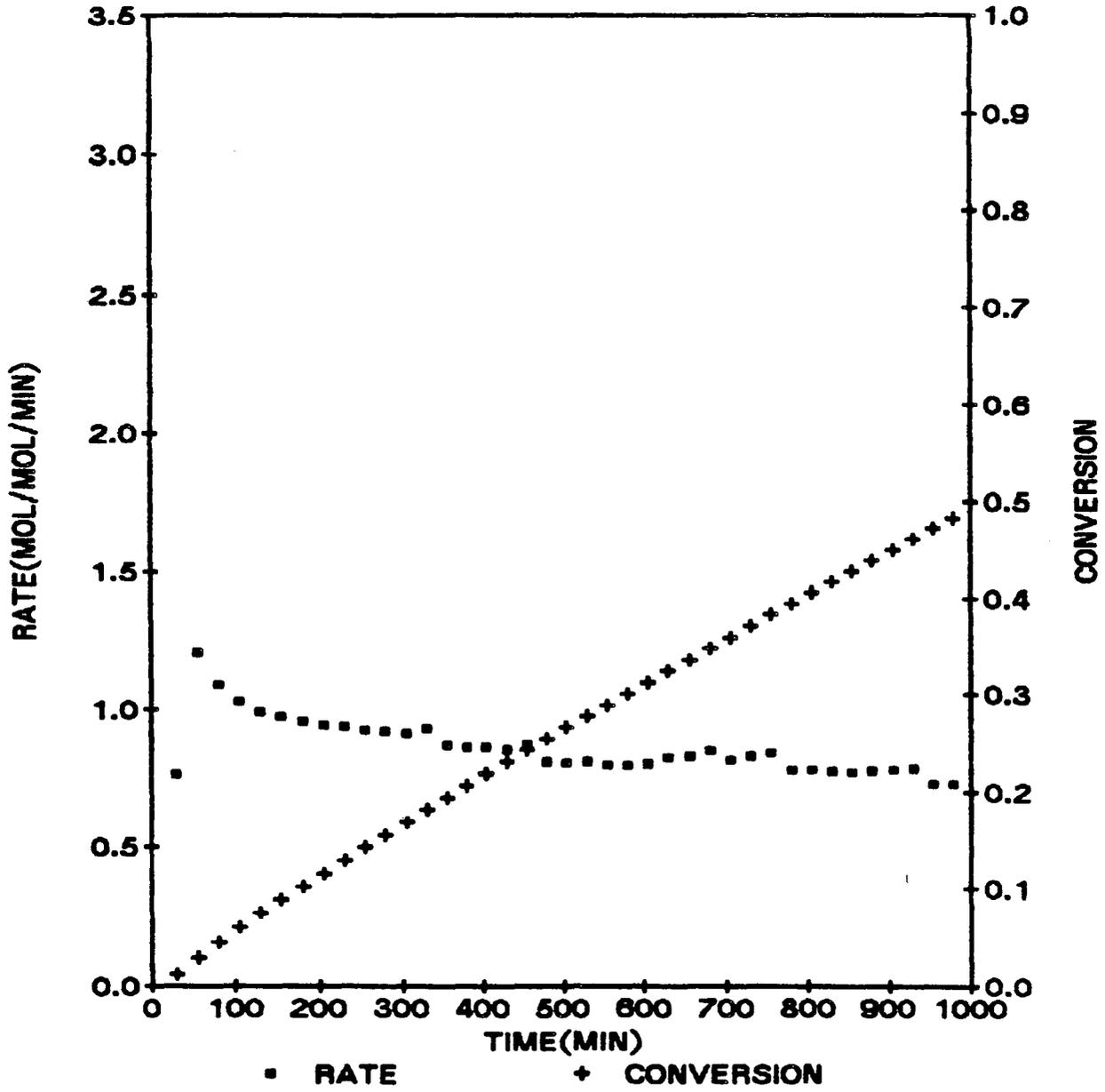


Fig. 4

Finally, Fig. 5 and Fig. 6 compare the conversion in the presence of K-Ca (Fig. 5) and of K-Ni (Fig. 6) for the various chars investigated, both before and after demineralization.

The chemical analysis of the KY No. 13 char (Table 1) shows close similarity to the other bituminous char investigated, OH Pitt No. 8, except for the lower pyritic sulfur content of the KY No. 13 char. Conversion of the K-Ca impregnated chars is about the same for the bituminous chars (Fig. 5). After demineralization the Ohio char performed somewhat better than the KY char. The subbituminous Rosebud char exhibited appreciably better conversion (Fig. 5). The demineralized OH No. 8 char performed better than other demineralized chars with K-Ca catalysts (Fig. 5).

In the case of K-Ni impregnated chars (Fig. 6) all the chars tested showed similar behavior except for the demineralized Rosebud char which gives much higher conversion.

Figure 7 compares K-Ca with K-Ni catalysts for both raw and demineralized subbituminous Rosebud char. It is obvious that K-Ca is much more active than K-Ni for the raw char. This can also be stated as an indication of poisoning by ash components for the K-Ni catalyst, which poisoning does not occur with K-Ca. The demineralized Rosebud char on the other hand performs somewhat better with K-Ni than with K-Ca, indicating that K-Ni is a more active catalyst but is also more subject to poisoning.

The most important conclusions to be drawn from the gasification experiments conducted thus far are:

- Ease of gasification increases: graphite < bituminous < subbituminous < lignite.
- K-Ca catalysts are almost as effective as K-Ni catalysts and are not as easily poisoned by ash components (Table 2).
- Demineralization often improves gasification performance, particularly for the K-Ni catalysts, indicating that ash components act as catalyst deactivating agents.

**K-Ca CATALYST  
COMPARED BEHAVIOR FOR DIFFERENTS CHARS**

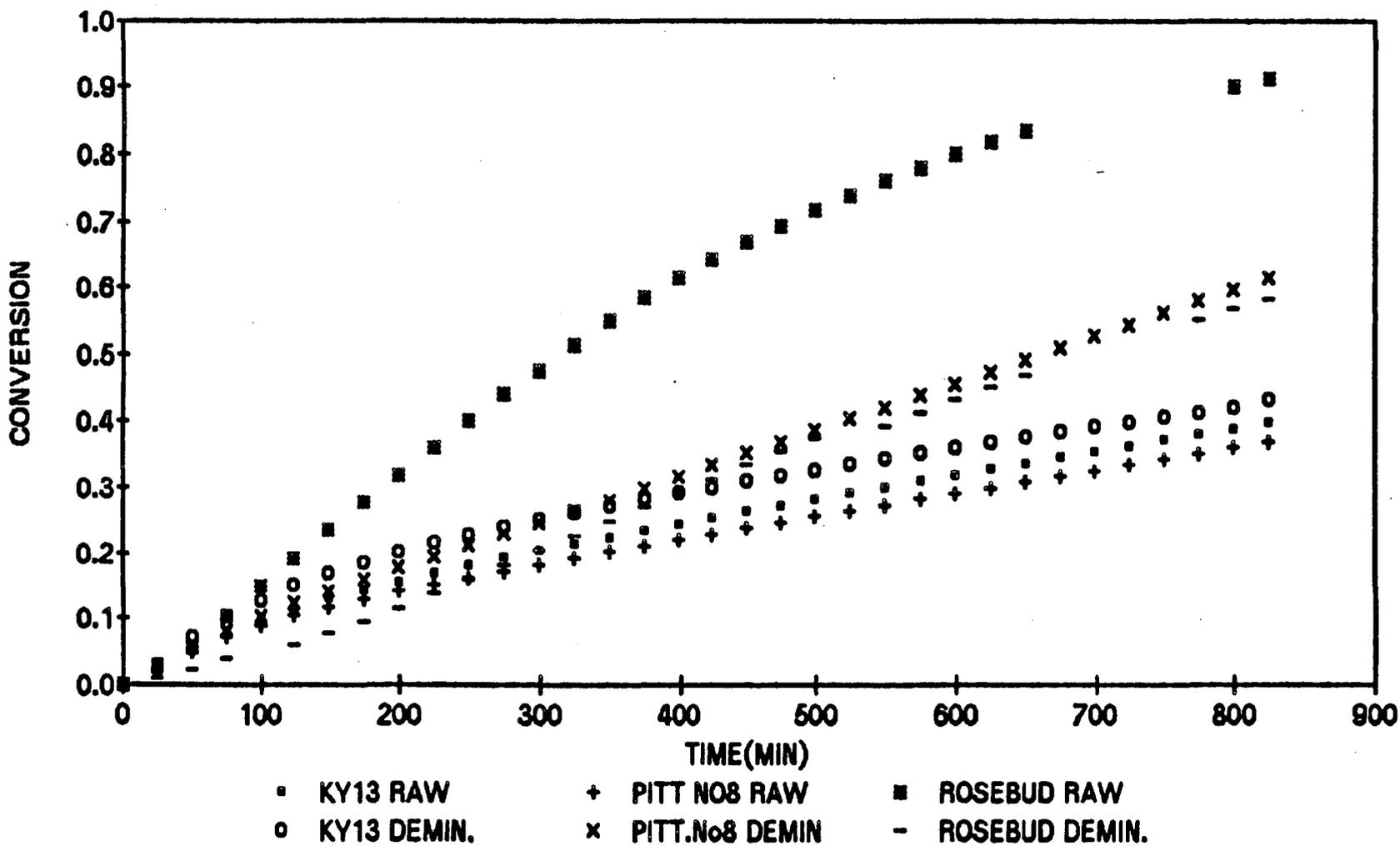


Fig. 5

K-NI CATALYST  
COMPARED BEHAVIOR FOR DIFFERENTS CHAR

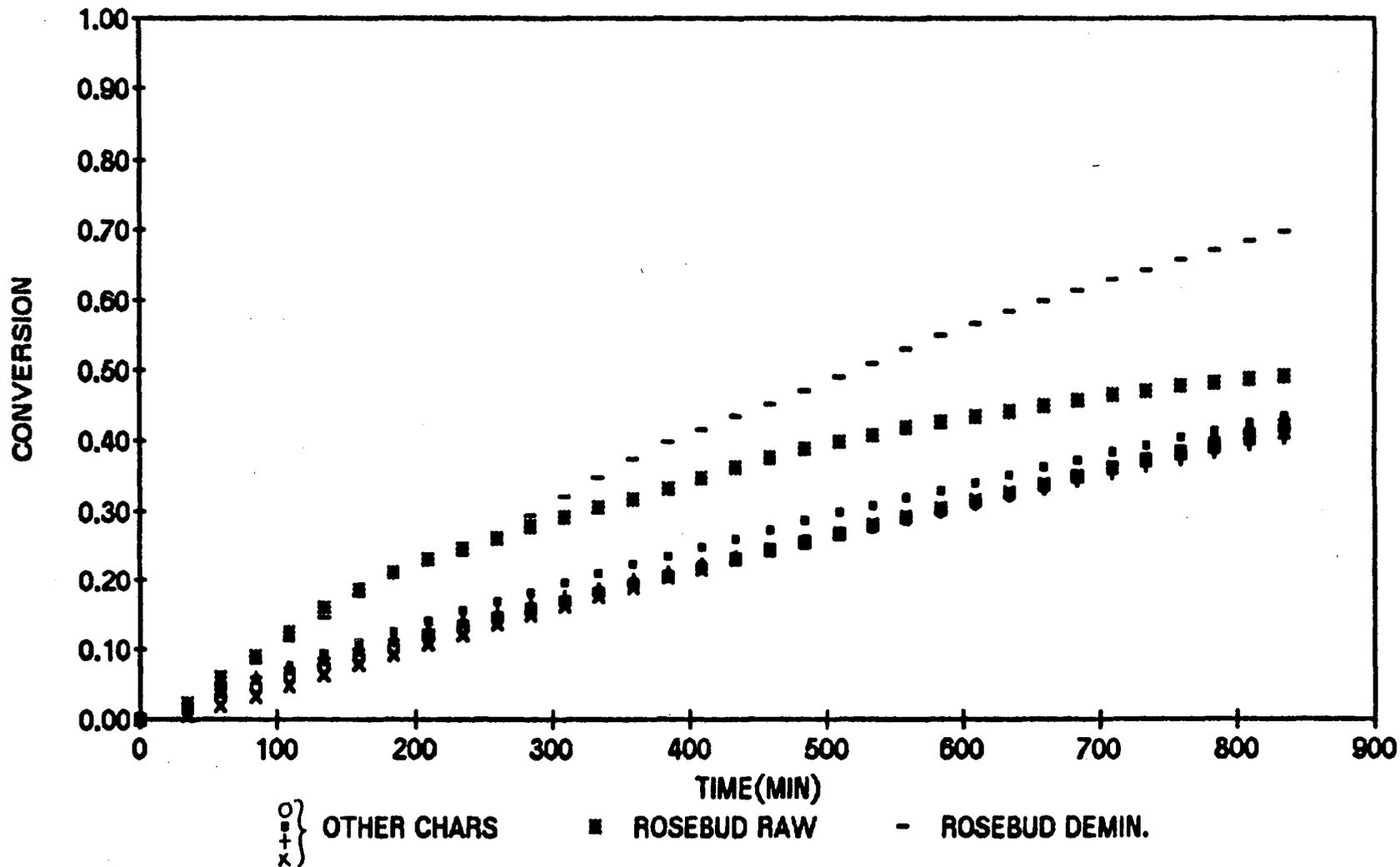


Fig. 6

TABLE 2  
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

b) Surface Area Determinations

Surface areas were determined of various chars before and after impregnation with catalysts and after their gasification to about 50% conversion. Results are presented in Table 3.

The surface area of the raw chars greatly decreases in the order of their activity, from 550 m<sup>2</sup>/g for the North Dakota lignite to ~ 25 m<sup>2</sup>/g for subbituminous, and 2-10 m<sup>2</sup>/g for bituminous char. Demineralization of the char has no major effect on the surface area.

Impregnation of the Rosebud char with catalysts of the K/Ca or K/Ni type oxides causes a major loss of surface area, probably due to blocking of pores by the catalyst material.

TABLE 3  
Surface Area of Chars

Char	Catalyst	Demineralized	Surface Area in <sup>2</sup> /g	
			Before Gasific.	After 50% Gasific.
N. Dakota	--	yes	552	--
Rosebud	--	no	27	--
Rosebud	--	yes	22	--
Rosebud	K/Ca	yes	0.22	446
Rosebud	K/Mg	yes	1.1	524
Rosebud	K/Ni	yes	2.2	410
OH Pitt No. 8	K/Ni	no	2.0	319
OH Pitt No. 8	--	yes	2.2	--
KY No. 13	K/Ca	no	9.3	330
KY No. 13	--	yes	9.9	--

Most surprising is the tremendous increase of surface area of the impregnated chars (1-3 orders of magnitude) after about one-half of the char has been gasified. This indicates an opening up of the char structure and increase of porosity during the partial conversion. It is not accompanied, however, by an increase in the rate of gasification with increasing conversion.

Surface area and porosity data for the impregnated bituminous chars will be obtained in the future.

c) Chemical Intermediates During Gasification

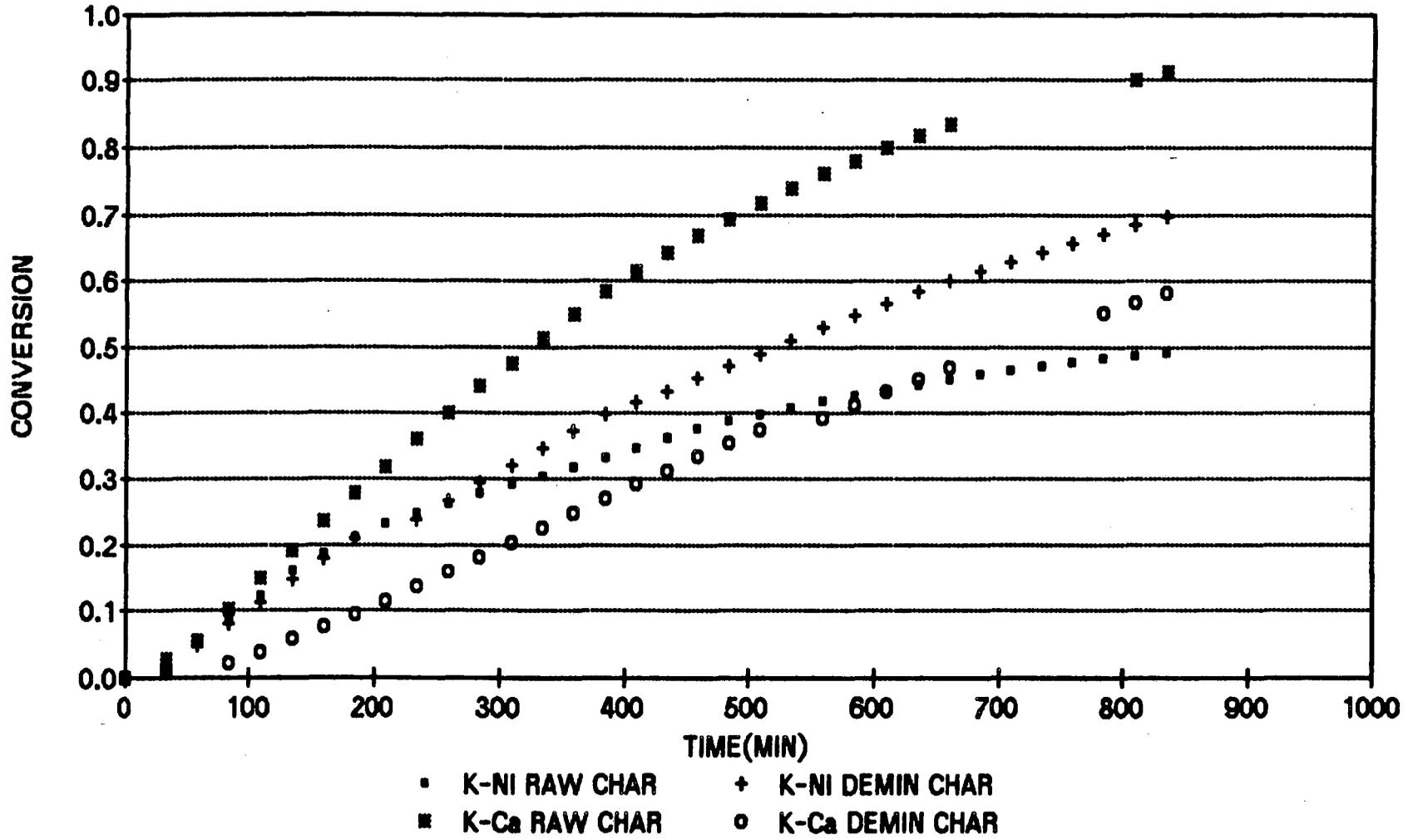
In order to obtain an indication of the potential presence of CO as a surface adsorbed intermediate during the catalytic steam gasification of K/Ca impregnated char to  $\text{CO}_2$  and  $\text{H}_2$ , a combined Auger-TPD (temperature programmed desorption) study of CO on K/Ca impregnated char was undertaken. The Auger spectrum (Fig. 8) before and after CO desorption is unchanged. It shows the same peaks of K, Ca, C, and O at about the same counts and therefore implies that there is no involvement of CO by either water gas shift or reverse Boudouard reaction on the catalyst surface.

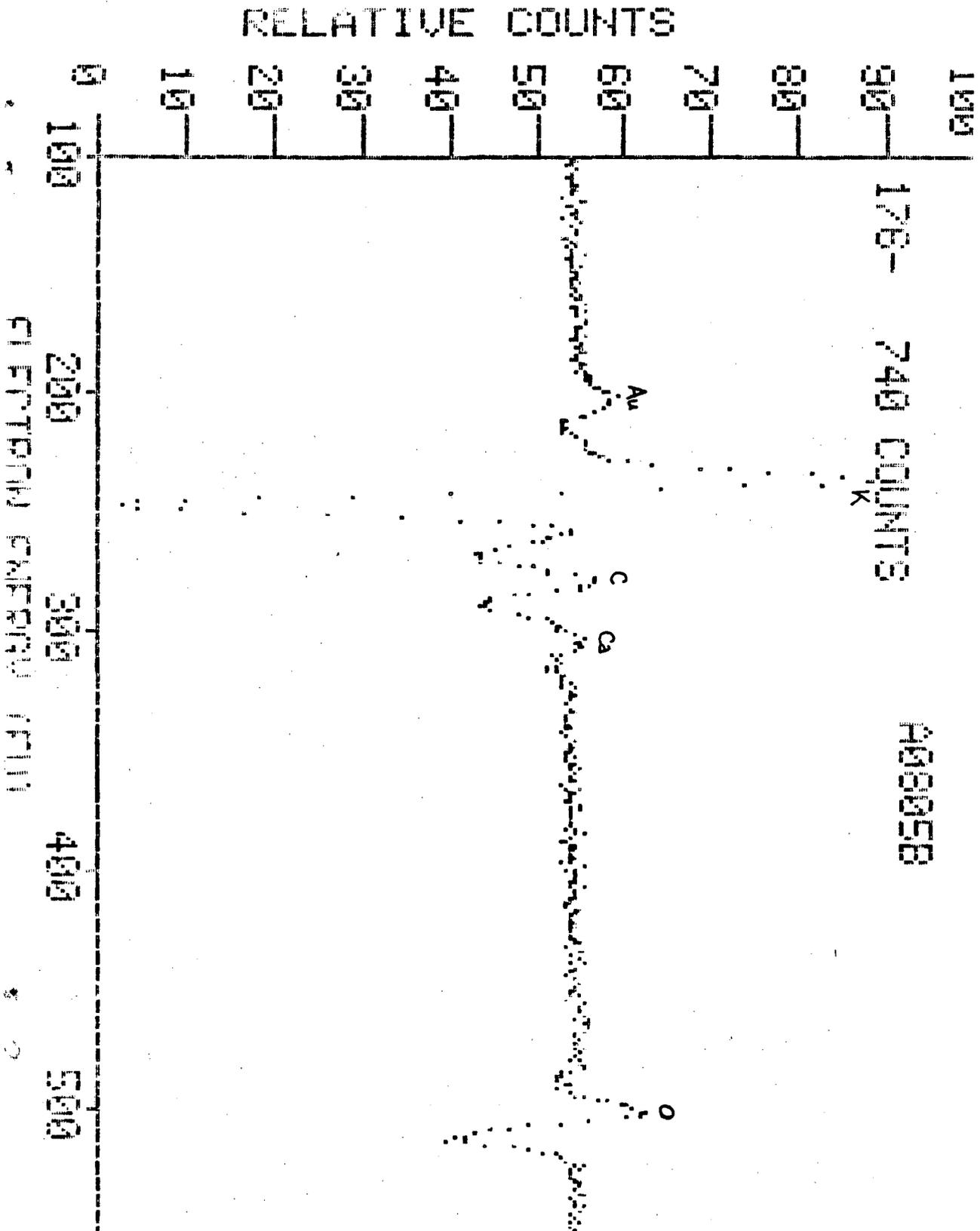
d) Controlled Atmosphere Electron Microscopy (CAEM)

We have previously reported CAEM studies of K/Ni catalysts during graphite gasification. They showed that gasification on K/Ni proceeds by an edge recession mechanism rather than a channeling mode which prevails for K or Ni catalysts alone.

Recently an additional CAEM study was undertaken (with cooperation of Roseann Csencsits of the National Center for Electron Microscopy) observing the steam gasification of a K/Ca impregnated graphite at temperatures in the 610-670°C. Wet argon ( $\text{Ar}/\text{H}_2\text{O} = 40/1$ ) at a total pressure of 40 mm was used as reacting gas. A magnetic tape of the gasification shows:

ROSEBUD CHAR STEAM GASIFICATION  
K-Ca AND K-NI COMPARED





Before TPD 25C

Fig. 8

- a good initial dispersion of the salts on the graphite
- an edge recession mode of gasification without preferential orientation, similar to the K/Ni case.

By measuring the extent of edge recession over a given time period, an activation energy of 60 Kcal/mol has been calculated which is in excellent agreement with the value obtained in the kinetic experiments in a flow reactor.

The magnetic tape has not yet been transferred to movie film and photographs are therefore not yet available.

#### V. Future Work

Additional surface area and porosity data on bituminous chars will be obtained.

Better interpretation of CAEM experiments will be possible when photographs become available .

A program has been started to investigate the poisoning of various gasification catalysts by adding potential poisons (pyritic or organic sulfur; ash minerals) to impregnated demineralized chars and observing their effect on the gasification reaction.

Rate and product distribution during gasification in the presence of various gases such as  $H_2$ , CO, or  $CO_2$  mixed with steam will be investigated.

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