

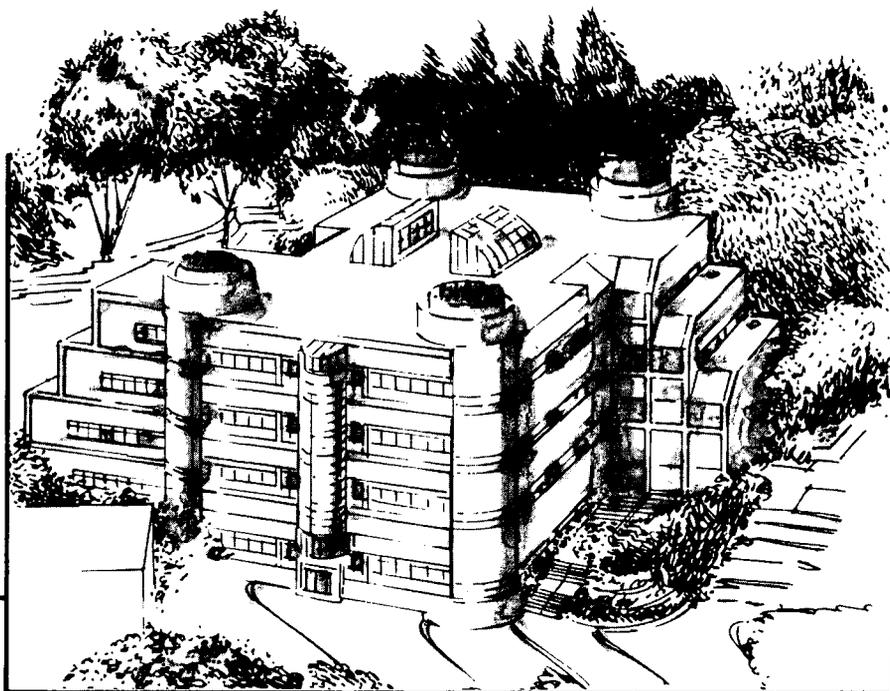
Center for Advanced Materials

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Fundamental Studies of Catalytic Gasification: Annual Report, October 1, 1988–September 30, 1989

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ANNUAL REPORT

October 1, 1988 - September 30, 1989

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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I. Task Description for FY 1989

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. Most of the mechanistic work has been done with graphite as a pure source of carbon. A number of chars with different ash contents and ash compositions have been gasified at relatively low temperatures (~800K). There is a major effect of the ash content on the catalyst. In some cases catalysts are being rapidly deactivated by ash components while in other cases gasification is promoted by ash. Demineralized chars can be gasified at low temperatures with the potassium-nickel catalyst without appreciable deactivation. In general chars are much easier to gasify than graphite. More recently it has been found that combinations of alkali and earth alkali catalysts, for instance mixtures of potassium and calcium oxides, are excellent gasification catalysts that cannot easily be poisoned by ash components. These catalysts are also considerably less expensive than transition metal compound containing materials. Future work will investigate the role of alkali-earth alkali catalysts which have been shown to be able to dissociate water at relatively low temperatures. A series of chars of different derivations will be gasified with these materials. The investigation will include the effect of oxidizing or reducing atmospheres. Poisoning of catalysts will be investigated by adding ash components back to demineralized chars.

II. Introduction

The "Highlight" section of this report summarizes the accomplishments of work during fiscal year 1989 and partially repeats

findings reported in the quarterly reports of December 1988 (LBL-26424), March 1989 (LBL-26891), and June 1989 (LBL-27330) along with new information obtained during the last quarter. The "Progress of Studies" section reports the results obtained during the June-September period of 1989.

III. Highlights

A. Steam Gasification

1) Graphite and Chars

- A controlled atmosphere electron microscopy (CAEM) study was completed for the steam gasification of graphite catalysed by KOH/CaO. This permits comparison with the earlier CAEM study with K/Ni catalysts. The present study (LBL-26424) showed that:
 - a) The potassium and calcium salts used were decomposed before loading into the electron microscope and that the catalyst can be presumed to be in the oxidized state at the start of gasification.
 - b) There is no evidence for a separate existence of the two oxides, but only for a mixture of them.
 - c) Edge recession without specific orientation was observed. The basal plane appeared to be non-reactive.
 - d) Higher partial pressures of hydrogen had an inhibiting effect.

- e) An evaluation of the activation energy from the CAEM study gave a value of 52.6 Kcal/mol (220 KJ/mol), close to the value reported previously in the flow reactor for the same catalyst.
- The effect of sulfur compounds on K-Ni and K-Ca catalyst activity during steam gasification of chars was studied. (LBL-26891)
 - a) Inorganic, pyritic sulfur showed only very minor activity inhibition even at high (3%) sulfur loadings for both types of catalyst.
 - b) Organic sulfur (Dibenzothiophene) showed little effect on the K-Ca catalyst, but severely poisoned the K-Ni catalyst. At a 3% S loading, it essentially killed the catalyst activity.
- A kinetic study of K, K-Ca, and K-Ni catalysts on graphite indicates that the catalyst susceptibility to H₂ decreases in the order K-Ni > K > K-Ca. It is suggested that hydroxide formation plays a role in hydrogen inhibition. (LBL-26891)
- A temperature programmed reaction (TPR) study of the decomposition of the nitrate salts used for deposition on chars has been carried out (LBL-26891). It shows that potassium nitrate alone results in a compound formation of carbon and potassium oxide and/or metal which may be intercalated and cannot react with edges of the carbon. In the case of binary catalyst, mixtures of specific oxides which can contain an alkali peroxide are formed, which can wet the carbon surface.

- Steam gasification of graphite impregnated with varying ratios of K and Ca at constant total catalyst to carbon ratio shows (LBL-27330):
 - a) Potassium alone and calcium alone give much lower activity than K-Ca mixtures.
 - b) A ratio of between 1:1 and 2:1 K:Ca gives better activity than either 3:1 or 1:3 K:Ca.
- A comparison of Na:Ca (1:1) with K:Ca and K-Ni catalysts in the steam gasification of a Rosebud subbituminous char gave higher activity for the Na:Ca and K:Ca than for K:Ni. Differences between Na-Ca and K:Ca are small with K:Ca being marginally better (LBL-27330).
- In a preliminary experiment it was shown that continuous gasification in a moving bed is feasible by feeding fresh char without catalyst to a reactor containing an original load of impregnated char (LBL-27330).

2) Coals

- Steam gasification of three coals in the presence and absence of catalysts showed:
 - a) K-Ca catalysts permit steam gasification of coals at lower temperature than is possible in the absence of catalysts.
 - b) K-Ca catalysts are about twice as effective as K alone.

- c) Coals are easier to gasify with K-Ca catalysts than the chars derived from these coals.
- d) Subbituminous coals gasify faster than bituminous coals.
- e) With all coals tested, a devolatilization period precedes actual carbon gasification. During this period, most of the hydrocarbons are steam reformed to H_2 and CO_2 .
- f) During the catalytic steam gasification of coals only small amounts (<2%) of CO and traces of CH_4 and C_2 hydrocarbons are formed.

3) Catalyst Modifications

- A catalyst in which sodium was substituted for potassium in admixture with calcium was at least as active for coal gasification as K-Ca. This may cut catalyst cost substantially and lead to the use of a throw-away catalyst.
- A cesium-calcium catalyst was not active.

B) Methane Coupling

- Addition of methane and oxygen to the feed during steam gasification of a K-Ca impregnated bituminous char has resulted in several interesting, but as yet not well defined observations (LBL-27330):
 - 1) C_2 hydrocarbons (apparently from methane coupling) begin to appear in the reactor affluent after about 80% of the char carbon has been gasified.

- 2) A fairly steady yield of 10% C₂ hydrocarbons is obtained after complete char conversion. About 70% selectivity can be obtained at 10% conversion by varying operating conditions. This is at a gasification temperature of 680°C, about 150° lower than reports in the literature for similar results.
- 3) The role of carbon, if any, is not understood. The presence of water seems essential for CH₄ conversion at these temperatures. Higher yields are indicated at higher temperature.
- 4) A large number of variables remains to be investigated.
- 5) During the last quarter of fiscal 1989, equipment modifications were undertaken to permit better product analysis. A mass spectrometer was installed.

IV. Progress of Studies

A) Methane Coupling

No experimental work was performed during the quarter because of equipment changes and long delay in delivery of ordered items. Analytical facilities have been improved by installation of a mass spectrometer and changes are being made to permit the reaction to be carried out at higher temperatures than the old equipment permitted.

B) Catalytic Steam Gasification of Coals

Samples of three coals were obtained from IGT. These are the parent coals of the chars which have been used in earlier work. They comprise a subbituminous (Rosebud) and two bituminous coals (Ohio, Pitt #8 and Kentucky #13). An analysis of these coals is given in Table 1.

TABLE 2
Proximate, Ultimate, and Inorganic Chemical Analyses
of Coals Used in Gasification Tests

Seam Mine	OH Pitt #8 <u>Franklin 125</u>	KY #13 <u>Ken #13</u>	Rosebud <u>Rosebud</u>			
Proximate Analysis, wt%						
Moisture	2.5	9.8	23.1			
Volatile Matter	38.6	32.2	28.5			
Ash	7.5	7.3	11.3			
Fixed Carbon	<u>51.4</u>	<u>50.7</u>	<u>37.1</u>			
Total	100.0	100.0	100.0			
Ultimate Analysis, wt% (dry basis)						
Ash	7.68	8.08	14.66			
Carbon	74.47	73.74	62.76			
Hydrogen	5.24	4.82	4.40			
Sulfur	3.21	1.40	1.29			
Nitrogen	1.50	1.8	0.99			
Oxygen (by difference)	<u>7.90</u>	<u>10.11</u>	<u>15.88</u>			
Total	100.0	100.0	100.0			
Ash Composition, wt%						
SiO ₂	41.6	58.5	48.8			
Al ₂ O ₃	20.9	26.9	23.5			
Fe ₂ O ₃	31.7	8.1	7.02			
TiO ₂	1.02	0.87	0.12			
P ₂ O ₅	0.07	0.16	0.25			
CaO	1.14	0.90	7.16			
MgO	0.36	1.21	2.57			
Na ₂ O	0.35	0.24	0.09			
K ₂ O	0.98	2.94	0.36			
SO ₃	<u>1.00</u>	<u>0.80</u>	<u>9.91</u>			
Total	99.2	100.6	99.78			
Ash Content (as ashed for analysis of ash, dry basis)						
Basic Ash Constituents, wt%	7.7	8.2	--			
Dolomite Ratio, wt%	35.2	13.4	19.2			
SiO ₂ /Al ₂ O ₃ Ratio	4.3	15.8	56.6			
	2.0	2.2	2.1			
Forms of Sulfur, wt% (dry basis)						
Pyritic	2.37	0.40	0.76			
Sulfate	0.21	0.10	0.015			
Organic	<u>0.97</u>	<u>1.03</u>	<u>0.52</u>			
Total	3.56	1.53	1.28			
Forms of Iron (dry basis)						
	wt%	%Fe	wt%	%Fe	wt%	%Fe
Pyritic	2.07	96	0.35	70	1.32	62 ^a
HCl-Soluble	<u>0.08</u>	<u>4</u>	<u>0.15</u>	<u>30</u>	<u>0.12</u>	<u>6</u>
Total	2.15	100	0.50	100	2.13 ^a	100
Acid-Insoluble	<0.10	--	<0.10	--	0.69	--
Pyritic, % of total Fe ^b	97		54		--	

^a Based on total iron including 0.69 wt% HCl-insoluble

^b Of 1/4-inch-top-size coal after storage.

The three coals were subjected to steam gasification at 640°C both in the absence of and in the presence of K-Ca-O catalyst. When the catalyst was used, it was impregnated on the coal by an aqueous nitrate solution containing equimolecular amounts of K and Ca. The procedure used and the nitrate decomposition treatment were the same as previously described for chars and graphite.

In the absence of catalysts no gasification occurred except for an evolution of light hydrocarbons (devolatilization) during the heat-up period. This was most pronounced for the subbituminous Rosebud coal.

In the presence of catalysts, gasification of all three coals was quite rapid and much faster than that of the corresponding chars, which in turn gasified better than graphite. Complete (100%) gasification of all coals was achieved at 640°C. The subbituminous Rosebud coal gasified better than the bituminous coals.

Fig. 1 plots the catalytic gasification of Rosebud coal at two temperatures, 580 and 640°C. The gasification occurring at the lower temperature is essentially only a devolatilization. However, while in the absence of catalysts the products of this devolatilization were mostly light paraffins and aromatics, in the presence of catalyst a majority of the products consisted of H₂ and CO₂, indicating that the catalyst has steam reforming activity at this low temperature.

For all the coals there is some devolatilization while heating up and before actual carbon gasification occurs. This explains why carbon gasification starts only after 10-25% conversion. Fig. 2 presents a comparison of the

three coals investigated. The two bituminous coals have the same steady gasification rate except for the devolatilization part. The Ohio Pitt #8 has more volatiles in the presence of steam and catalyst than Kentucky #13. This is somewhat different than the volatile matter content given in Table 1 determined in the absence of steam. The subbituminous Rosebud coal shows a better gasification rate than the bituminous coal.

Fig. 3 presents a plot of conversion vs. rate in which the rate is expressed as mol of carbon conversion/min rather than as mol of carbon conversion/mol of catalyst/min as in Fig. 2. The overall appearance of both, the shape and relative positions of the curves is the same in both figures. Fig. 3 also contains a rate picture for the devolatilization part of the Rosebud coal.

Fig. 4 presents percent conversion of the three coals as a function of time. It shows that the Rosebud subbituminous coal is fully gasified in about one-half the time required for the bituminous coals. Fig. 5 demonstrates the advantage of a K-Ca catalyst over K alone for the Rosebud coal. Complete gasification is achieved with K-Ca in about 60% of the time required for K.

A comparison of the Rosebud coal with the Rosebud char (gasification of which as reported in earlier reports, LBL-25416, June 1988) is shown in Fig. 6A and 6B. The coal gasifies at a much higher rate than the char. Complete carbon conversion occurs in 450 min for the coal, 900 min for the char (Fig. 6B).

The distribution of gases produced from the coals in the presence of K-Ca is illustrated in Fig. 7 and 8, plotting

conversion vs. molar fractions of gases on a logarithmic scale. Hydrogen and carbon dioxide production is steady at a 2:1 ratio over the whole range of conversions (Fig. 7), while CO, CH₄, and C₂ production gradually decline. CO production amounts to about 2%, CH₄ to 0.5% and C₂ to less than 0.01%. Rosebud coal gives slightly higher yields of CO, CH₄, and C₂ than the other coals.

While Fig. 7 shows gas distribution after devolatilization, Fig. 8 includes the devolatilization period. During this period (first 30% of conversion) larger amounts of CH₄ and C₂ hydrocarbons (and somewhat higher amounts of CO) are produced. It is remarkable, however, that the major products are again H₂ and CO₂, indicating that steam reforming of paraffins and aromatics must occur.

C) Catalyst Modifications

In order to test the necessity of using relatively expensive potassium as a catalyst component, gasification of the Ohio Pitt #8 coal was undertaken employing a Na-Ca catalyst. The proportions of Na in the catalyst were the same as in the case of K-Ca. As shown in Figs. 9 and 10, the Na-Ca catalyst was at least as active as K-Ca, increasing the likelihood that the catalyst maybe used on a throw-away basis.

A catalyst comprising cesium-calcium was also tested. It exhibited almost no gasification activity. The reason for this may lie in the large atomic size of the Cs relative to Ca. A Cs-Ba or Bs-Sr catalyst will be tested in the future.

STEAM GASIFICATION OF ROSEBUD COAL WITH K-Ca CATALYST
K:Ca:C=0.01:0.01:1, T=580 & 640 C, P=ATM

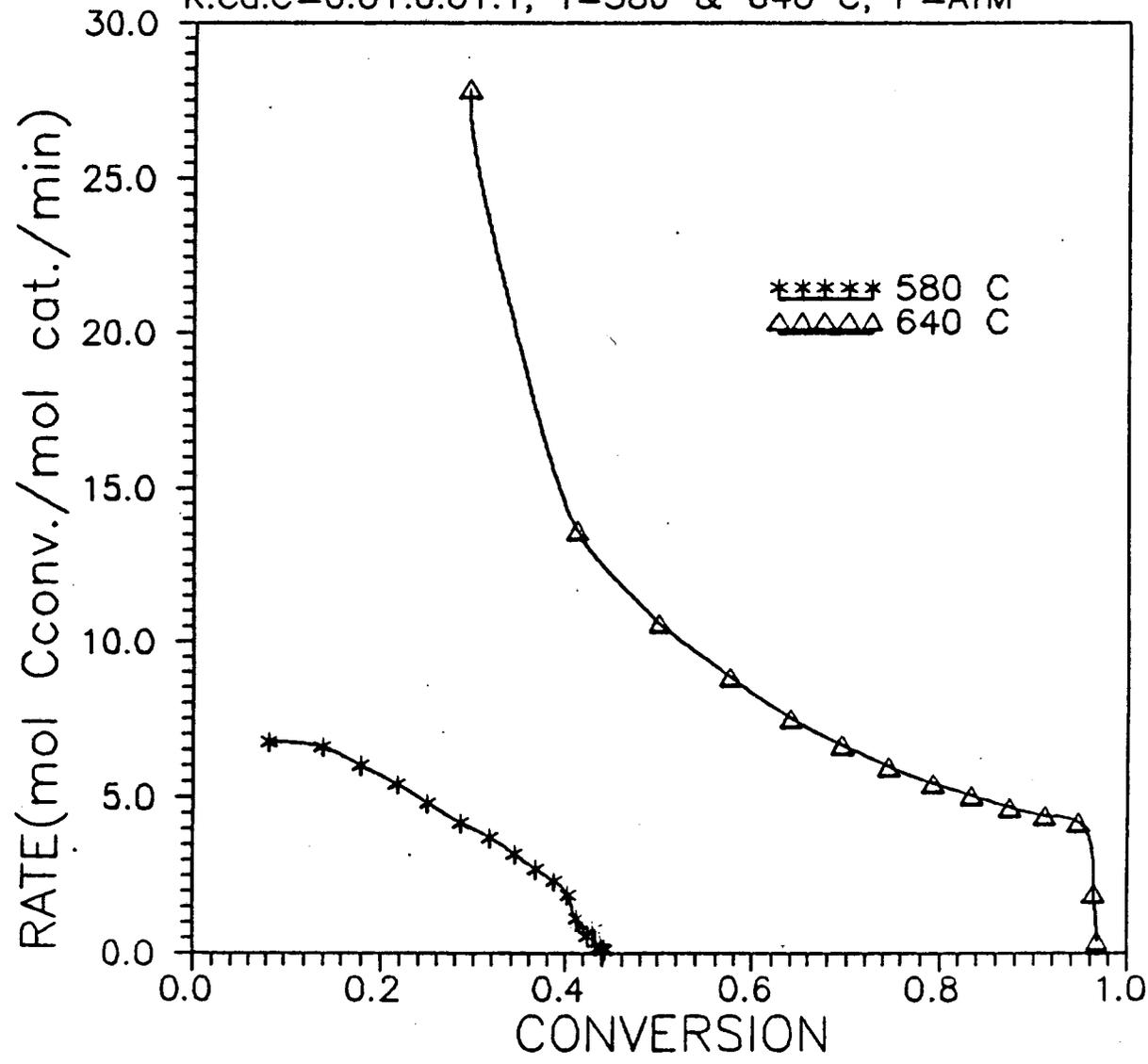


Fig. 1

STEAM GASIFICATION OF DIFFERENT COALS WITH K-Ca CATALYST
K:Ca:C=0.01:0.01:1, T= 640 C, P=ATM

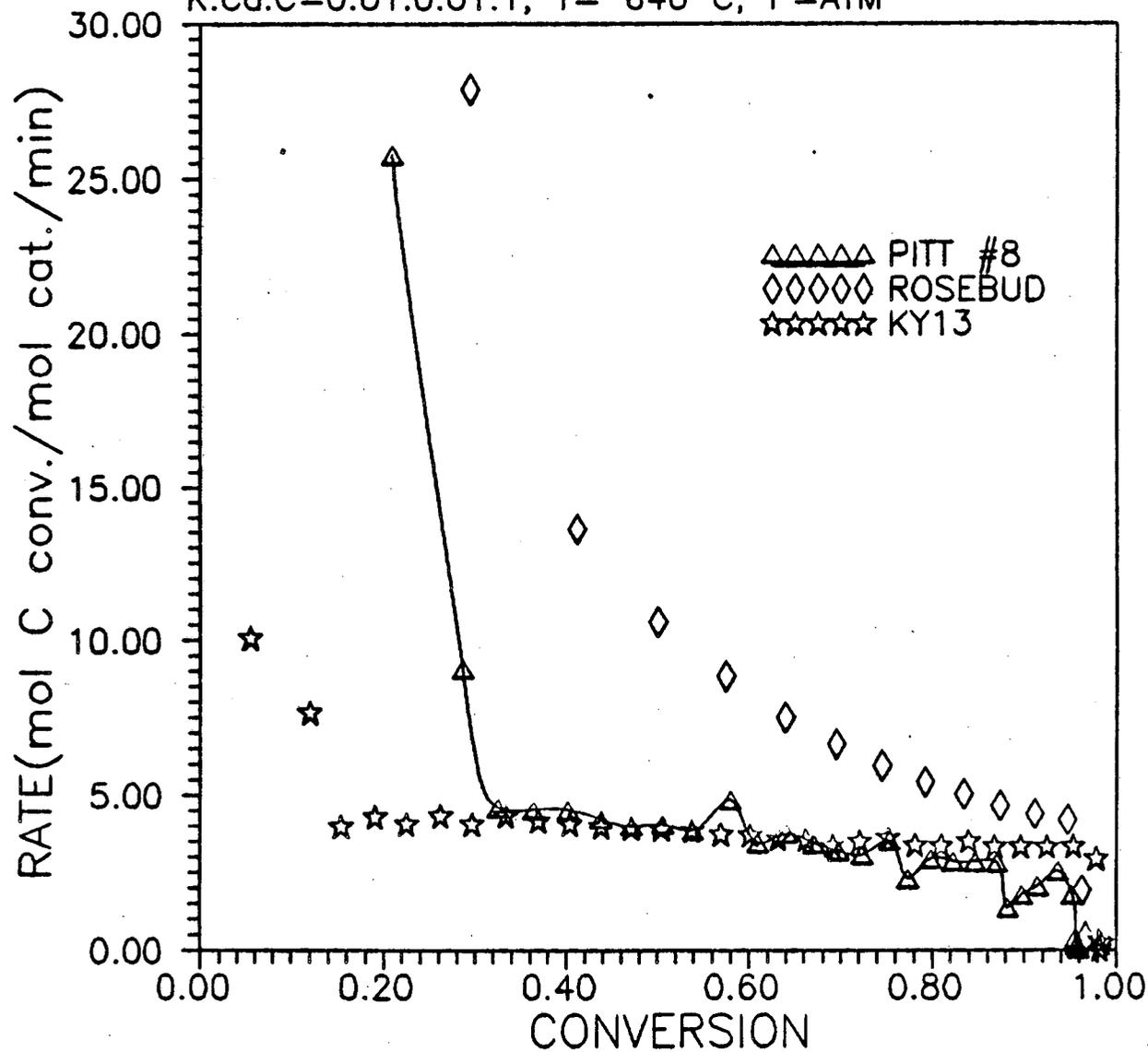


Fig. 2

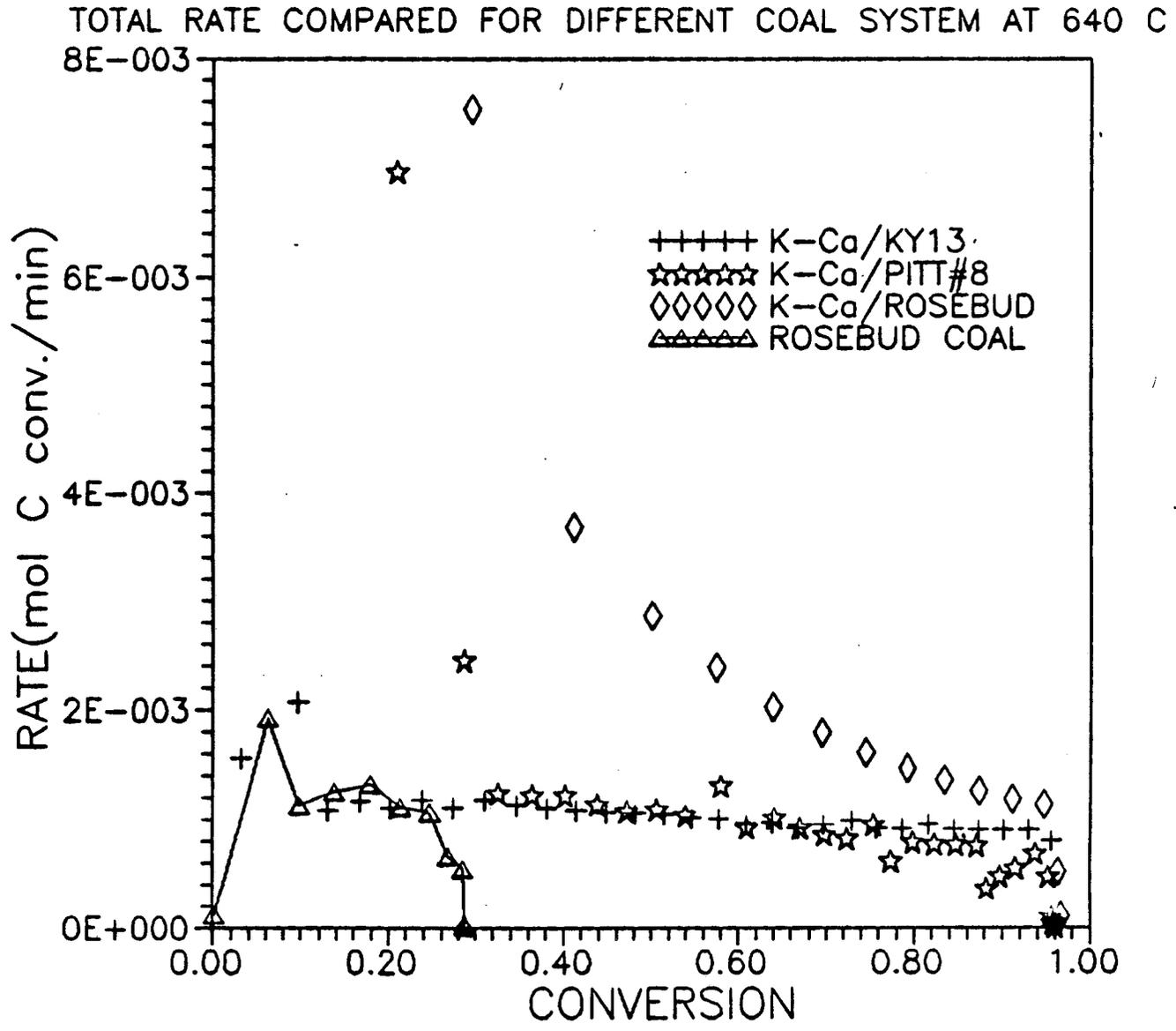


Fig. 3

STEAM GASIFICATION OF COALS WITH K-CA CATALYST
K:Ca:C=0.01:0.01:1, T= 640 C, P=ATM

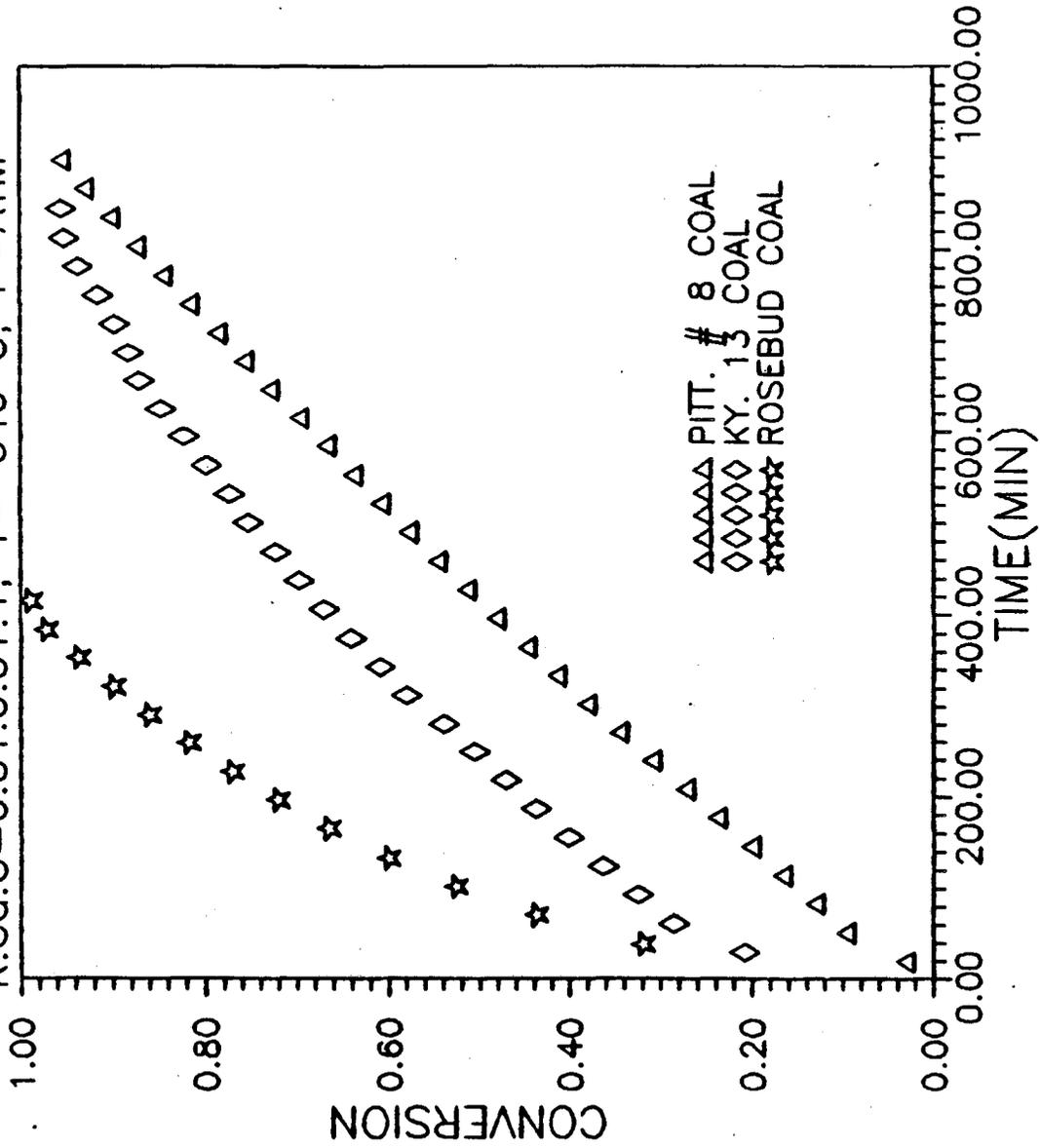


Fig. 4

STEAM GASIFICATION OF ROSEBUD COAL WITH K AND K-Ca CATs.
K:K or Ca:C=0.01:0.01:1. T=640 C . P:ATM.

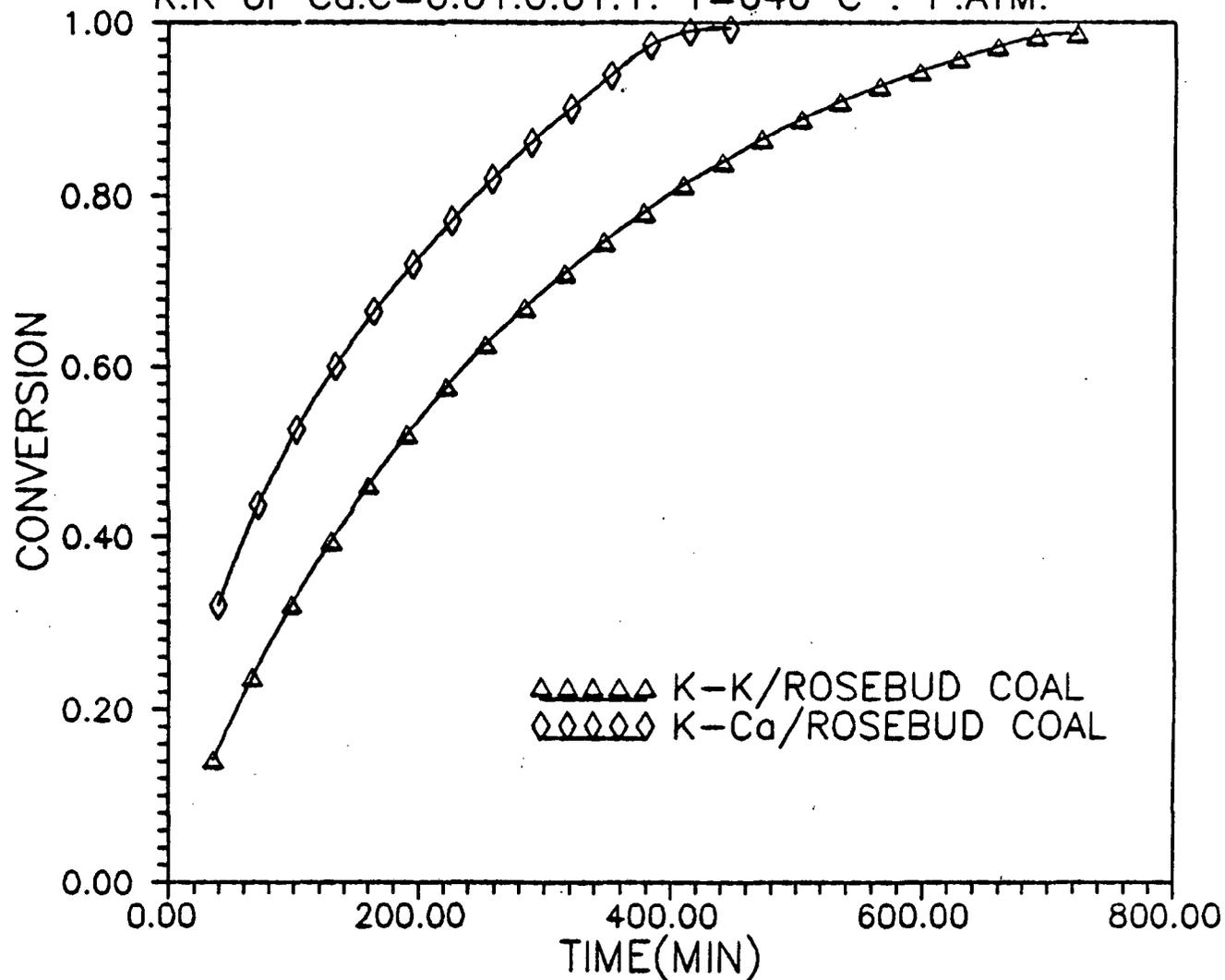


Fig. 5

STEAM GASIFICATION OF ROSEBUD COAL AND ROSEBUD CHAR
K:Ca:C=0.01:0.01:1, T= 640 C, P=ATM

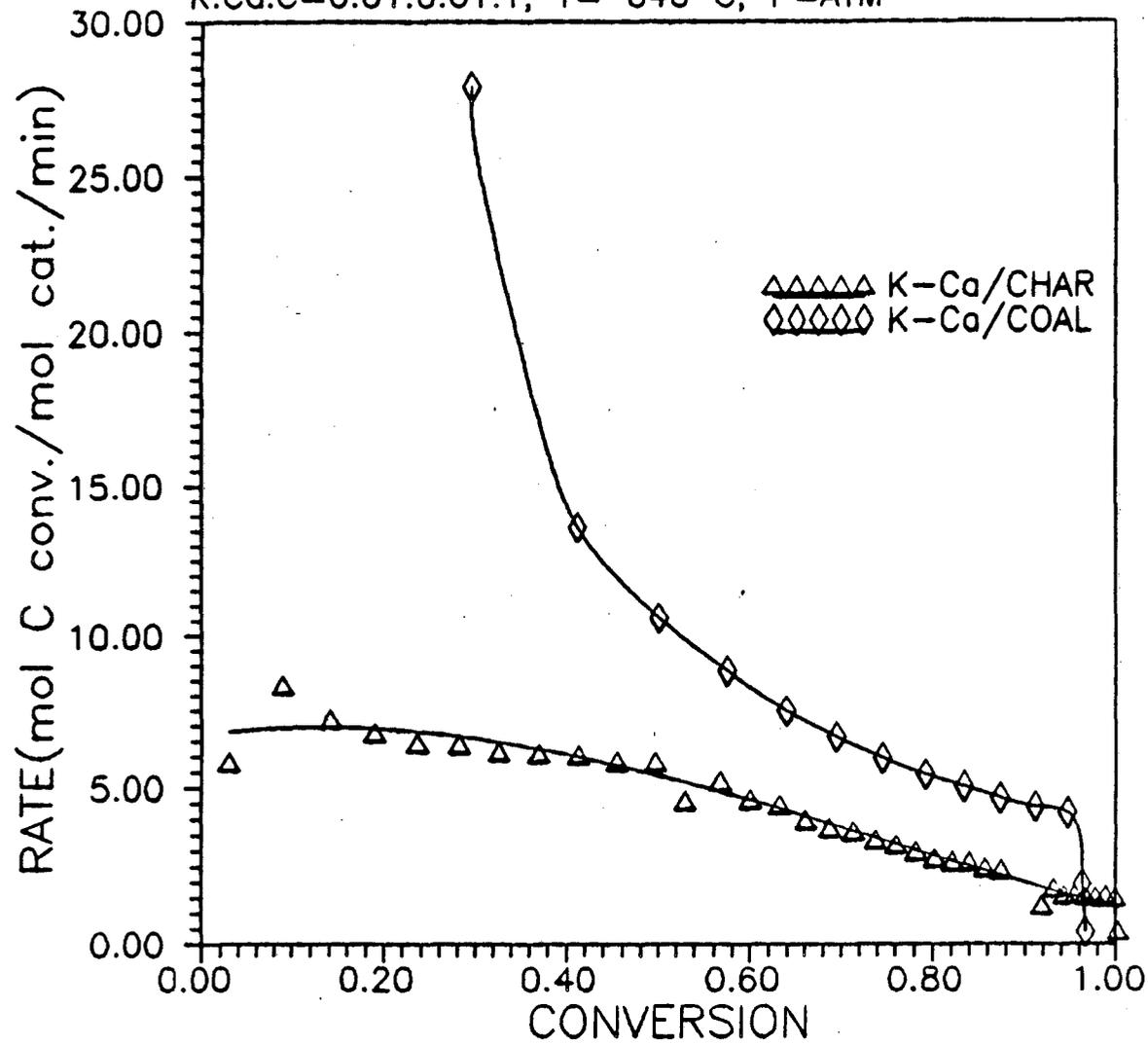


Fig. 6A

STEAM GASIFICATION OF ROSEBUD COAL AND CHAR WITH K-Ca
K:K or Ca:C=0.01:0.01:1. T=640 C . P:ATM.

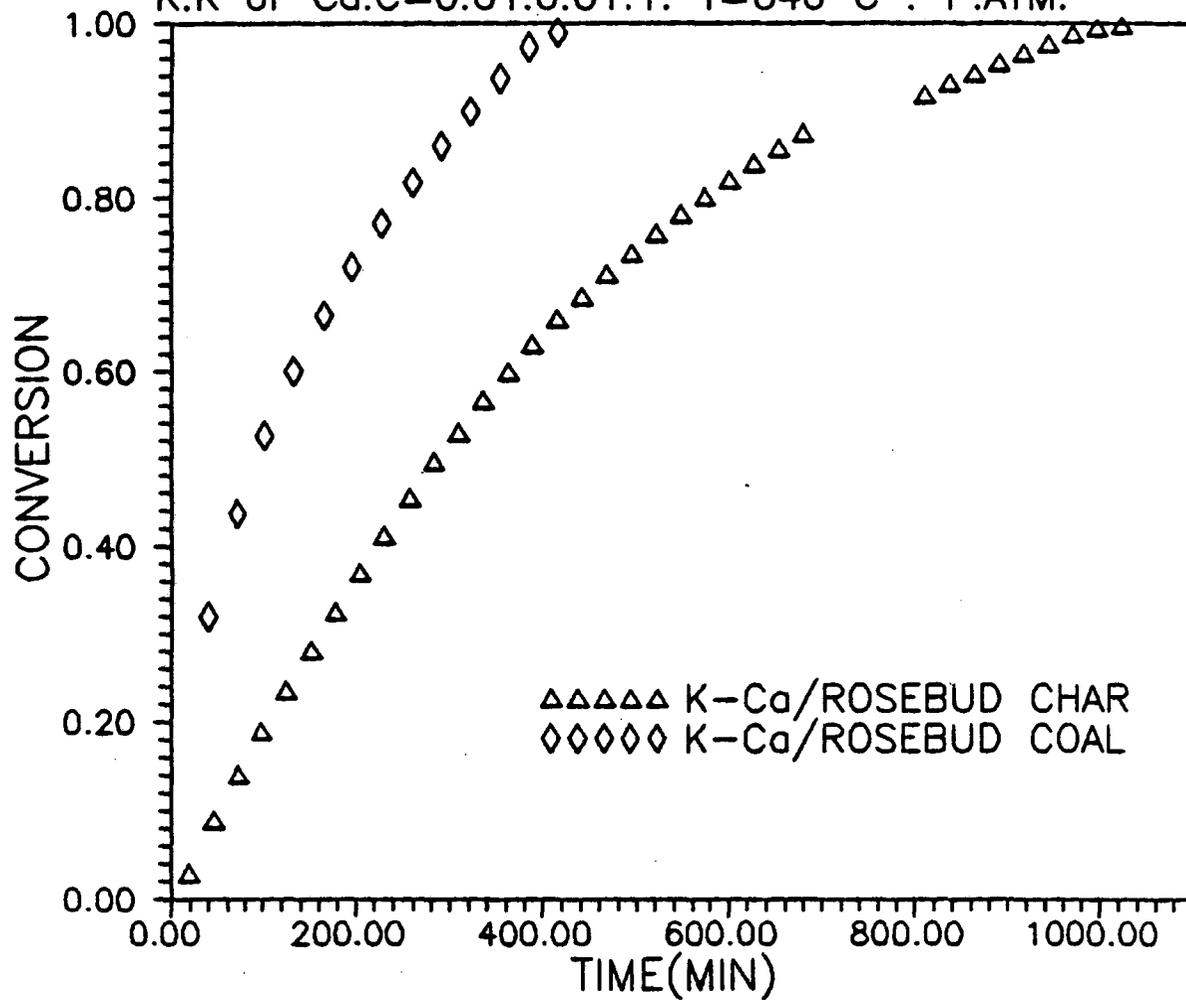


Fig. 6B

MOLAR FRACTION OF GASES PRODUCED DURING THE STEAM GASIFICATION OF DIFFERENT COALS WITH K-Ca CATALYST AT STANDARD CONDITIONS

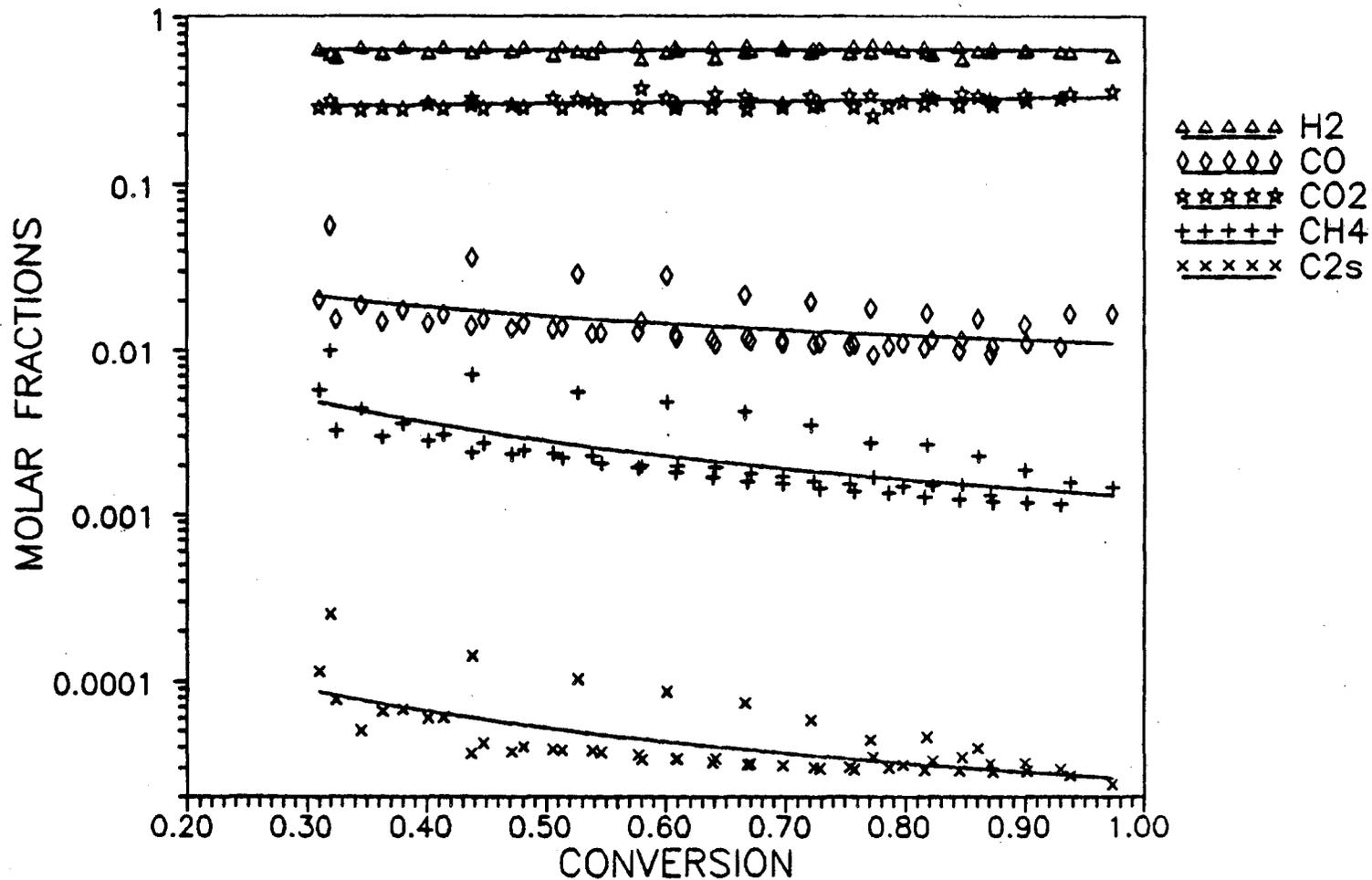


Fig. 7

MOLAR FRACTION OF GASES PRODUCED DURING THE STEAM GASIFICATION OF DIFFERENT COALS WITH K-Ca CATALYST AT STANDARD CONDITIONS

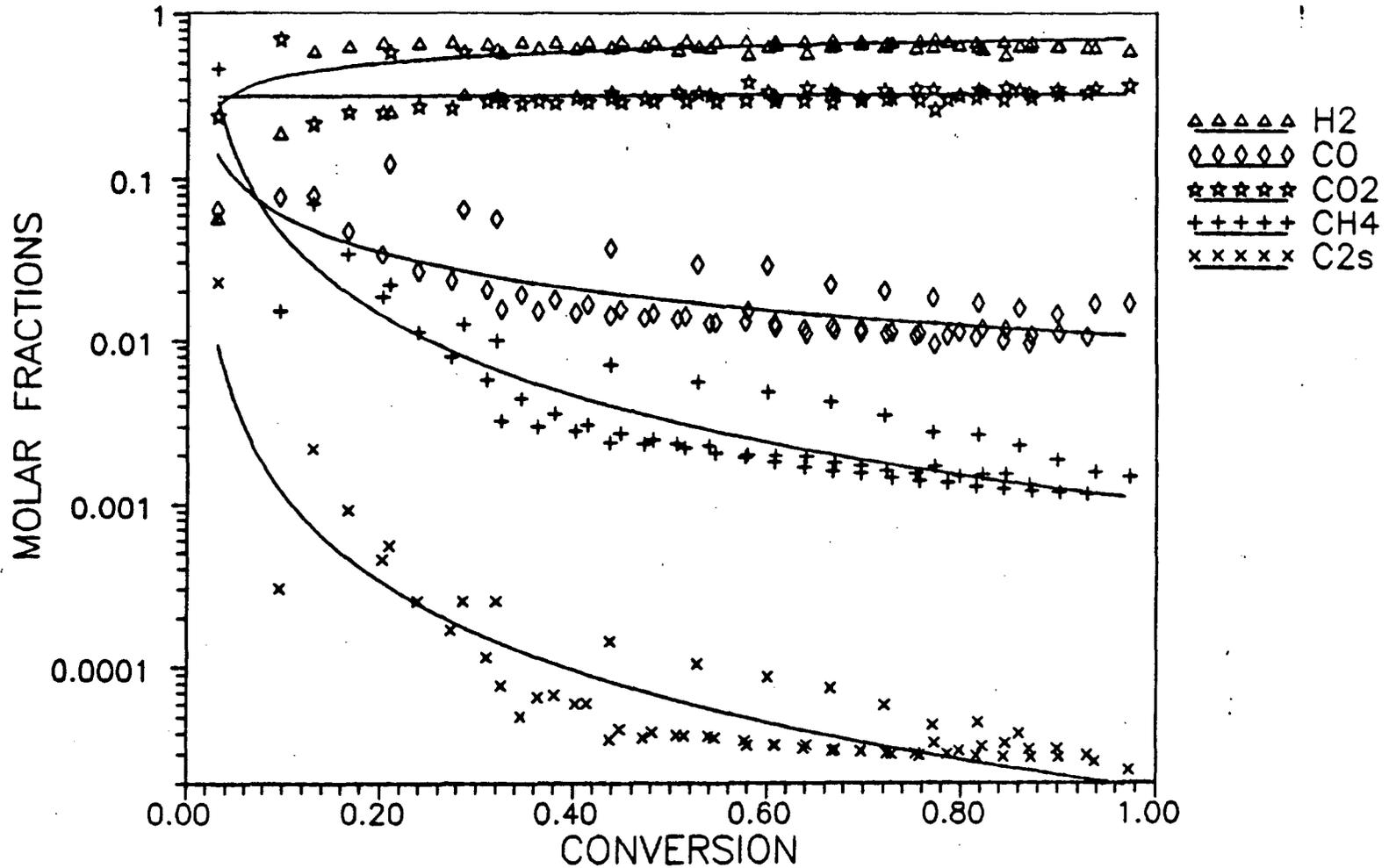


Fig. 8

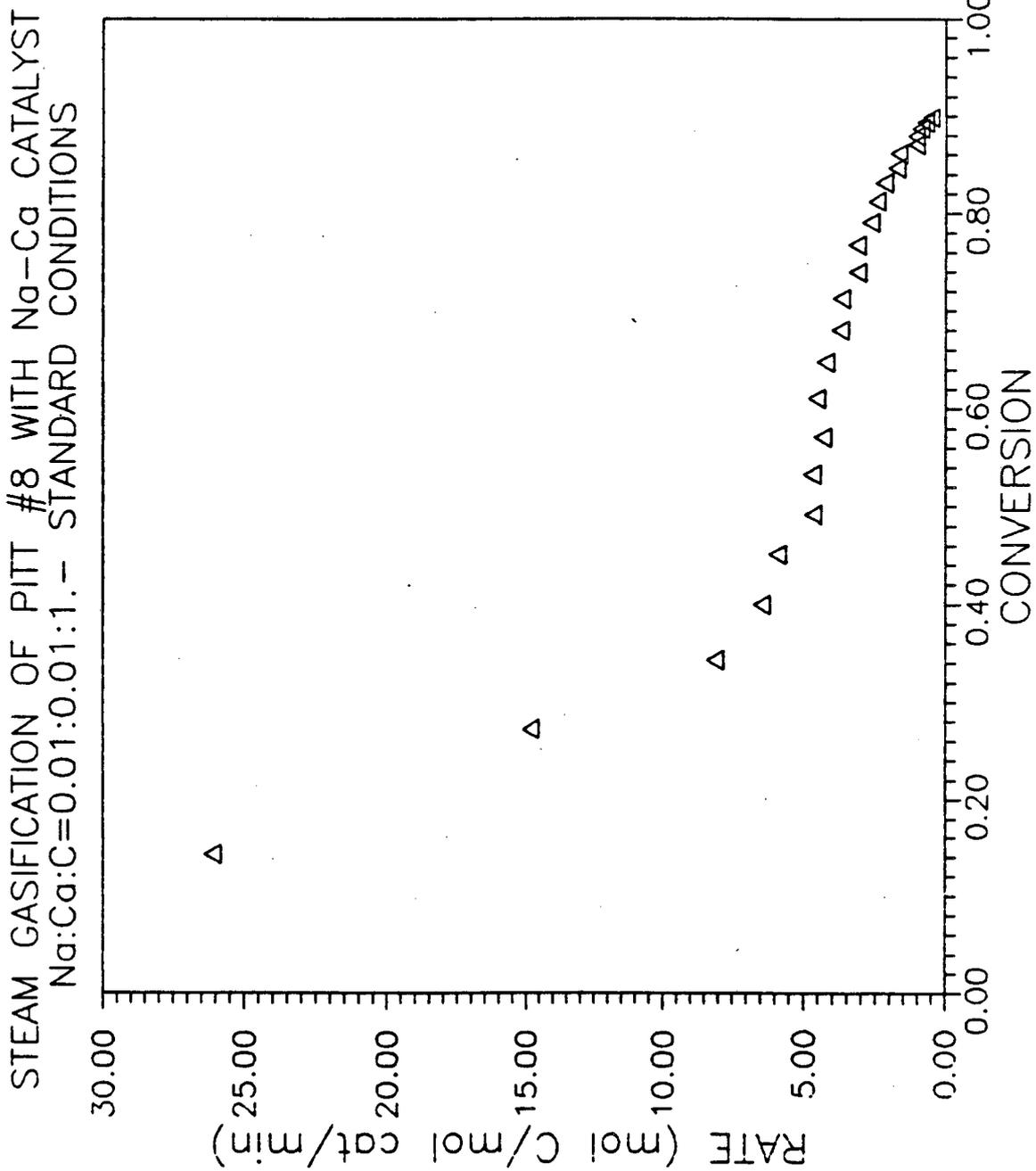


Fig. 9

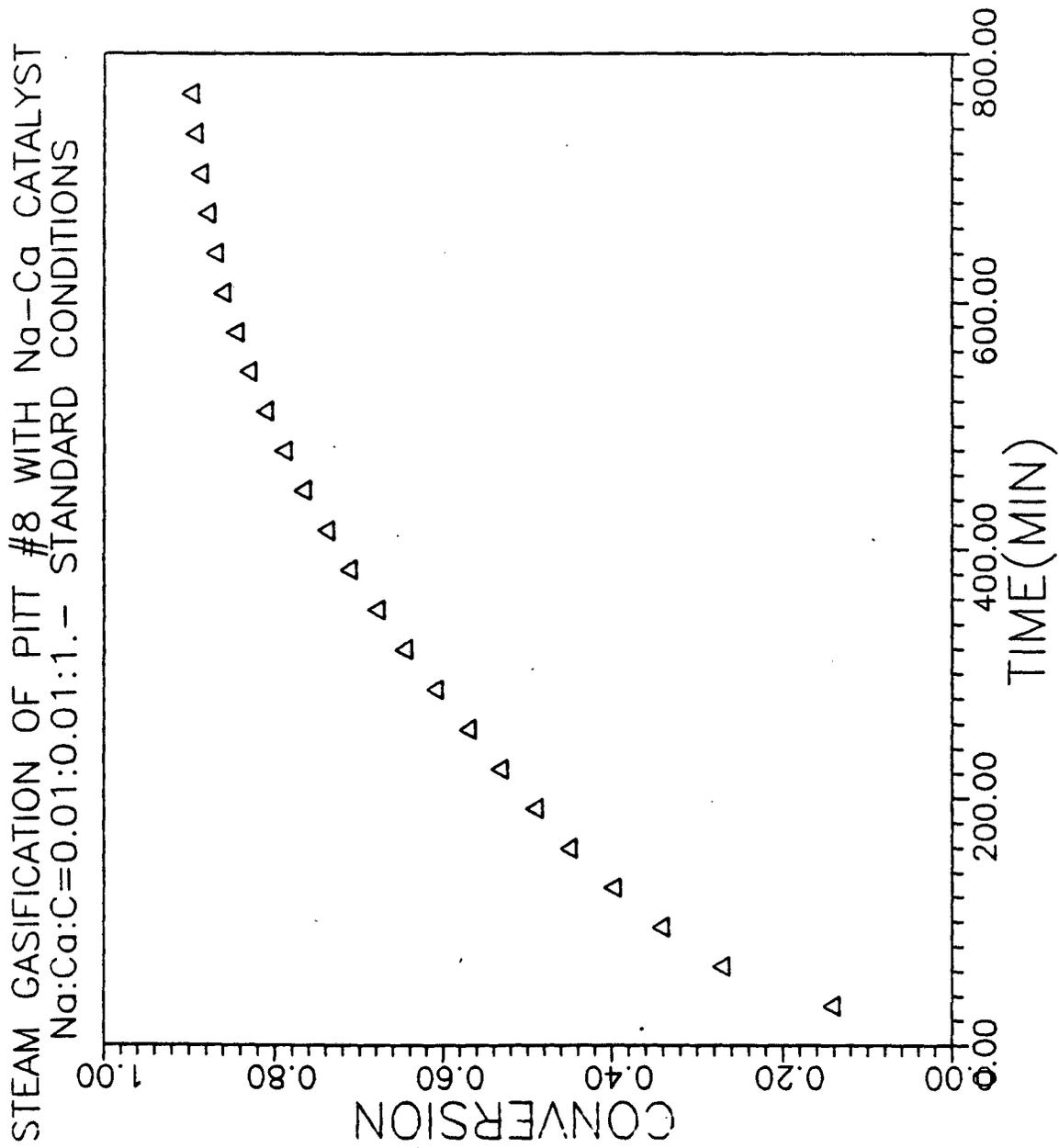


Fig. 10

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