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# FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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## I. Task Description for FY 1990

Our previous work has shown that chars and coal can be gasified with steam in the presence of alkali-transition metal oxide catalysts or alkali-earth alkali catalysts at relatively low temperatures. These studies are to be extended to the investigation of the amounts of catalysts required and whether a throw away catalyst can be used. Fresh versus stored char will be gasified to determine the role of oxidation of the char on gasification rates. Less expensive catalyst materials such as sodium instead of potassium and iron instead of nickel will be explored. Reaction rates will be determined in the presence of nitrogen, CO and CO<sub>2</sub>. Reactions of methane and carbon solids in the presence of an oxidizing agent such as water, oxygen, and/or carbon dioxide will be explored in the presence of similar catalysts. It is expected that hydrocarbon liquids and C<sub>2</sub> plus gases will be produced along with hydrogen. These studies will be performed over a wide range of reaction pressures and reaction temperatures in a flow reactor using a GC-MS detector. Pure paraffinic and cyclic hydrocarbons of high carbon to hydrogen ratio will be gasified to have an indication of the ease of gasification of different carbonaceous materials.

## II. Introduction

The **Highlights** section of this report summarizes the accomplishments of work during FY 1990 and partially repeats findings reported in the quarterly reports of December 1989 (LBL-28298), March 1990 (LBL-28710) and June 1990 (LBL-29812) along with new information obtained during the last quarter. The **Progress of Studies** section reports the results obtained during the July-September period of 1990.

Much of the work performed in FY 1990 on the oxidative coupling of methane has been summarized in a paper which will be published in *CATALYSIS LETTERS* in October, 1990, and a copy of which is reproduced in the Appendix. Patent applications on this work have been filed.

### III. Highlights

#### a) Catalytic Steam Gasification

- Substitution of other alkali and/or earth alkali oxides for K and Ca showed that sodium is equivalent to potassium. A cesium-barium oxide catalyst is comparable to  $\text{KCaO}_x$  in overall performance. It is less active initially, but more active in the later stages of gasification. (LBL-28298)
- A third metal component was introduced into the  $\text{KCaO}_x$  catalyst in an attempt to enhance carbon-carbon bond breakage. Using Ni as the third component, poorer results were obtained than with  $\text{KCaO}_x$  alone. (LBL-28298)
- The superiority of  $\text{KCaO}_x$  over  $\text{KNiO}_x$  for char gasification has also been demonstrated for the gasification of the parent coals. (LBL-28298)
- In the catalytic steam gasification of coals, it has been shown that there is no appreciable difference in rate or time of gasification between a "Premium" freshly mined coal preserved in an inert atmosphere and a coal which has been subject to air oxidation at ambient conditions. (LBL-29182)

#### b) Conclusions of Catalytic Gasification Project to Date:

- Good steam gasification catalysts must:  
Wet the carbonaceous material  
Attack by edge recession  
Dissociate water at reaction temperature
- $\text{K-CaO}_x$  (or  $\text{Na-Ca}$ ) catalysts equal  $\text{K-Ni}$  catalysts
- $\text{K-CaO}_x$  catalysts are not poisoned by S

- K-CaO<sub>x</sub> catalysts have good gasification rates at 800-900K (527-630°C) giving H<sub>2</sub> and CO<sub>2</sub> from lignite > subbituminous > bituminous coals
- Coals gasify at better rates than their chars
- The catalysts may be used on a throw-away basis
- The catalytic gasification mechanism involves water dissociation forming H<sub>2</sub> and carbon surface oxygenates (lactones; quinones), C-C bond breakage forming CO<sub>2</sub>

c) Oxidative Methane Coupling

- A novel catalyst (KCaNiO<sub>x</sub>) has been discovered that will permit oxidative coupling of methane at close to 100% selectivity to C<sub>2</sub> hydrocarbons at 10% CH<sub>4</sub> conversion. Essentially no CO<sub>x</sub> production occurs. Temperatures below 600°C are used. (LBL-28710)
- The presence of water has been found important for oxidative coupling of CH<sub>4</sub> over either KCaNiO<sub>x</sub> or KCaO<sub>x</sub> catalysts. (LBL-28710)
- Absence of CO<sub>x</sub> in the products from coupling greatly effects economics because of lower oxygen demand, less methane loss and less recycle purification. (LBL-28710)
- Calcination conditions of the KCaNiO<sub>x</sub> catalysts are important factors in their performance. (LBL-28710)
- High selectivity to C<sub>2</sub> hydrocarbons was maintained over CaNiKO<sub>x</sub> catalysts for extended periods of time. (LBL-28710)
- The preparation of KCaNiO catalysts for the oxidative coupling of methane with high selectivity to C<sub>2</sub> hydrocarbons is difficult. A large

variety of factors in catalyst preparation and reaction operation contribute to catalyst performance. (LBL-29182)

- CaNiK $O_x$  catalysts giving ~100% selectivity at 9-11% conversion can now be produced at will. The relative proportion of the catalyst components is of major importance, as are the calcination conditions of the catalysts. (LBL-29182)
- Oxidation pretreatment conditions of the catalyst are critical. (LBL-29182)
- The best operating conditions are temperatures of 560-600°C and low space velocity at atmospheric pressure. (LBL-29182)
- The presence of steam is essential for selectivities approaching 100% as well as for stable operation over extended periods of time. (LBL-29182)
- A large number of potential methane coupling catalysts have been prepared. In general silica or alumina supported catalysts are less active than unsupported bi- or tri-metallic oxides. (LBL-28710)
- Deposition of carbon on the catalyst during initial phases of operation may be important for the reaction.
- With prolonged oxidative treatment of the CaNiK $O_x$  catalyst, appreciable amounts of C<sub>3</sub> and C<sub>4</sub> hydrocarbons can be produced from methane along with C<sub>2</sub> olefins and paraffins. The oxidative pretreatment also increases the olefin/paraffin ratio.
- The optimum ratio of the catalyst components was found to be Ca:Ni:K atomic ratio of between 4:1:1 and 2:1:1. The very small amounts of K $O_x$  increase both selectivity and stability of the catalyst.

- A study of the effect of space velocity shows that selectivity goes through a maximum at about 6-7 mmol total feed/g catalyst/hr.
- The mechanism of the coupling of methane in the presence of oxygen and of steam over KCaNi catalyst appears to be different from the mechanisms proposed in the literature for coupling at higher temperatures and with lower selectivities. A homogeneous gas phase mechanism does not appear to exist in the present work and a reaction on the surface appears to be predominant.

#### IV. Progress of Studies

The best catalysts found so far for the oxidative coupling of methane have a composition of Ca:Ni:K in an atomic ratio of 2-4Ca:1Ni:.1K. A study was undertaken with catalyst prepared in the absence of potassium and with varying Ca:Ni ratios and with the calcium oxide derived from either nitrate or carbonate. Figure 1 and 2 show conversion, resp. selectivity as a function of time for this series of catalysts. The selectivity data in Fig. 2 show a decline with time for all catalysts, which had a high selectivity at the start. This instability is attributed to the absence of potassium in these catalysts. Both, conversion (Fig. 1) and selectivity (Fig. 2) are highest for Ca<sub>4</sub>Ni<sub>1</sub> catalysts prepared from either nitrates or carbonates, if the precursors had been decomposed at 900°C. A Ca<sub>8</sub>Ni<sub>1</sub> and a Ca<sub>9</sub>Ni<sub>1</sub> catalyst performed less well. While it had previously been shown that catalysts from nitrates perform well after decomposition at 750°C, the data in Figs. 1 and 2 show that for carbonate derived catalysts the higher decomposition temperature of 900°C is required, since calcium carbonate is stable up to 890°C. All catalysts in this work were oxidized in flowing oxygen at 700° prior to use.

The importance of contact time for a Ca<sub>4</sub>Ni<sub>1</sub>K<sub>0.1</sub> catalyst is shown in Fig. 3. For total feed rates of CH<sub>4</sub>, O<sub>2</sub> and H<sub>2</sub>O, an optimum selectivity is obtained at 600°C at about 6 mmol/g catalyst/hr. The conversion appears to increase with space velocity and the yield of hydrocarbons increases slightly. This suggests that a methane space velocity of about 2 may give better results than the space velocity of 4 mmol/g/hr normally used.

An exploratory run was carried out to study the conversion of propane over a Ca:Ni:K oxide catalyst 4:1:.1. At a lower temperature than used for methane conversion (480°C) both

higher and lower hydrocarbons than C<sub>3</sub> were observed with little CO<sub>2</sub> formation. It is apparent that a detailed study of operating conditions and catalyst composition would be required to evaluate the potential of propane or ethane conversion.

Work is currently in progress on methane conversion using C<sup>13</sup>H<sub>4</sub> and H<sub>2</sub>O<sup>18</sup> isotopes to determine the role of carbon deposition on the catalyst and of water in the reaction chemistry. Results are too incomplete at this time to permit any conclusions.

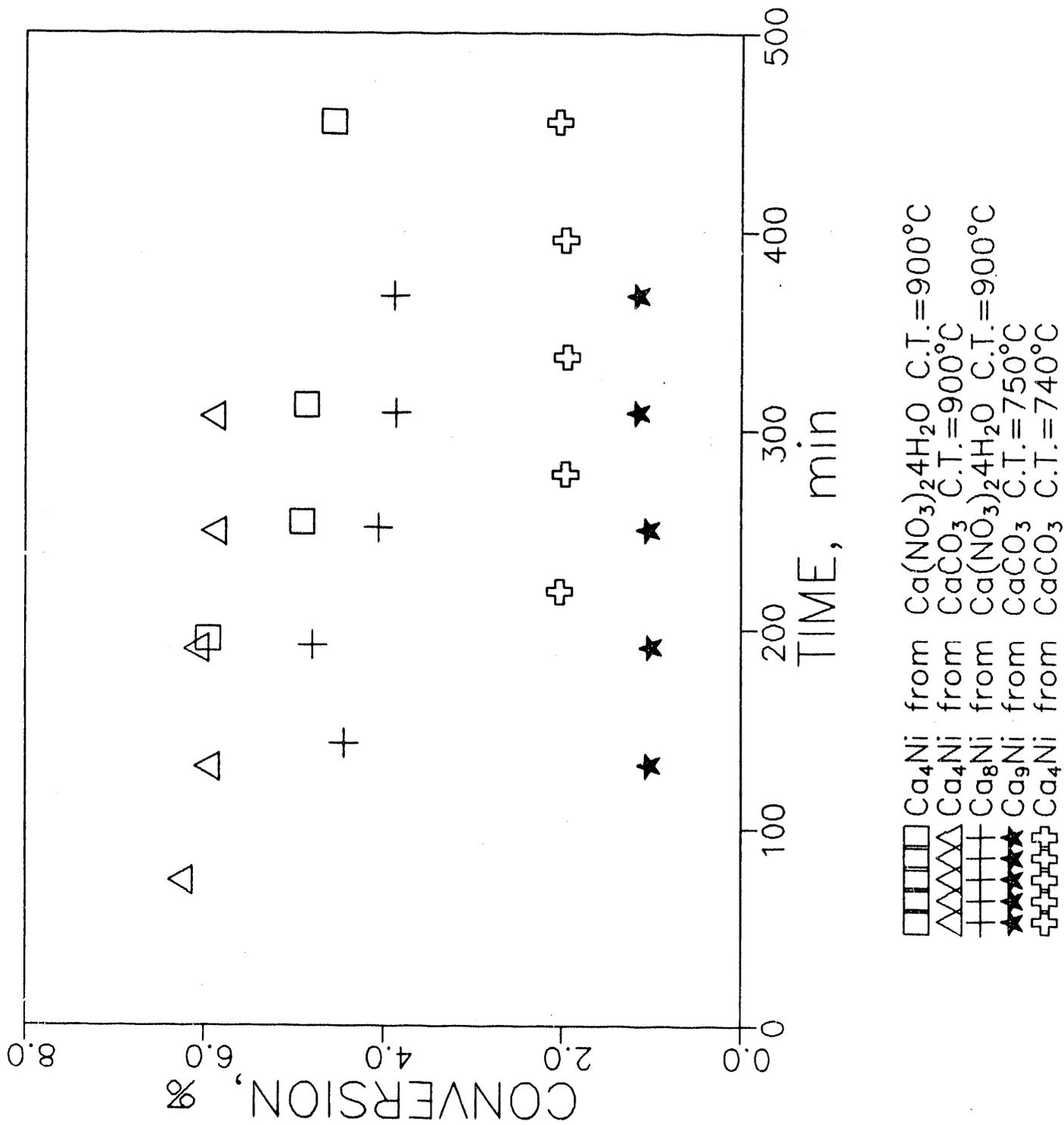


Fig. 1

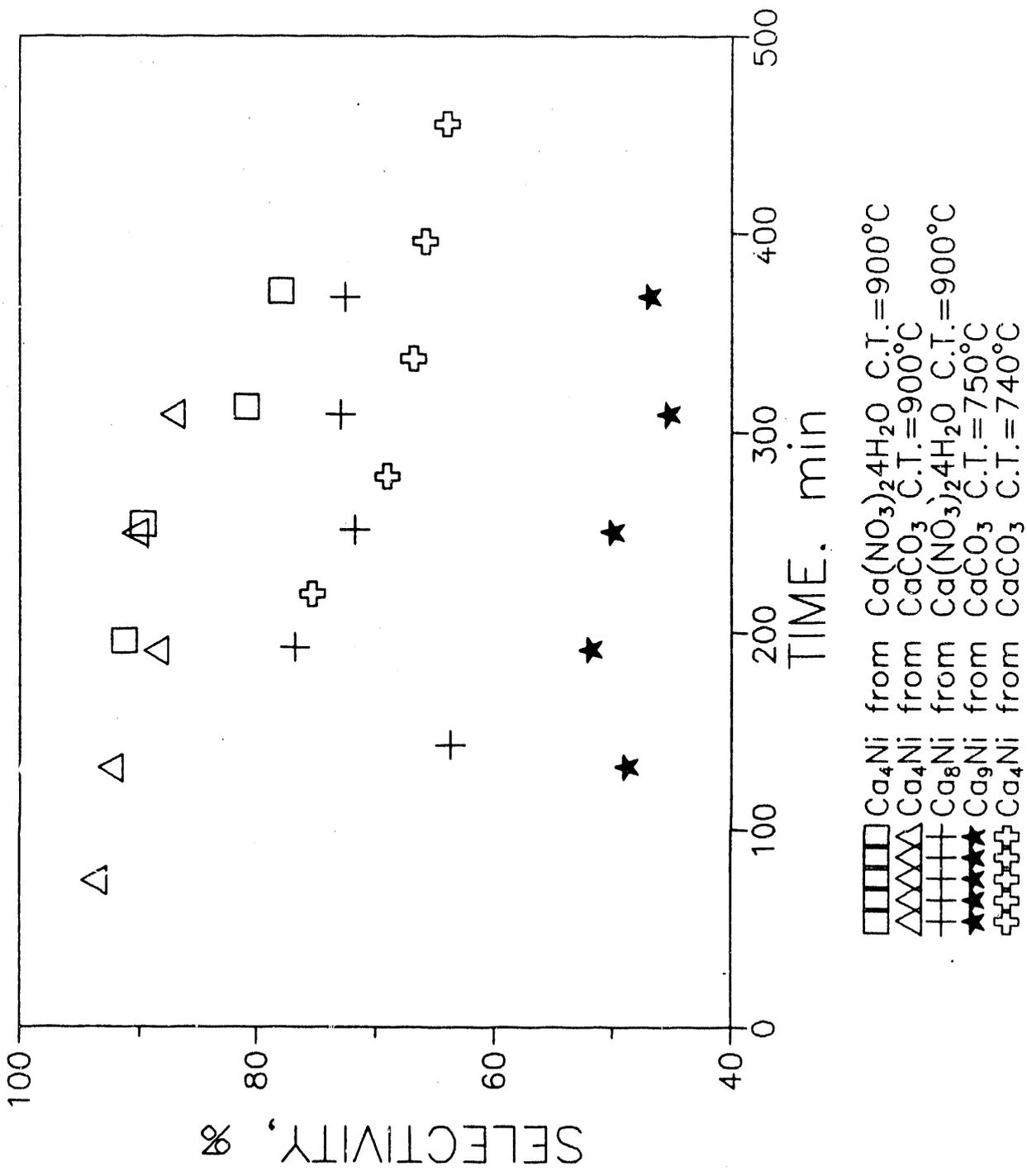


Fig. 2

Ca<sub>4</sub>Ni<sub>1</sub>K<sub>.1</sub> CATALYST

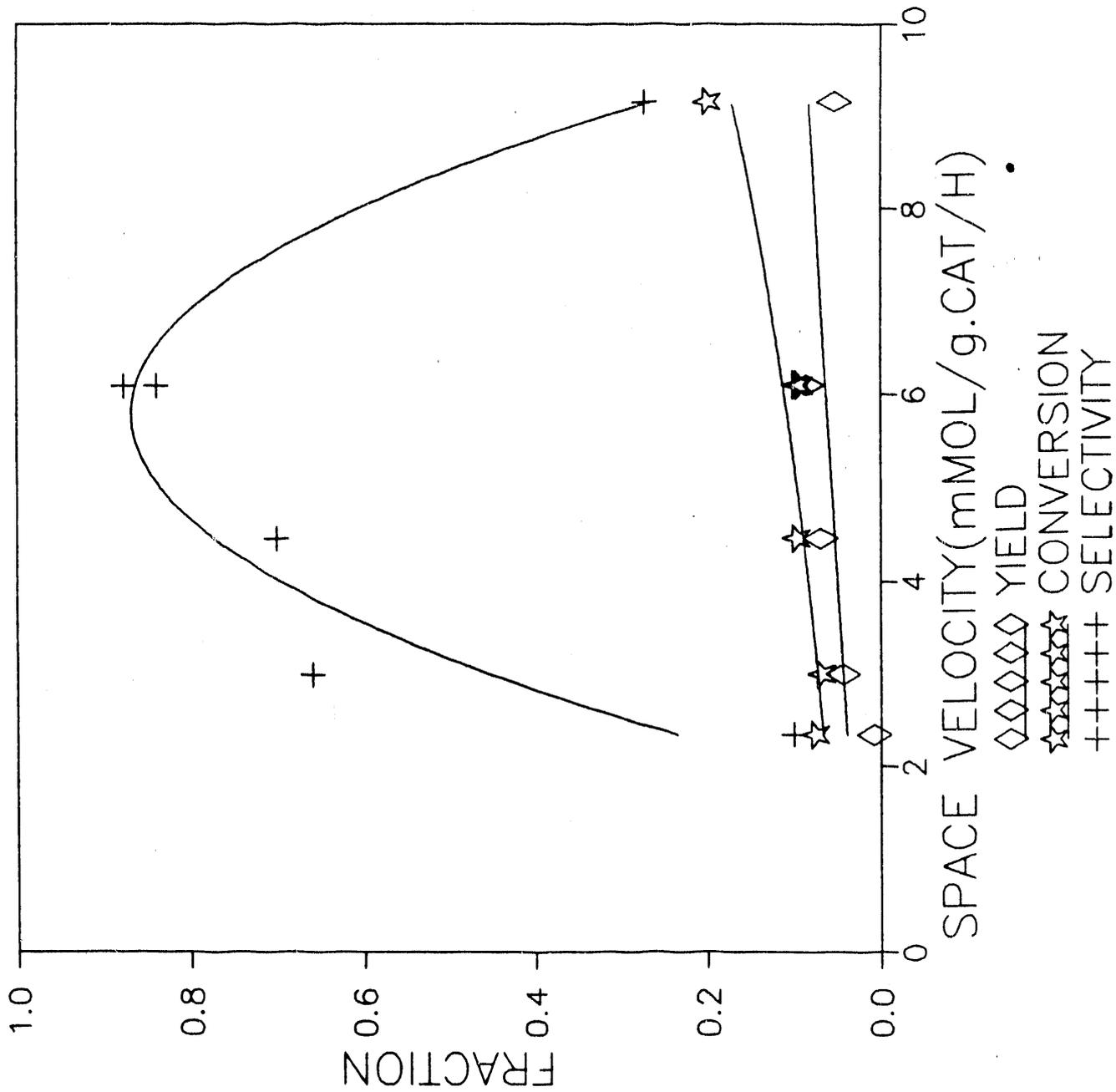


Fig. 3

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