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CATALYTIC GASIFICATION OF GRAPHITE OR CARBON:
Quarterly Report, January 1 - March 31, 1985

H. Heinemann

March 1985

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Quarterly Report

January 1 - March 31, 1985

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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I. TASK DESCRIPTION FOR FY 1985

This program is designed to look at the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Much of the work is being carried out with graphite as a carbon source to insure that hydrogen or hydrogen in hydrocarbons is derived from water. Relatively low temperatures are being used to favor the equilibrium $C+2H_2O \rightarrow CH_4+CO_2$, which is almost thermally neutral. Our earlier work has shown that, in the presence of KOH as catalyst, higher hydrocarbons up to C_6 can be formed. This raises the question whether hydrocarbons are a primary product and syngas a secondary one formed by steam reforming. The formation of hydrocarbons is a stoichiometric reaction in which each H_2 in water reacts to form a phenolate and a hydrocarbon: $5C+4KOH \rightarrow 4COK+CH_4$. We have shown the presence of phenolate by surface spectroscopy and have found that it can be decomposed over metal oxides to make the reaction truly catalytic: $4COK \xrightarrow{MeOx} 2K_2O+2C+2CO$; $2K_2O+2H_2O \rightarrow 4KOH$. Future work is directed toward combining flow reactor studies with ultrahigh vacuum surface studies to follow the mechanism, to find the best catalysts for phenolate decomposition, to measure and improve kinetics, and to study the effect of added gases, such as CO or COS.

II. HIGHLIGHTS

1. A char derived from Illinois #6 coal was gasified after impregnation with KOH-NiO. The gasification with steam resulted in almost identical results with those obtained from graphite. Gaseous products were hydrogen and CO₂ in a ratio of about 2:1. The char gave larger, but still small amounts of methane (about 1% of gas products) than graphite at gasification temperatures of up to 900K.
2. Addition of CO to the steam feed to KOH-NiO impregnated graphite resulted in a 25% increase in the rate of gasification. While the gaseous products were hydrogen and CO₂ in a ratio of 2:1 as observed in previous experiments without added CO, the new data show that formation of H₂ and CO₂ in a 2:1 ratio is not due to a water gas shift reaction.
3. Addition of hydrogen to the steam feed caused about a 25% decrease in the rate of gas production as did the addition of CO₂ instead of hydrogen.

III. PROGRESS OF STUDIES

A. Gasification of Char with Steam Catalyzed by KOH-NiO

The gasification of char with steam was studied using KOH-NiO as a catalyst. The char-coal was prepared by pyrolyzing Illinois #6 coal at 1300K for 6 hours under a He atmosphere. The catalyst was loaded by impregnation to incipient wetness of water solutions of KOH and $\text{Ni}(\text{NO}_3)_2$. The sample was dried in an oven at 373K for 10 minutes and introduced into the reactor. The nickel salt was decomposed at 673K under He to form the oxide.

The results obtained for a char sample with 13.0% w/w KOH loading and 17.35% w/w NiO loading (KOH/NiO molar ratio equal to 1.0) are shown in Figure 5. The activity for gasification of char is almost identical to the activity for gasification of graphite. The gas products are mainly H_2 and CO_2 in an H_2/CO_2 molar ratio equal to 1.8 ± 0.3 .

The main differences between the results obtained with char and with graphite lies in the fraction of CH_4 in the gas products. In the case of graphite, almost no CH_4 is present after 1% graphite conversion, while in the case of char a molar ratio of CH_4/H_2 equal to 6.2×10^{-3} (about 1% of the gas products) is present even at temperatures as high as 920K after 5% graphite conversion. This can be explained by

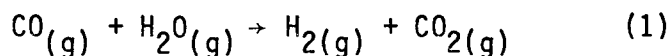
considering that char has a larger fraction of edges and non-aromatic carbon sites. These sites have weaker C-C bonds, and therefore, when hydrogen atoms are adsorbed, it is easier to break the C-C bonds to form CH₄ than in the case of C atoms in an aromatic structure of graphite. On the other hand, since the CH₄/H₂ molar ratio is much smaller than 1.0, it is clear that recombination of hydrogen atoms is still favored over breaking of the C-C bond.

B. Effect of Gas Addition on Gasification

The effect of added H₂, CO and CO₂ on steam gasification of graphite catalyzed by KOH/NiO has been studied during the report period.

Figure 1 shows the result obtained for the addition of CO to the reactant stream. The inlet flow of CO was 1.2 ml/min and the flow of steam was equal to 1.0 ml of condensed water/min. An increase in the rate of gas (H₂ and CO₂) production of the order of 25% was observed after deduction of the added CO relative to the rate obtained with steam only in the feed (Figure 2). The product distribution of the outlet gases shows a ratio of H₂ to CO₂ of 2.0. The same ratio was observed when steam was the only gas in the reactant stream.

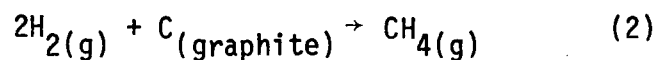
The total outlet flow of CO remains relatively constant as a function of temperature (Fig. 1). Therefore, the increase in the total production of H₂ and CO₂ cannot be due to the water gas shift reaction:



A ratio of H_2 to CO_2 equal to 2.0 also suggests this conclusion. The ratio of H_2 to CO_2 obtained when only the steam gasification of graphite is taking place is 2.0. If in addition to this reaction, we had the reaction of CO with steam to produce H_2 and CO_2 in a ratio of 1.0, we would expect an overall H_2 to CO_2 ratio less than 2.0 in the outlet gases, which is not the case at our reaction conditions.

At present, we do not have enough evidence to explain this increase on the steam gasification activity of the NiO/KOH catalyst when CO is present. One hypothesis is that CO is increasing the dispersion of the catalyst, improving the total contact area with the graphite. Surface science and electron microscopy studies will be done to test this hypothesis.

Another hypothesis for the increase in rate of gas production by addition of CO to the reactant stream is that CO is reducing the NiO to Ni metal, which is a more active catalyst for this reaction. If this were the case, we would expect an even greater effect by adding H_2 to the reactant stream. Figure 3 shows a completely opposite effect. When an inlet flow of H_2 of 0.7 ml/min was added to steam and passed through a graphite sample loaded with KOH and NiO, a decrease of nearly 25% in the rate of gas production was observed. If the initial amount of H_2 added is subtracted from the product gases, the ratio of H_2 to CO_2 obtained is 2.0, as in the previous experiments. A small amount of CH_4 in the gas products was observed (less than 1%) below 900K, possibly due to the gasification of graphite with hydrogen according to equation (2).



The presence of NiO, even in an H₂ containing atmosphere, supports our previous results suggesting that KOH stabilizes the presence of NiO at our reaction conditions.

Just as in the case of the addition of CO, we did not have enough evidence to explain the reduction on activity when H₂ is added to the reactant stream. Our working hypothesis, based on the effect of these gases on the catalyst dispersion, would suggest that H₂ is favoring a sintering process that reduces the contact area between the catalyst and graphite. It has been reported that a similar situation is found in the case of a Ni metal catalyst. Yamada et al. reported (1) that in the presence of H₂, the particle size of Ni metal deposited on graphite was larger than when steam alone was present in the reactant stream.

Figure 4 shows the results obtained when CO₂ was added to the reactant stream. A reduction in the rate of reaction of about 25% was observed. As in the case of H₂, if the inlet flow of CO₂ is subtracted from the gas products, the ratio of H₂ to CO₂ produced is equal to 2.0.

In order to draw more definite conclusions about the effect of adding these gases on the activity of the NiO/KOH catalyst for the gasification of graphite with steam, new experiments have to be carried out. First, the flow reactor will be modified to allow the addition of smaller flows of these gases. In the present experiments, the flows are

relatively large and reactions involving small amounts of these gases are hard to detect. Also, the use of different isotopes to identify the sources of hydrogen and carbon in the gas products will show if these gases are taking part in the gasification process or if they are only changing the physical properties of the catalyst (e.g., dispersion).

Surface science studies are in progress to determine the oxidation state of the Ni in the NiO-KOH catalyst and its particle size. Also, electron microscopy studies will be undertaken to verify the hypothesis made on the effect of H₂ and CO on the catalyst dispersion in our reaction conditions.

Reference

1. T. Yamada, A. Tonita, Y. Tamai and T. Homma, Fuel 62, 246 (1983).

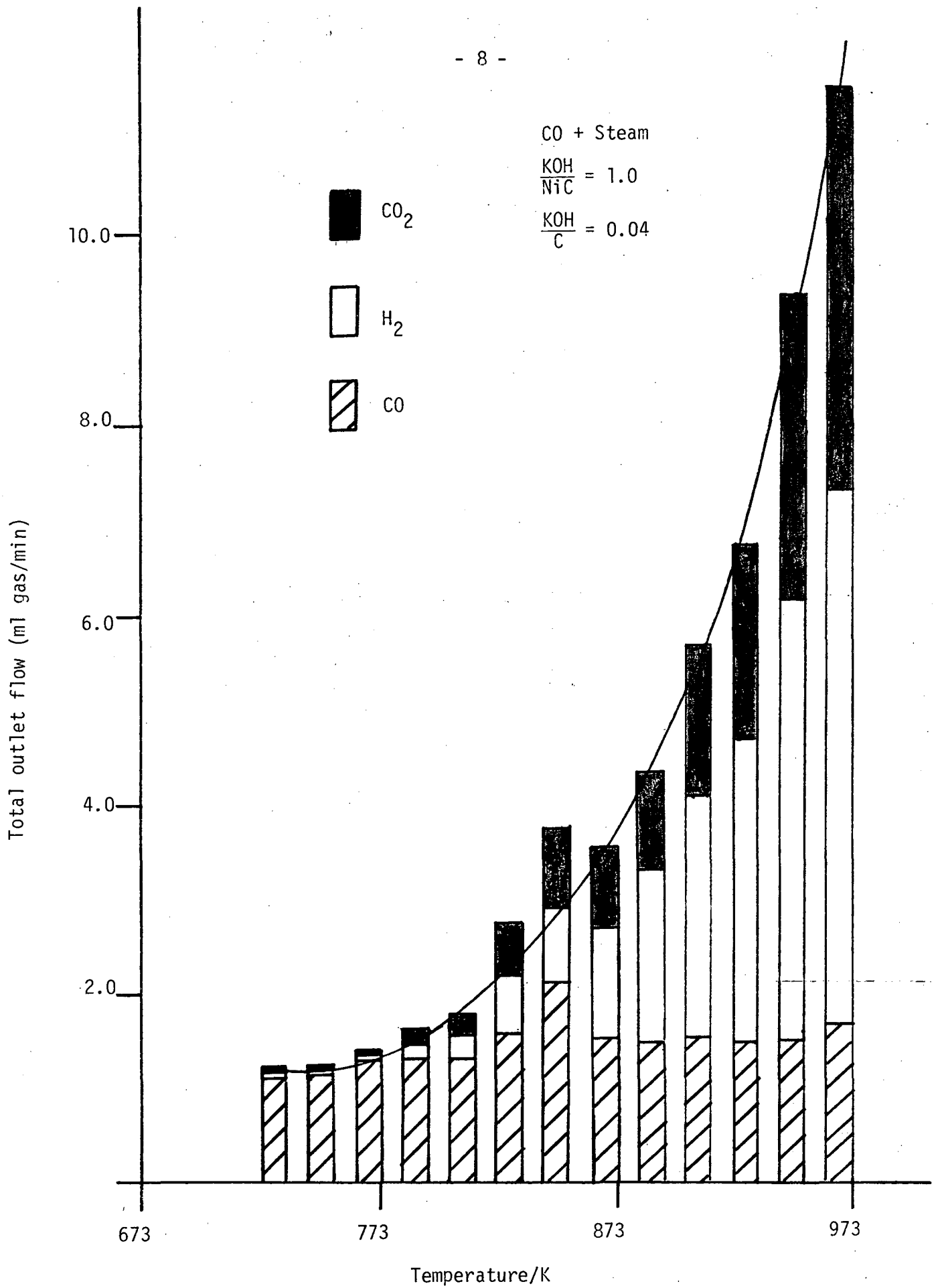


Figure 1

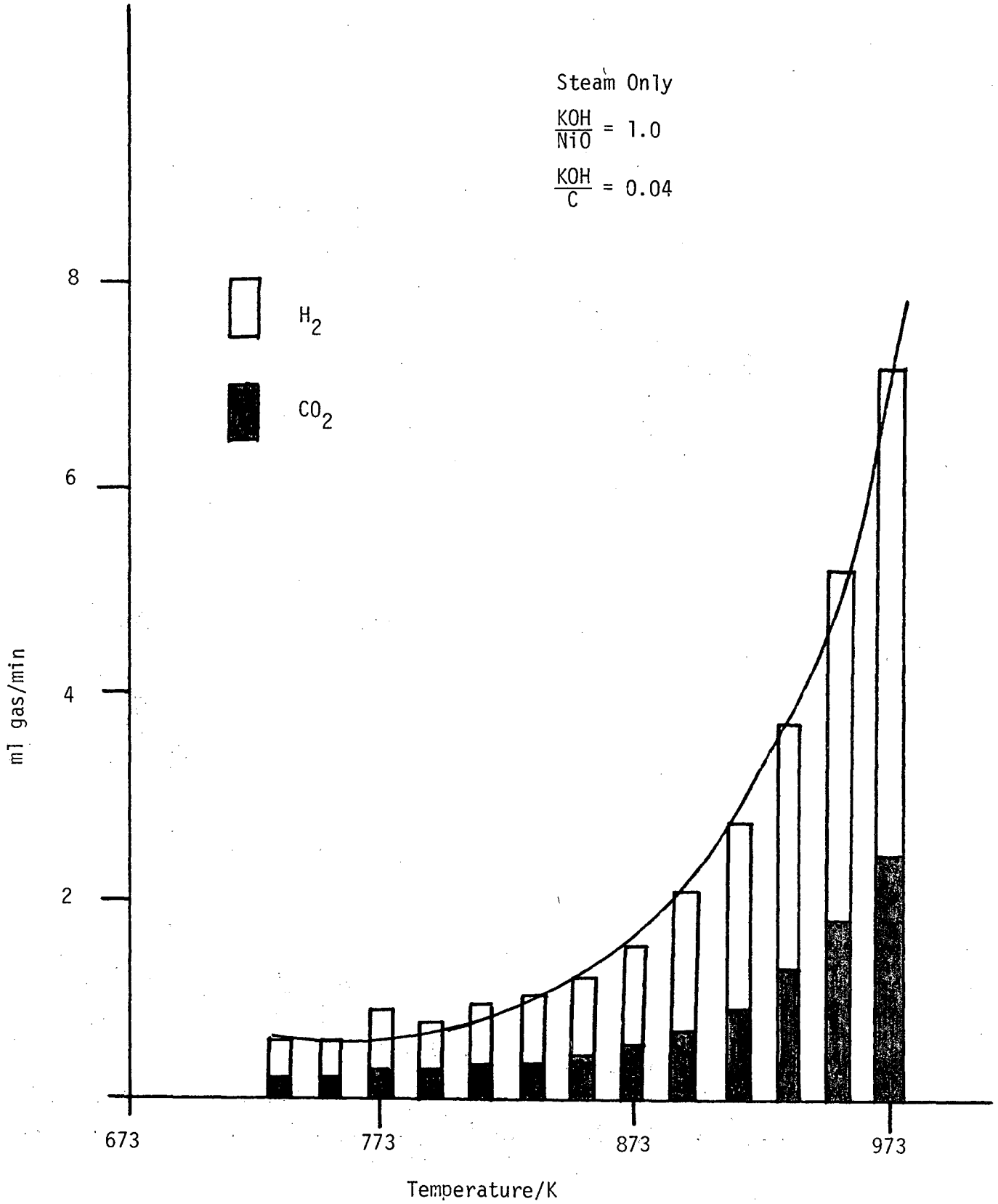


Figure 2

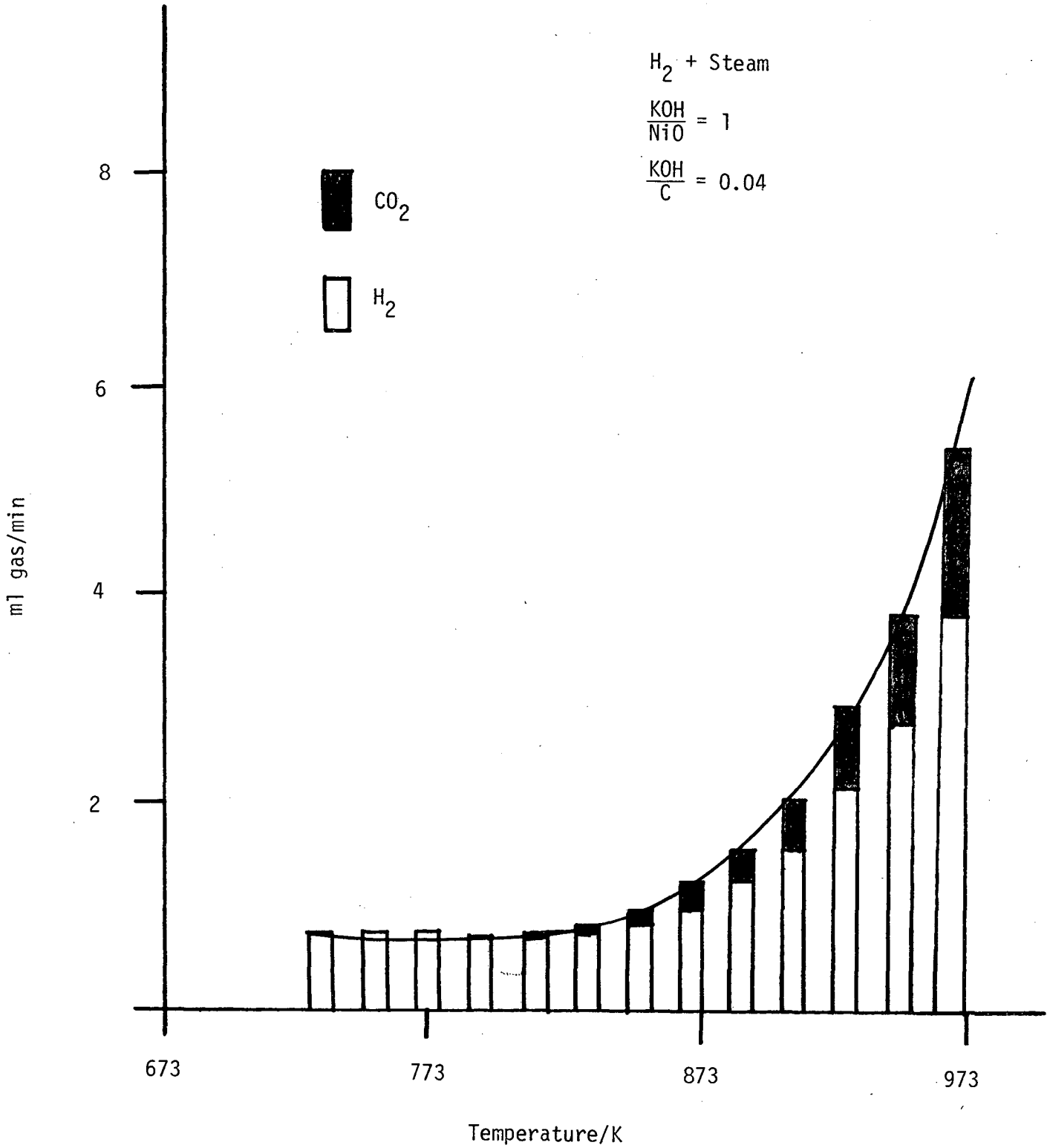


Figure 3

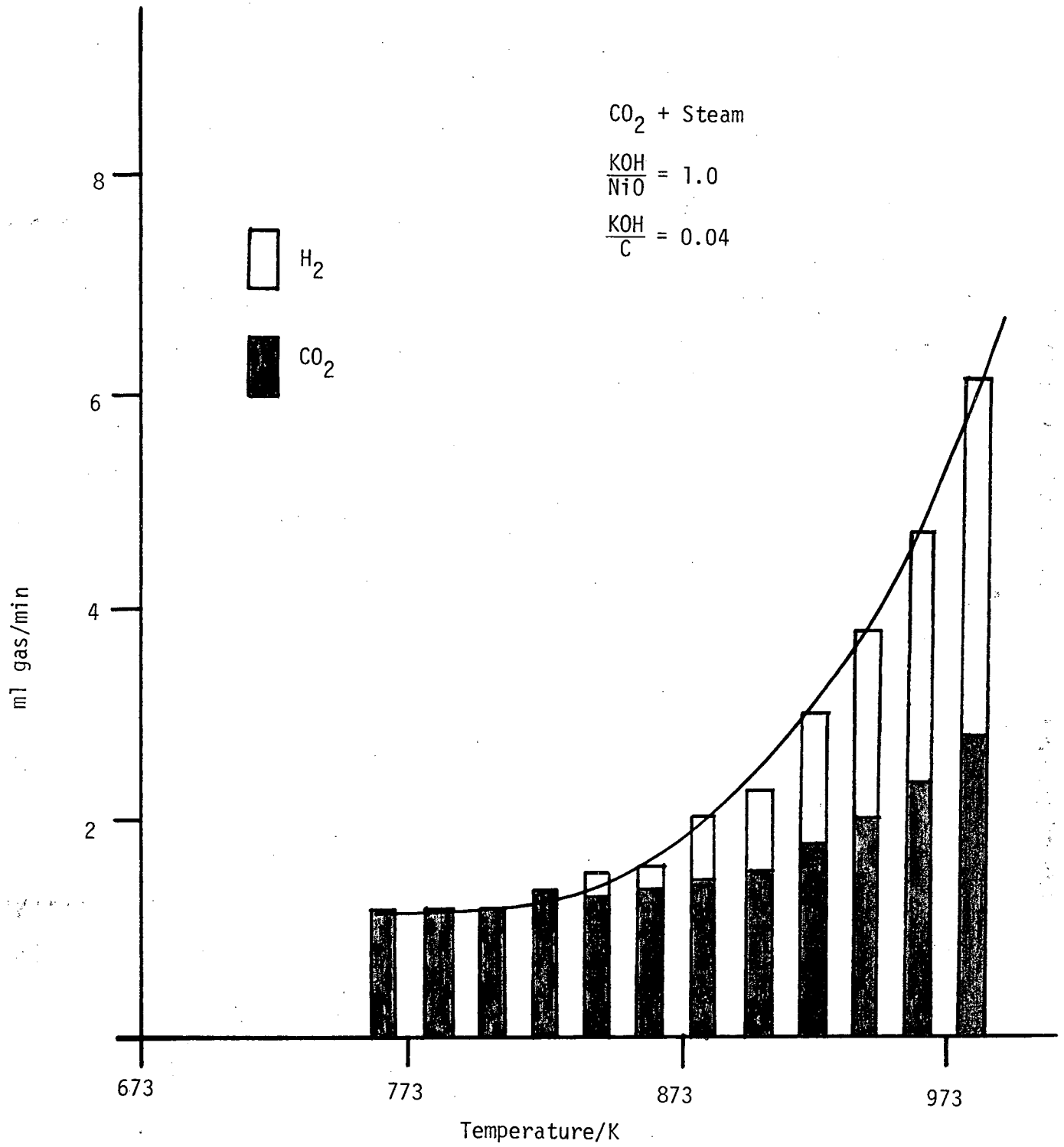
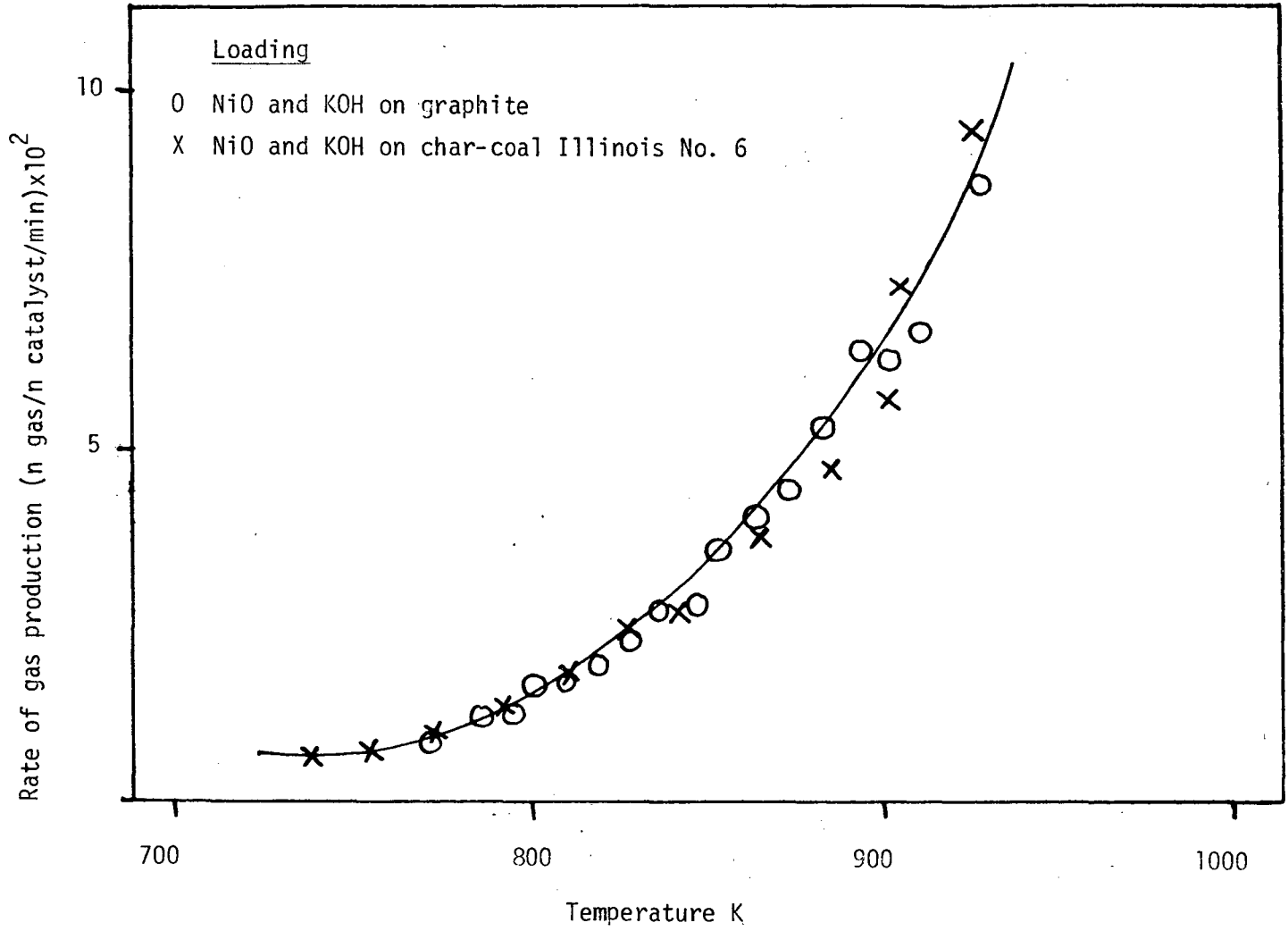


Figure 4

Figure 5



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