LBL-16050
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY
AUG 10 1983
LIBRARY AND
DOCUMENTS SECTION

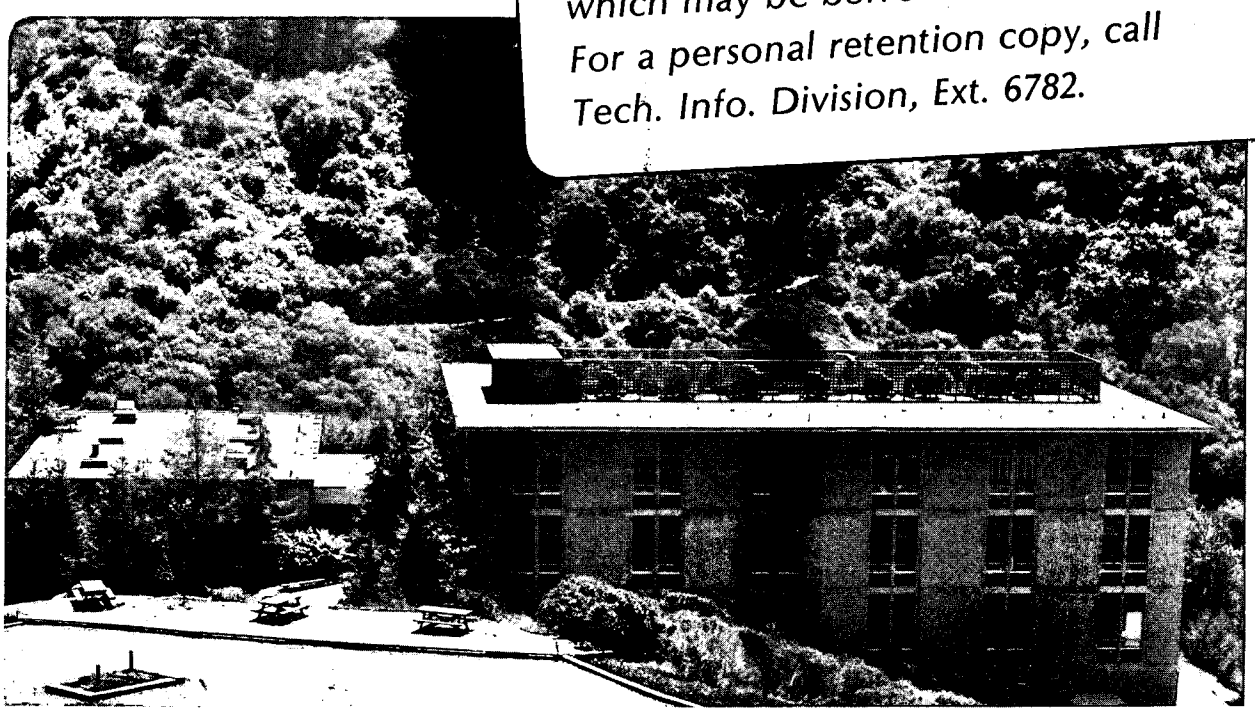
Submitted to Applied Catalysis

DISTRIBUTION OF REACTION PRODUCTS IN THE KOH INITIATED LOW TEMPERATURE STEAM GASIFICATION OF GRAPHITE

F. Delannay, W.T. Tysoe, H. Heinemann,
and G.A. Somorjai

May 1983

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-16050 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-16050

DISTRIBUTION OF REACTION PRODUCTS IN THE KOH INITIATED LOW TEMPERATURE STEAM GASIFICATION OF GRAPHITE

F. Delannay*, W.T. Tysoe, H. Heinemann, and G.A. Somorjai

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemistry
University of California, Berkeley
Berkeley, California, 94720, USA

*On leave from the Groupe de Physico-Chimie Minérale et de Catalyse,
Université Catholique de Louvain, Belgium

Distribution of Reaction Products in the KOH Initiated Low Temperature Steam Gasification of Graphite

By F. Delannay*, W.T. Tysoe, H. Heinemann and G.A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and
Department of Chemistry, University of California, Berkeley, CA 94720

Abstract

Powdered graphite samples loaded with various amounts of KOH have been reacted with atmospheric pressure of steam in the temperature range 700-900K. Significant amounts of C_1 to C_6 hydrocarbons are found in the gaseous products of this reaction. Both the abundance of these hydrocarbons with respect to hydrogen and their relative distribution varies as a function of reaction time, KOH loading and temperature. A model for their production is proposed according to which C-H groups are stabilized by the formation of a potassium phenolate type compound at the prismatic edge of graphite. Hydrocarbon would then be produced from the direct hydrogenation of surface carbon atoms. The hydrocarbon distribution shows large deviations from the ideal Schulz-Flory distribution, giving little support to a chain growth type mechanism.

*On leave from the Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Louvain, Belgium

1. INTRODUCTION

The production of hydrogen and carbon monoxide from the reaction of carbon with water vapor is endothermic and thus requires high temperatures. In contrast, the synthesis of hydrocarbons from carbon monoxide and hydrogen is exothermic and is thus favored at lower temperatures. Our research aims at investigating possible catalytic routes for the direct production of hydrocarbons from the reaction of carbon and steam. As most hydrocarbons are unstable at high temperature, this reaction requires a relatively low reaction temperature.

It has been known for many years that alkali metals catalyse the steam gasification of carbon [e.g. 1]. In most studies reported in the literature, alkalis are deposited over carbon in the form of a salt, usually a carbonate [2]. We have found that, in the temperature range 700-900K, the gasification of graphite powder under atmospheric pressure of steam is more efficiently promoted by potassium hydroxide than by potassium carbonate.[3] The only gaseous products from the reaction are then hydrogen and hydrocarbons. This hydrogen is produced from the splitting of H_2O; the corresponding amount of oxygen remains in the sample to form a compound with potassium. As a consequence, the reaction rate decreases drastically when all potassium hydroxide has been converted into this compound. CO evolves when the latter is decomposed thermally by heating up to 1300K in an inert atmosphere. The original reactivity is partially recovered after this heat treatment. This suggests that the decomposition of this compound consisting of C-OK groups may be the rate limiting step in the catalytic reaction conducted at higher temperatures.

Few studies have been concerned with the product distribution obtained during gasification reactions. Only the evolution of H_2, CO and a few percent of CO_2 and CH_4 has been reported [e.g. 4]. The CH_4 formed is usually thought to arise from the hydrogenation of CO by H_2, this reaction also being catalyzed by potassium carbonate [5]. However, Cabrera et al. [6] have shown that KOH may directly catalyse the production of CH_4 from the reaction of steam with graphite in the temperature range 500-800K. In this case, a reaction of the type

$$2C + 2H_2O \longrightarrow CH_4 + CO_2$$

was postulated.

In this paper, we discuss the distribution of gaseous products collected during the reaction of a KOH loaded graphite powder under atmospheric pressure of steam in the temperature range 700-900K. It will be shown that significant amounts of C_2 to C_6 hydrocarbons are formed in addition to hydrogen and methane. Such a production of higher hydrocarbons has not been reported previously in the literature. Possible reaction mechanisms will be discussed.

2. EXPERIMENTAL

A diagram of the experimental setup is shown in Figure 1. The reactor consisted of an 3.7 mm ID alumina tube containing 0.5 g of KOH loaded graphite powder. Either pure argon or pure steam could be flowed through the reactor. Steam was produced by forcing water from a reservoir

into a copper tube heated to above 400K. At the outlet of the reactor, an open ended U-shaped tube immersed in water condensed the steam and allowed the gaseous products to be collected in a graduated burette. This enabled the volume of gas products to be measured accurately. The volume of cooling water was kept as small as possible to minimize solution of products. However, it should be borne in mind that a variation in solubility of outlet gases may slightly affect the product distribution. A septum was attached to the top of the burette for the extraction of gas samples during the reaction. Gas from the burette was periodically transferred to a vacuum container for analysis after the reaction was completed.

The products were analysed by gas chromatography and mass spectrometry. A thermal conductivity detector with column consisting of six feet Chromosorb 102 + six feet Chromosorb 101 with argon as carrier gas was used for the measurement of the relative proportions of H_2, CO, CO_2 and CH_4. The hydrocarbon distribution was more conveniently determined using flame ionization detection with a six foot long Chromosorb 102 column. This experimental apparatus is discussed in greater detail in reference 3.

3. RESULTS

The experiments discussed in this paper were all performed under isothermal conditions. After exposing the sample to steam at 400K, the reactor temperature was quickly raised (at $\sim$ 160K min^{-1}) to that chosen

for the reaction. Figure 2 shows a plot of the volume of gas produced as a function of time during the reaction at 800K for a sample having a KOH/C molecular ratio of 0.043 (which corresponds to a C/KOH ratio of 24). The shape of this plot is typical for a reaction in the temperature range 700-900K for KOH/C ratios between 0.01 to 0.065 (corresponding to C/KOH ratios of 100 and 16 respectively). After a short initial burst, the gas evolved at a fairly constant rate during a period of a few hours. (This first steady-state will be referred to in the following as reaction I). The reactivity of the sample then changed, and the gas production proceeded at a much reduced rate (reaction II).

During reaction I, the products were almost exclusively hydrogen and hydrocarbons, whereas during reaction II, CO was also produced. In this case the CO/H_2 ratio was approximately unity. Fig. 3 presents a typical flame ionization detection (FID) chromatogram of a gas sample extracted via the septum during the reaction. Hydrocarbons up to C_6 can be detected. Alkenes are more abundant than alkanes. The major C_2 and C_4 peaks on this chromatogram are ethene and butene respectively. (The three C_3 compounds are not separated on this chromatogram. Operation of the GC at lower oven temperature indicated that propene was the dominant C_3 product). No acetylene was detected.

Figure 4 gives the variation of the volume concentration of CH_4 in H_2 for the same reaction illustrated in Figure 2. The amount of CH_4 exceeded 2% of the amount of H_2 during the initial burst. However, the proportion of methane then decreased steeply during reaction I and once again increased slowly during reaction II. The average concentration CH_4 in H_2 in the products after 7 hours was 0.4%.

The corresponding variation of the distribution of the hydrocarbons is shown in Figure 5 as weight % of total hydrocarbon. The proportion of methane ranged between more than 80% at the start and about 50% at the end of reaction I. The proportion of higher hydrocarbons increased progressively during reaction I, with C_4 becoming the most abundant. Little change in the hydrocarbon distribution occurred during reaction II.

Figure 6 and 7 present the variations of the volume concentration of CH_4 in H_2 and the weight distribution of hydrocarbons respectively for the reaction at 800K for a sample having a KOH/C loading equal to 0.01. As discussed in [3], the gas production rate decreased drastically as the loading was decreased. In this case, reaction I lasted about 20 hours. The transition between reactions I and II is gradual. Decreasing the KOH loading by a factor of 4 significantly increased the CH_4/H_2 concentration ratio. This ratio again exhibits a decrease during reaction I. Furthermore, the results displayed in Figure 7 indicate that the proportion of higher hydrocarbons decreased with respect to methane when the KOH loading is decreased. The trends also differ from the previous case (ie. with KOH/C=0.043) as a continuous increase of the proportion of CH_4 with respect to the higher hydrocarbons is now observed. Figure 8 summarizes the dependence of the mean CH_4/H_2 concentration ratio of the products of reaction I on the KOH/C loading of the samples.

The temperature dependence of the product distribution was investigated in the temperature range 700-900K for samples with K/C ratio=0.043. The

experimental points in Figure 9 are for an analysis of gas samples which were extracted via the septum when the amount of hydrogen produced equalled 20% of the potassium loading in each case. The results have been plotted on a semilog scale as a function of the inverse of the absolute temperature. The solid points refer to the volume concentration of CH_4 in H_2, and the open circles ratio to the $(C_2 + C_3)/CH_4$ weight ratio. As the temperature was increased, the proportion of CH_4 was found to decrease both with respect to hydrogen and higher hydrocarbons. The reproducibility of these measurements was not very high, owing probably to the strong dependence of the product distribution on the extent of reaction. No accurate activation energy differences between products may thus be extracted from these data. An order of magnitude estimate may be made, however, and indicates that the activation energy for CH_4 formation is about 5 to 10 kcal/mole lower than for H_2 production.

4. DISCUSSION

Whereas the production of a few percent of methane during steam gasification of carbon is not a new phenomenon, the production of higher hydrocarbons has not been reported before. The high rate observed during reaction I cannot be sustained because of the formation of an oxygen containing (K-O-C) intermediate which is stable at the reaction temperature.[3] However, Figures 5 and 7 indicate that hydrocarbons are produced during both reactions I and II. This supports the suggestion that these two stages of the reaction essentially operate via identical mechanisms, the difference merely being due to a change in the rate controlling step. [3].

According to the model developed [3], under reaction conditions, the prismatic edges of graphite would be covered, as indicated in Figure 10, by K-O-C and H-C groups. The binding within the K-O-C entities may be sufficiently strong to induce C-C bond scission. Hydrogen molecules can desorb as a result of the recombination of two C-H groups.

According to this picture, the simplest mechanism that may be proposed for the production of hydrocarbons would be the formation of multiple $C\text{-}H_m$ groups by sequential addition of hydrogen and simultaneous scission of C-C bonds. The formation of such groups on neighboring surface atoms would eventually result in the desorption of hydrocarbon molecules heavier than CH_4. According to this mechanism, the role of potassium would be to effectively increase the number of available hydrogen atoms (by preventing the back-reaction $C\text{-}H + C\text{-}OH \longrightarrow 2C + H_2O$). Potassium would have little influence on the subsequent formation of the $C\text{-}H_m$ groups.

However, our experiments indicate that the product distribution does vary with potassium loading. Although this may merely be due to a dependence of product distribution on gasification rate, this behaviour is somewhat analogous to the role of alkalis in Fischer-Tropsch reactions. Indeed, it is well known that, for example, iron or nickel catalyzed Fischer-Tropsch reactions are influenced by the presence of alkalis in three ways: it (i) decreases the overall rate of hydrogenation, (ii) increases the rate of chain growth and (iii) increases the proportion of alkenes with respect to the alkanes [7.8]. In a similar way, the present results show that increasing the amount of potassium (i) decreases the ratio CH_4/H_2, and

(ii) increases the proportion of higher hydrocarbons with respect to methane. Also, the proportion of alkenes remains fairly high in all cases.

This analogy suggests an alternative possible mechanism for the hydrocarbon formation that would involve, as in Fischer-Tropsch reactions, as shown in [12] the hydrogenation of a carbidic carbon at an active site of the catalyst surface (potassium in the present case) and the subsequent growth of a hydrocarbon chain by sequential addition to the initial $C-H_m$ group of carbon atoms diffusing to this active site. In such a case, the formation of hydrocarbons would be directly catalyzed by potassium.

It is known that potassium has some activity as a catalyst for hydrogenation reactions. It has been reported that, at elevated pressures, a mixture of K_2CO_3 and coal is a good catalyst for the methanation of CO by H_2[5]. Also, Bonzel and Krebs [9] have shown that, after depositing potassium onto an iron foil, Fischer-Tropsh activity was still maintained even though the surface of the catalyst was completely covered by more than ten monolayers of carbon. Auger analysis indicate that, in this case, potassium still lays on top of the carbon deposit.

The distribution of Fischer-Tropsh products can be described by means of a chain growth polymerization mechanism, ie. the so-called Schulz-Flory (SF) distribution [10]. If W_n is the weight fraction of hydrocarbons containing n carbon atoms, this formalism implies that the logarithm of the ratio W_n/n should vary linearly with n. Figure 11 shows such a plot for a typical product

distribution for the reaction of a KOH loaded graphite sample at 800K. The dependence of $\ln(W_n/n)$ on n is obviously not linear. In general, this non-linearity is due either to a larger CH_4 and C_4 yield that expected theoretically or alternatively to a somewhat diminished C_2 and C_3 yield.

However, deviations of Fischer-Tropsch product distribution from the ideal SF model have often been reported in the literature. Various possible reasons for these deviations have been proposed, for example mass transfer limitations, coexistence of different types of active sites, or shape/size selectivity of the support [11]. The fact that the product distributions in this work do not obey the ideal SF dependence on n is thus not a very strong argument for ruling out the existence of a chain growth polymerization mechanism. The first mechanism proposed (namely the direct hydrogenation of the carbon surface) would, however appear more likely.

Previous papers have studied the influence of KOH on the production of CH_4 in the temperature range 500-800K from the reaction of 20 Torr of water vapor with a piece of highly oriented pyrolytic graphite (HOPG, Union Carbide) in a recirculation type reactor [6,12]. The product gas was not analysed for hydrogen and hydrocarbons other than CH_4 in these studies. However, their production using a flow reactor has been reported more recently [13] and the present results are thus in qualitative agreement with these previous ones. Owing to the low water pressure and temperature of these previous measurements, only a few percent of the KOH reacted and hence only the so-called reaction I

was studied since the transition to reaction II would have required excessively long times (several days).

Assuming that all carbon atoms exposed on the geometric surface area of the HOPG sample have an identical activity, a turnover frequency of about $5x10^{-3}CH_4$ molecule per carbon surface atom per second was calculated for the reaction with 20 Torr of water vapor at 800K [12]. The production of methane was also found to be first order with respect to water pressure up to 600 Torr [13]. The rates of CH_4 production measured in the present work (ie. in the flow reactor) are several orders of magnitude lower than the rate that can be calculated by extrapolation from the data of these earlier works. The origin of this discrepancy is unknown. Invoking differences in KOH loadings is obviously not sufficient to justify such a difference in activity. We hope that further work will allow us to clarify this problem.

5. CONCLUSION

This study shows for the first time that hydrocarbons heavier than CH_4 can be directly produced from the reaction of carbon with steam. This production appears to be promoted by the presence of KOH which allows a high rate of gasification at relatively low temperature. Two possible mechanisms for the formation of the hydrocarbon have been discussed: a chain growth polymerization mechanism and a sequential hydrogen addition to the prismatic planes of graphite.

The obvious limitation of this process is the fact that the high rate of gasification induced by KOH is not a catalytic reaction, owing to the

formation of a highly stable oxygen containing intermediate. The present results open however new prospects for a possible alternate route to the production of valuable hydrocarbons from carbonaceous materials. Future work will aim at studying other alkalis and transition metal hydroxides that might play a simlar role to KOH without involving deactivation.

ACKNOWLEDGEMENTS

This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, Pa. We also acknowledge partial support of this research by the Air Products Corporation.

The authors are indebted to G.T. Yee for experimental assistance. F.D. acknowledges Fulbright and NATO research fellowships.

REFERENCES

1. H.S. Taylor and H.A. Neville, J. Am. Chem. Soc., 43, 2065 (1921).
2. D.W. McKee, Carbon, 20, 59 (1982).
3. F. Delannay, W.T. Tysoe, H. Heinemann and G.A. Somorjai, submitted to Carbon.
4. M.J. Veraa and A.T. Bell, Fuel, 57, 194 (1978).
5. N.C. Nahas, Fuel, 62, 239 (1983).

6. A.L. Cabrera, H. Heinemann and G.A. Somorjai, J. Catalysis, 75, 7-22 (1982).

7. R.B. Anderson, in "Catalysis, Vol 4" (P.H. Emmett ed.), Reinhold, New York, 1956.

8. H.H. Storch, N. Golumbic and R.B. Anderson, The Fischer-Tropsch and Related Syntheses, Wiley, New York, 1951.

9. H.P. Bonzel and H.J. Krebs, Surface Science, 109, L527 (1981).

10. G. Henrici-Olive and S. Olive, Angew. Chem., 88, 144 (1976).

11. P.A. Jacobs and D. Van Wouwe, J. Molecular Catalysis, 17, 145 (1982).

12. R. Casanova, A.L. Cabrera, H. Heinemann and G.A. Somorjai, Fuel, in press.

13. F. Delannay, W.T. Tysoe, H. Heinemann and G.A. Somorjai, Proceedings of the 1983 Intern. Conf. on Coal Science, in press.

FIGURE LEGENDS

Figure 1: Diagram of experimental apparatus.

Figure 2: Plot of the gas production as a function of reaction time at 800K for a KOH/C loading equal to 0.043 (KOH/C molecular ratio).

Figure 3: Typical gas chromatogram for hydrocarbon products.

Figure 4: Plot of dependence on reaction time of the CH_4 concentration in H_2 the gas products for a KOH/C loading equal to 0.043 (mol).

Figure 5: Plot of dependence on reaction time of the proportion (wt %) of hydrocarbons for a KOH/C loading equal to 0.043 (mol).

Figure 6: Plot of dependence on reaction time of the CH_4 concentration in H_2 the products for a KOH/C loading equal to 0.01 (mol)

Figure 7: Plot of dependence on reaction time of the wt % proportion of hydrocarbons for a KOH/C loading equal to 0.01 (mol)

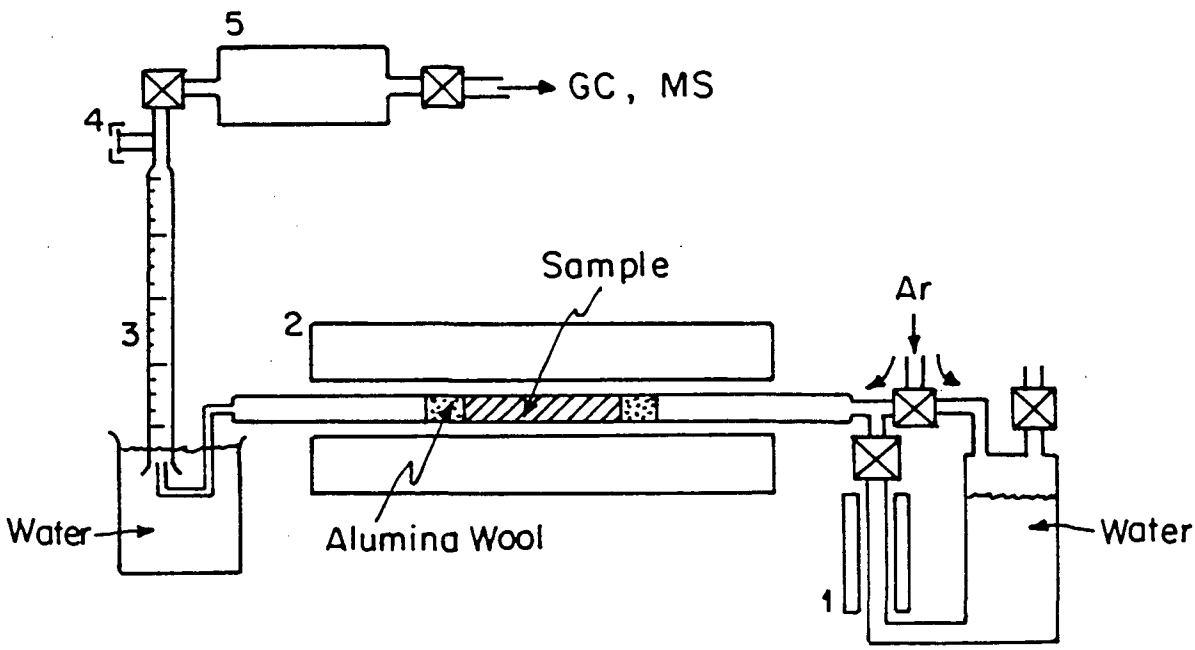
Figure 8: Plot of dependence of the CH_4 concentration in H^2 in the products on the KOH/C loading.

Figure 9: Semilog plot of the $(C_2+C_3)/CH_4$ weight ratio (0) and CH_4/H_2 volume ratio (•) as a function of the inverse of the absolute

temperature of the reaction.

Figure 10: Schematic diagram of the various species present on the prismatic edges of graphite during reaction.

Figure 11: Schulz-Flory plot of a typical hydrocarbon distribution in the products. n is the number of carbon atoms in the molecule and W_n is the total weight percent of the C_n hydrocarbons.



1 Steamer
2 Reactor
3 Burette
4 Septum
5 Vacuum Container

XBL 832-5326

Fig. 1

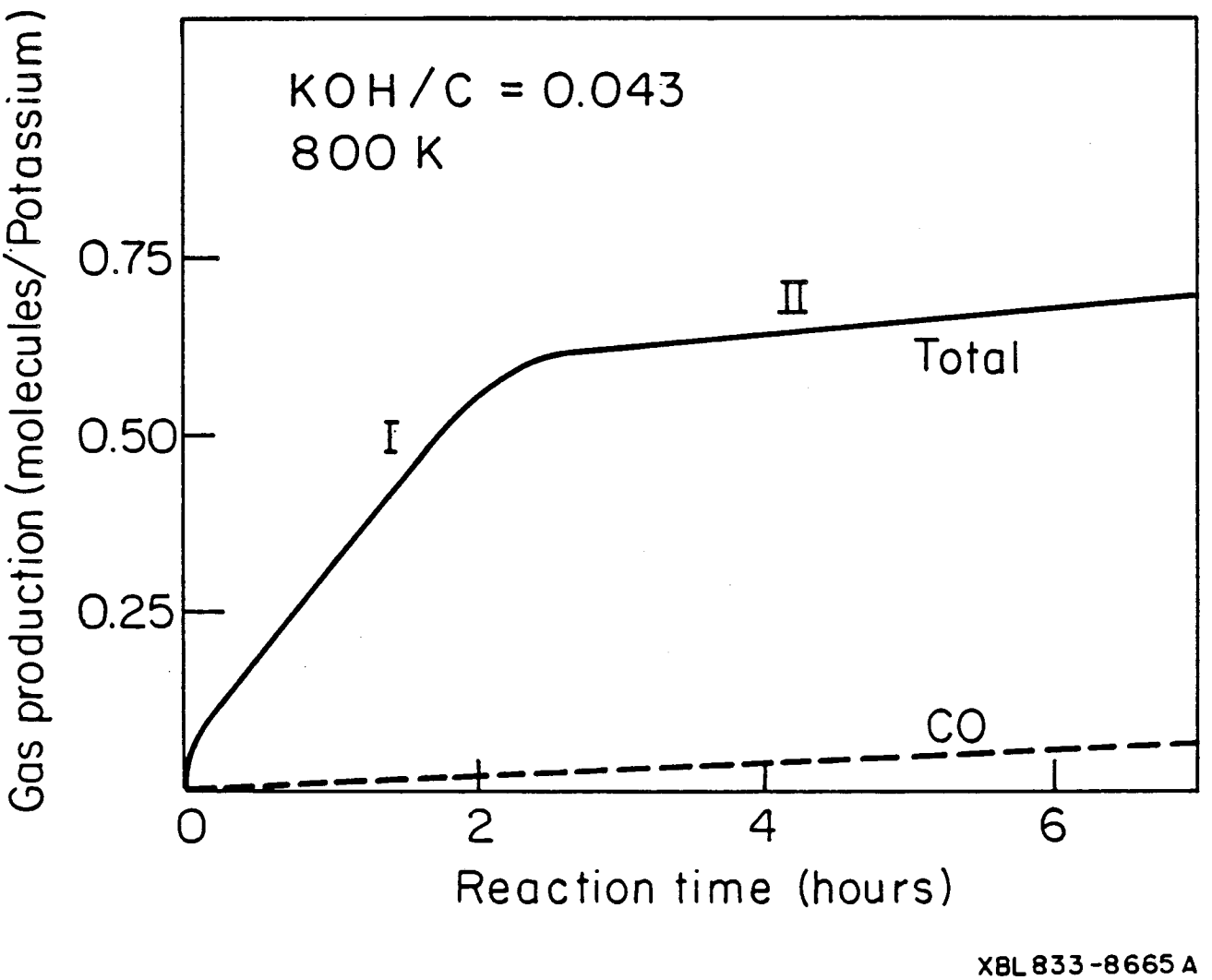
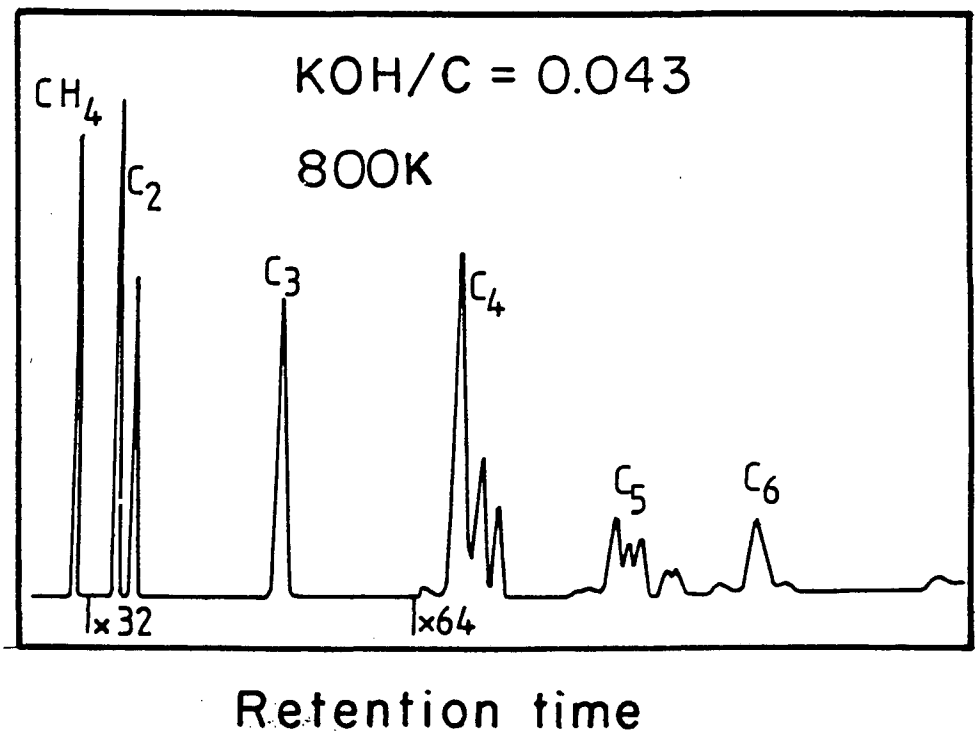
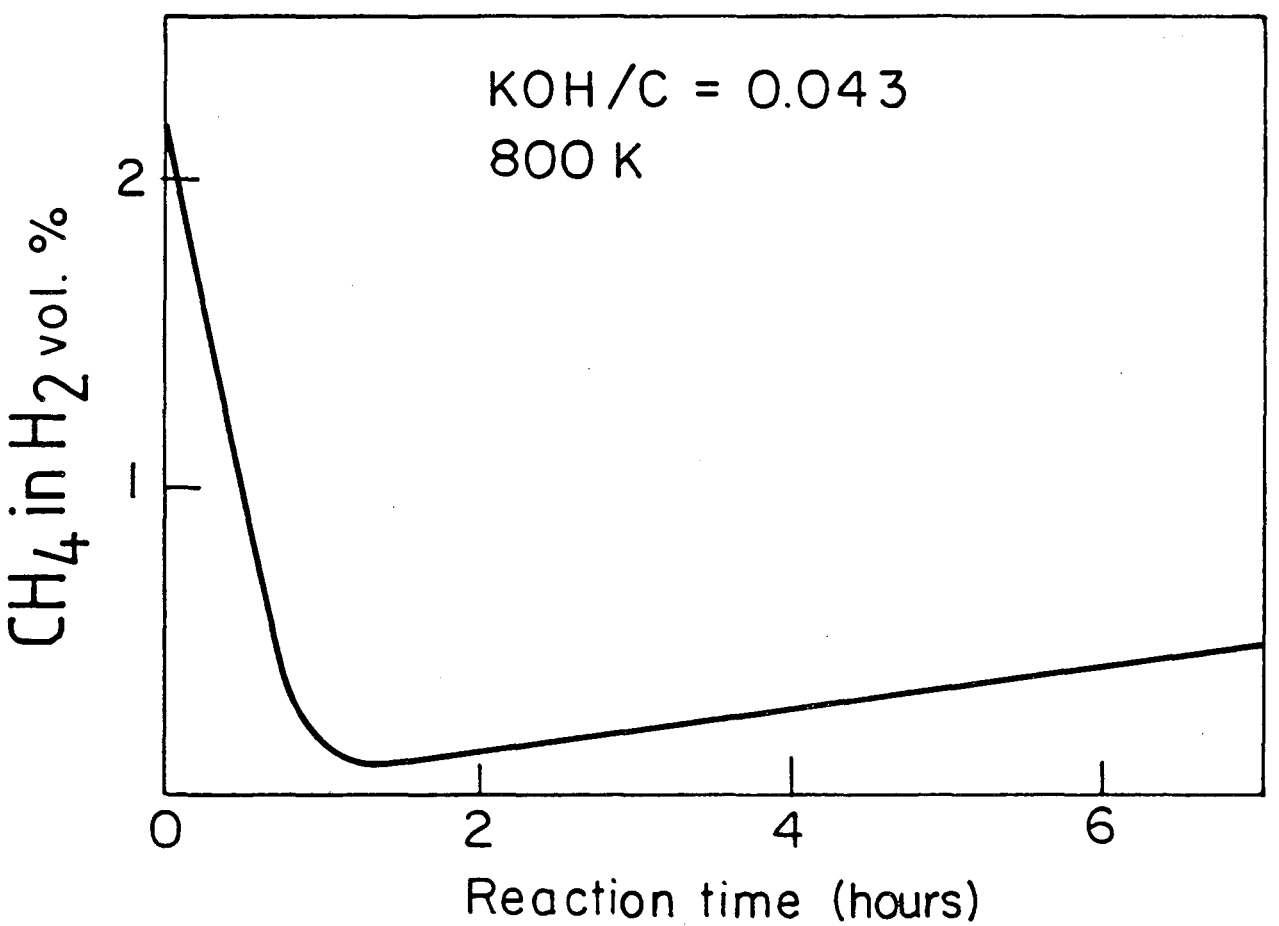

KOH/C = 0.043
800 K
0.75
0.50
0.25
I
II
Total
CO
0
2
4
6
Gas production (molecules/Potassium)
Reaction time (hours)
XBL 833-8665 A

Fig. 2



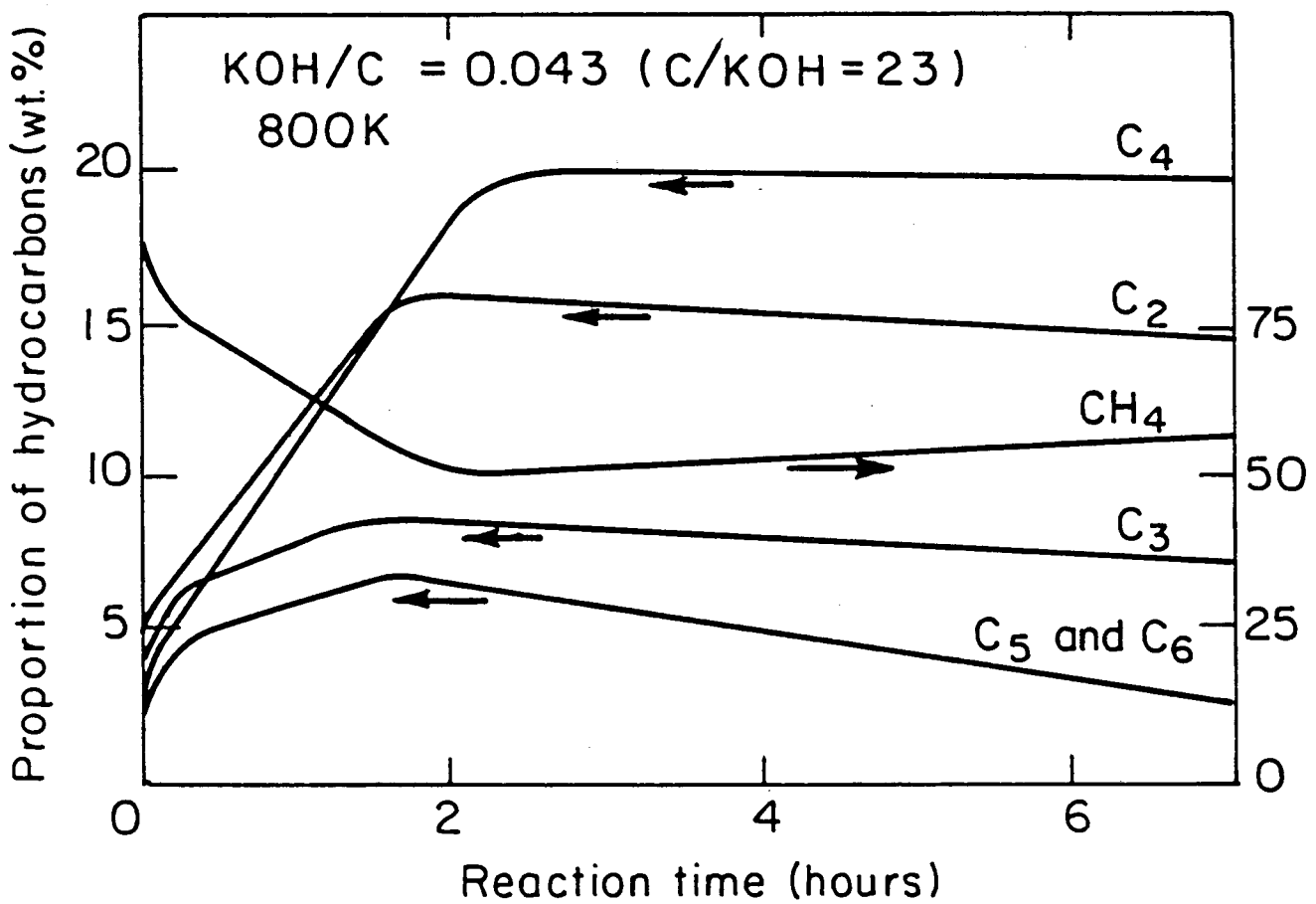
-- XBL 833-8664 A --

Fig. 3



XBL 833-8663A

Fig. 4



XBL833-8659B

Fig. 5

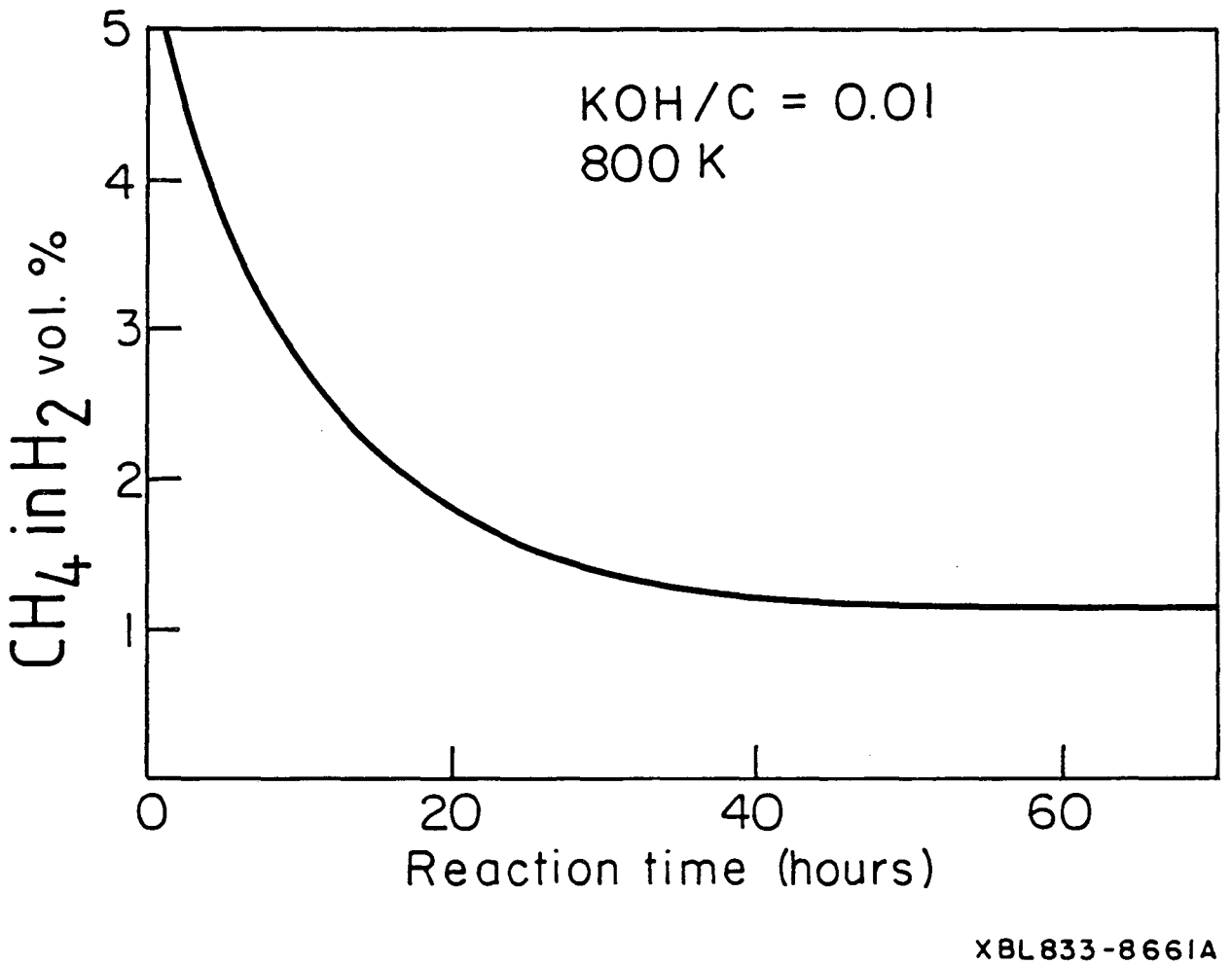
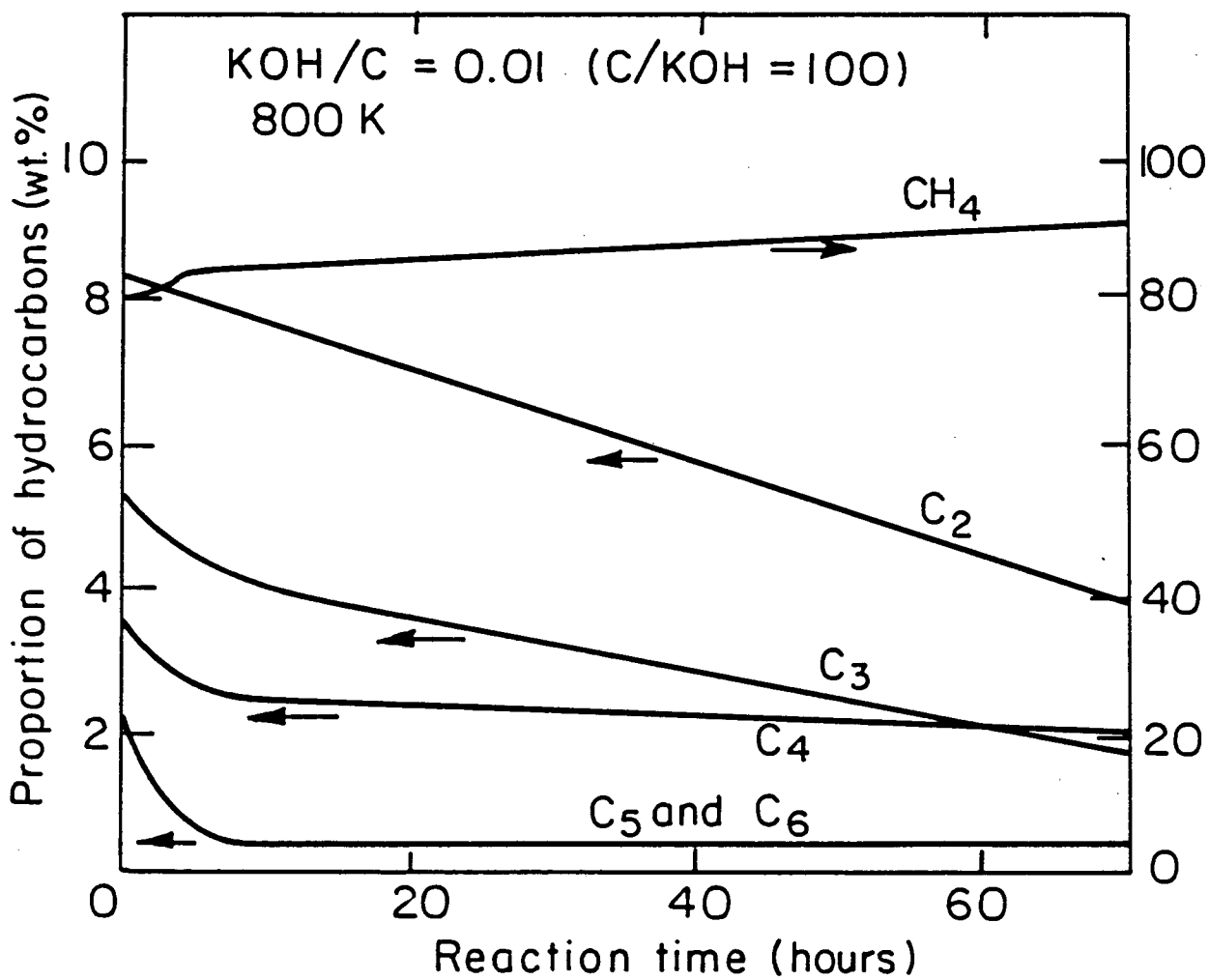

KOH/C = 0.01
800 K
CH_4 in H_2 vol. %
5
4
3
2
1
0
20
40
60
Reaction time (hours)
XBL833-8661A

Fig. 6



XBL833-8660B

Fig. 7

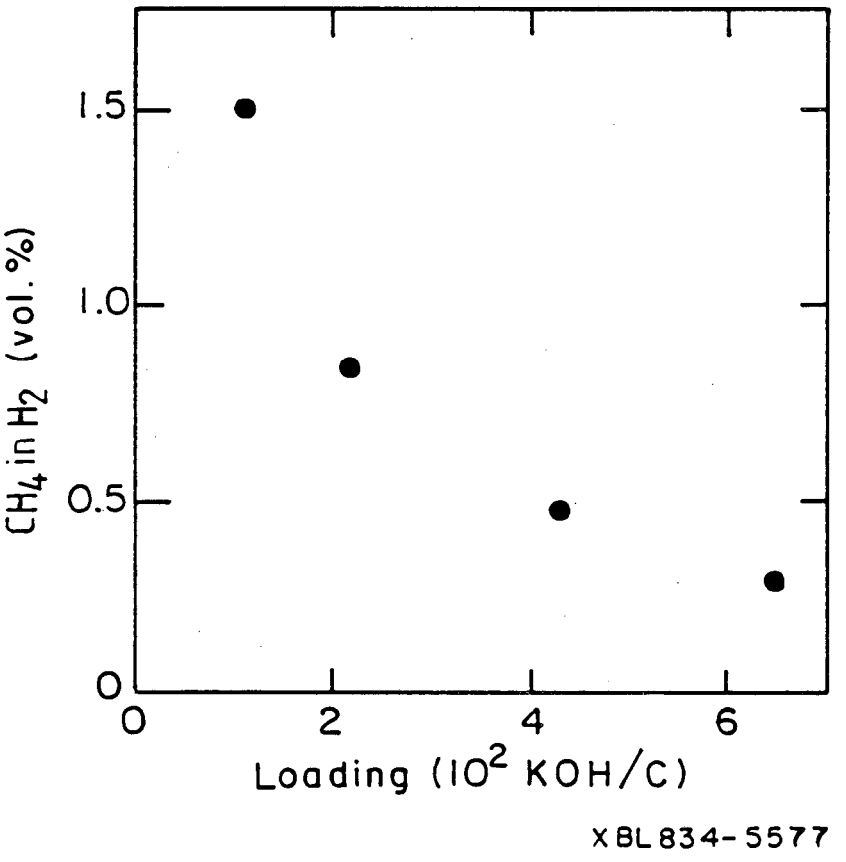


Fig. 8

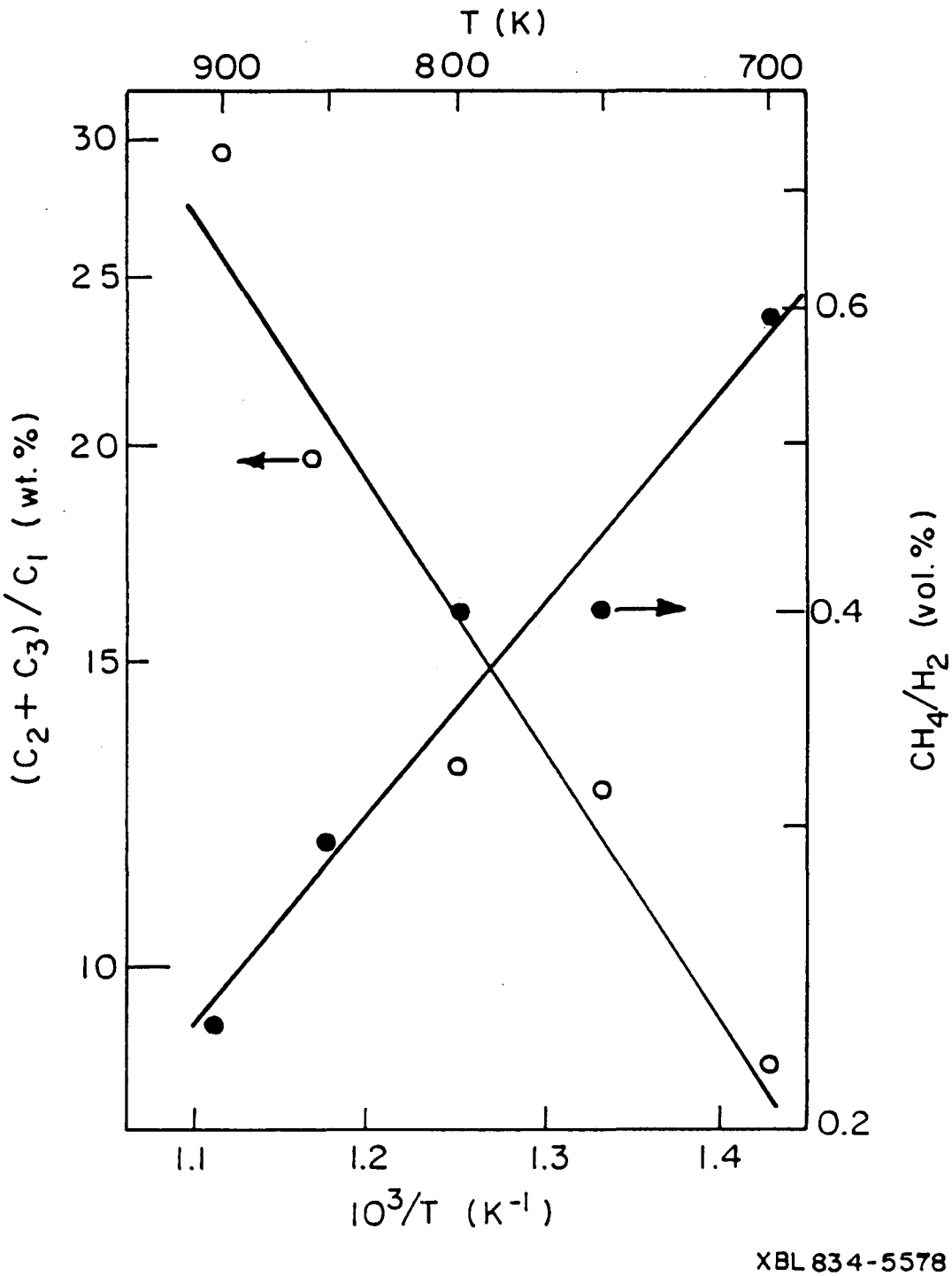
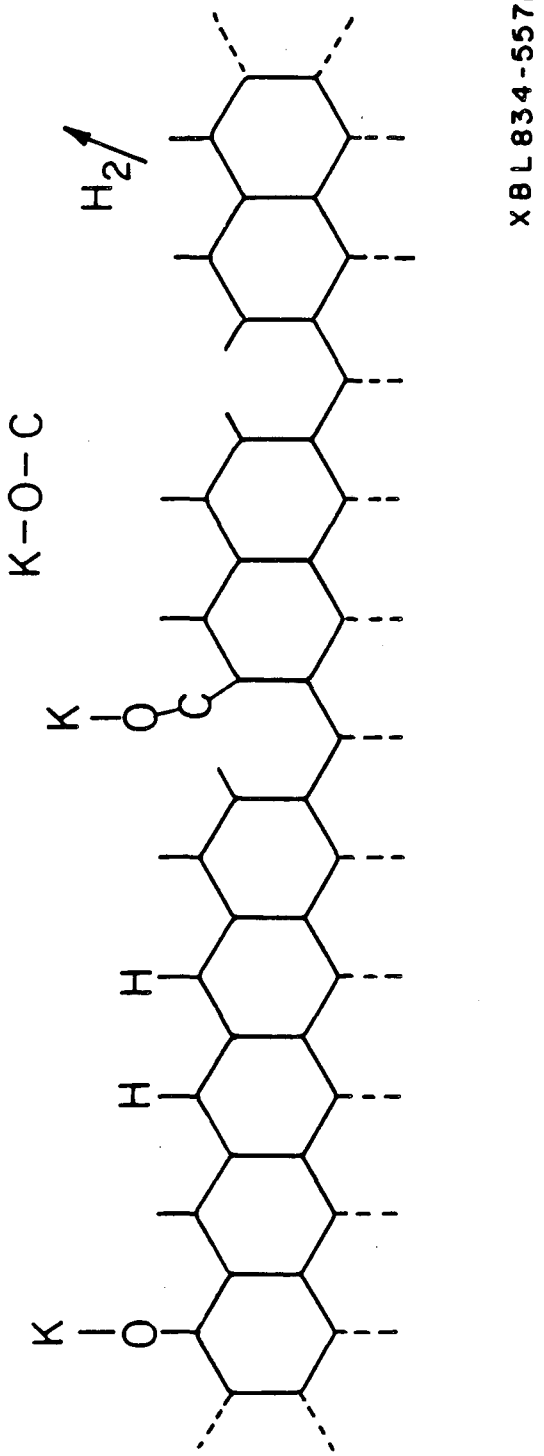

T (K)
900
800
700
30
25
20
15
10
0.6
0.4
0.2
1.1
1.2
1.3
1.4
$(C_2 + C_3)/C_1$ (wt. %)
CH_4/H_2 (vol. %)
$10^3/T$ (K^{-1})
XBL 834-5578

Fig. 9



XBL834-5571

Fig. 10

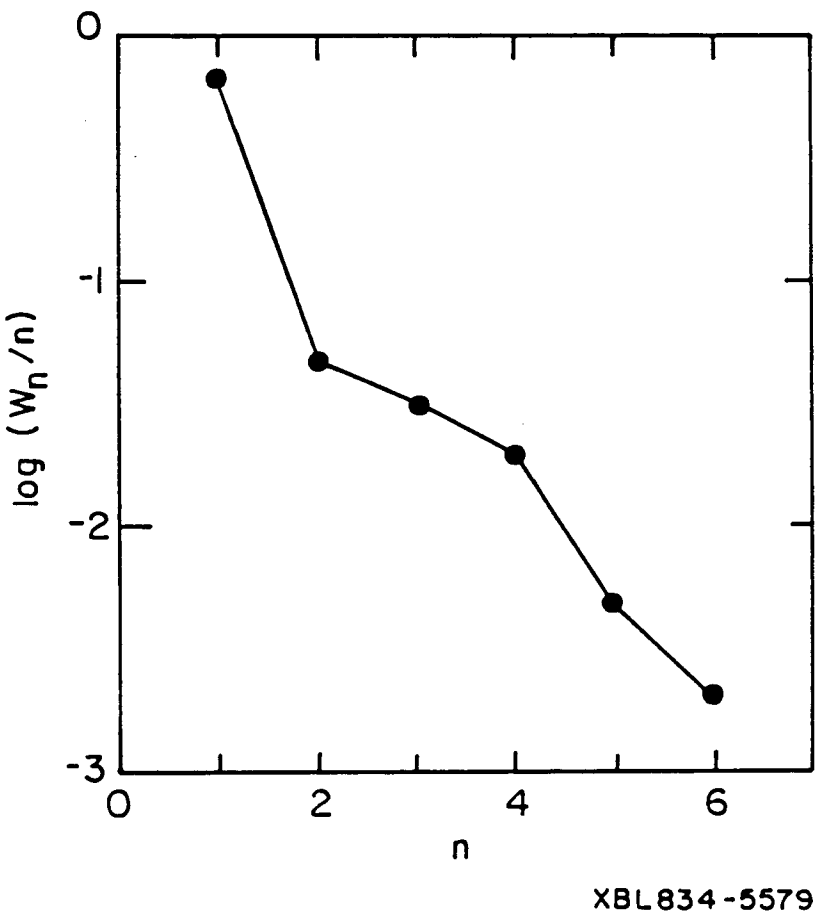


Fig. 11

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720