DOE/PC/93213--T12

Technical Progress Report
"Rate Inhibition of Steam Gasification by Adsorbed Hydrogen"
DOE Grant #DE-FG22-93PC93213
Reporting Period 7/1/96 - 9/30/96

Dennis J. Miller, Principal Investigator

"US-DOE Patent clearance is not required
prior to the publication of this document"

Introduction

In this twelvth quarter of the grant period, experiments have focused on the effects of char oxidation on gasification rate in steam/hydrogen mixtures. Experiments have been conducted primarily on annealed Saran char at temperatures of 1000 K and 1120 K, and the quantity of hydrogen adsorbed on the char surface both prior to and following oxidation has been measured.

Stability of Adsorbed Oxygen Groups on Char Surface

Before examining potential gasification rate enhancement via oxidation, we have examined the concentration and stability of char surface oxides following oxidation and gasification. The CO and CO_2 desorption profiles (Exp. 9624) for annealed Saran char following gasification in 3.1 MPa H_2 and then 1.7 hr in 10% O_2 in Ar at 475°C are given in Figure 1. The hydrogen desorption profile is given as the lower curve in Figure 2 along with those for chars oxidized at less extreme conditions. It is clear from the quantities of CO + CO_2 and H_2 present following reaction with and without oxidation that surface oxides are displacing hydrogen groups on the char surface. The sum of the quantities of the three gases present following oxidation is about 28 cm^3/g, close to the quantity of hydrogen present (31 cm^3/g) following gasification in H_2 only (Fig. 2, top curve).

We have also measured the quantity of surface oxides present following gasification in steam/hydrogen mixtures. When hydrogen was present in the reactant gas during gasification at 1120 K, only very small quantities of CO (<1.0 cm^3/g) and no CO_2 were observed in TPD following reaction. When reactant gas contained only steam/argon, slightly greater quantities of CO (up to 1.8 cm^3/g) and again no CO_2 were observed in TPD. For all reactant gases, the CO desorption peak was symmetric with a peak maximum at 1200 K. The CO desorbed represents "stable" surface oxides on the char at gasification conditions [21,22] as opposed to the unstable or reactive oxides that lead to CO formation in gasification.

We also conducted several gasification experiments at 1000 K and again monitored CO and CO_2 desorbing during TPD. Again, when hydrogen was present in the reactant gas, less than 1.0 cm^3 CO/g and no CO_2 was observed during TPD. Following gasification in steam/argon only, in contrast, 5.2 cm^3 CO/g was observed to desorb during TPD. The shape and location of the CO TPD peak following gasification at 1000 K was the same as following gasification at 1120 K, signifying that the nature of the surface oxides on the char are the same at the two temperatures. The high desorption temperature of the oxides following gasification in steam at 1000 K suggests

DISCLAIMER

that the oxides are present at their maximum surface concentration at these conditions. Adsorbed hydrogen concentrations following gasification at 1000 K were the same, within experimental uncertainty, as those following gasification at 1120 K.

In summary, surface oxide groups are present in low concentrations in steam and steam/hydrogen gasification and hydrogen predominates on the surface. Upon oxidation, surface oxides remove adsorbed hydrogen and the concentration of surface oxygen can approach that of adsorbed hydrogen. These results lead us to attempt rate enhancement via oxidation to remove adsorbed hydrogen.

Rate Enhancement via Oxidation

The effect of oxidation by molecular oxygen on hydrogasification rate of annealed Saran char is given in Figure 3. It is clearly seen that rate is enhanced approximately three-fold upon oxidation, but that the enhancement is apparently not propagated (the rate declines over the course of conversion between 400 and 500 minutes of gasification time). This is in accordance with our work published some time ago on enhancement of coal char and Saran char gasification rates.

We postulate that the rate enhancement is a result of surface oxides making the surface more reactive for hydrogasification, not as one would expect, via removal of strongly-bound hydrogen. We are currently pursuing this further and will report at a later date.

The effect of oxidation on steam gasification rate is given in Figure 4. Again, some enhancement of rate is observed, but the enhancement is transient and results mainly from greatly enhanced CO_2 production upon reintroduction of steam to the gasification chamber. It is likely that a large quantity of surface carboxylates and lactones, groups that desorb as CO_2, are produced during oxidation. Thus, the rate enhancement is not really of intrinsic steam gasification but is only caused by desorption of excess oxides formed during oxidation.

Summary

We have now completed essentially all aspects of the grant program, and will work for the remainder of the grant period to analyze the experimental data and prepare manuscripts for publication. The work we have conducted over the three-years of the grant has provided significant new insight into the role of hydrogen inhibition in gasification and has been well-received at technical meetings. While it appears that the extent of rate enhancement via molecular oxidation is not significant, that is now an expected results based on the mechanism for rate inhibition that we have developed. We will discuss this mechanism in the next progress report. We hope to publish two papers resulting from this work in early 1997.

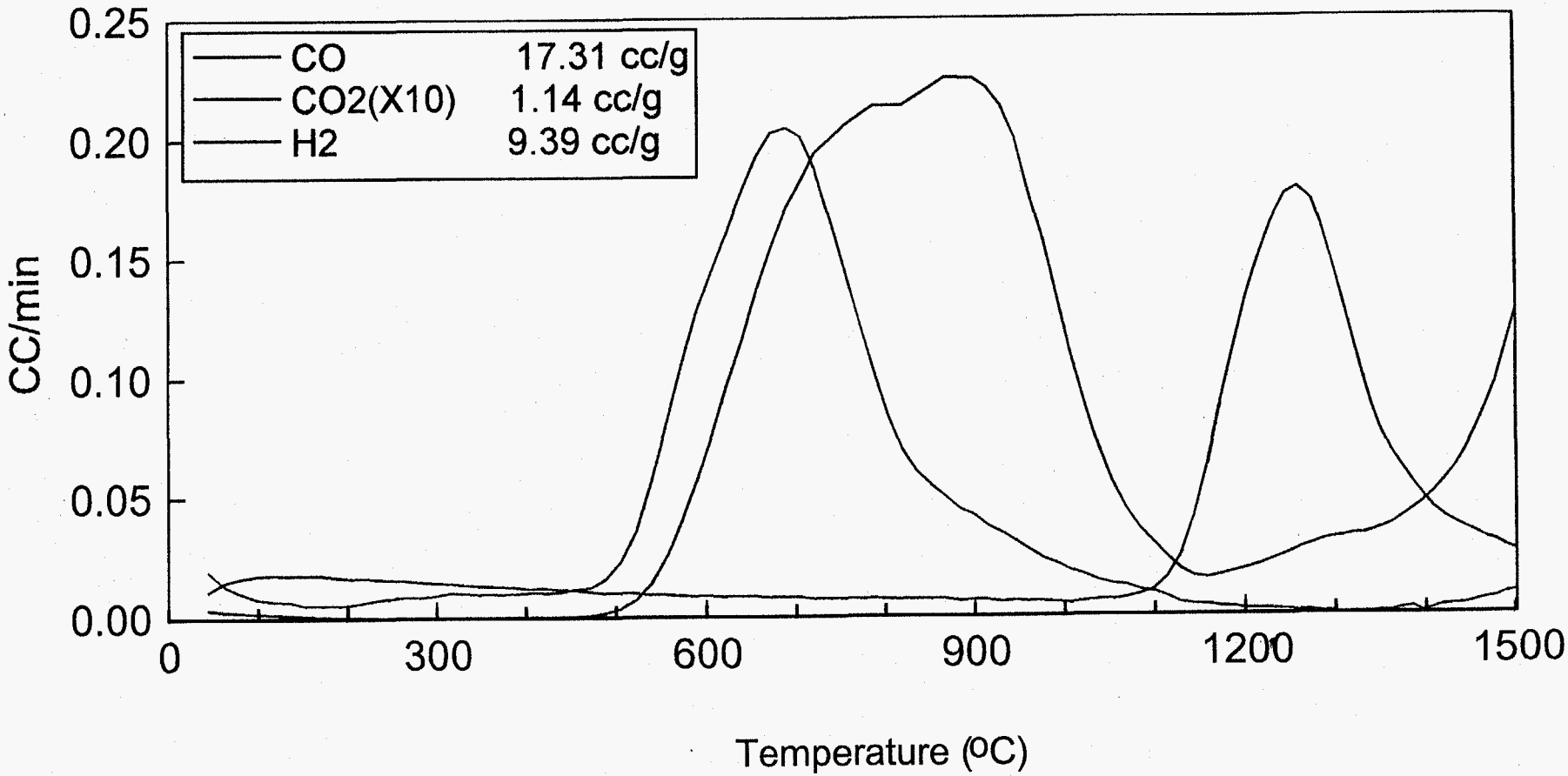

Figure 1. H_2, CO and CO_2 desorption profiles from annealed Saran char following gasification in H_2 for 4 hr at 850 °C and then oxidation in 10% O_2 in Ar at 475 °C for 1.7 hr.

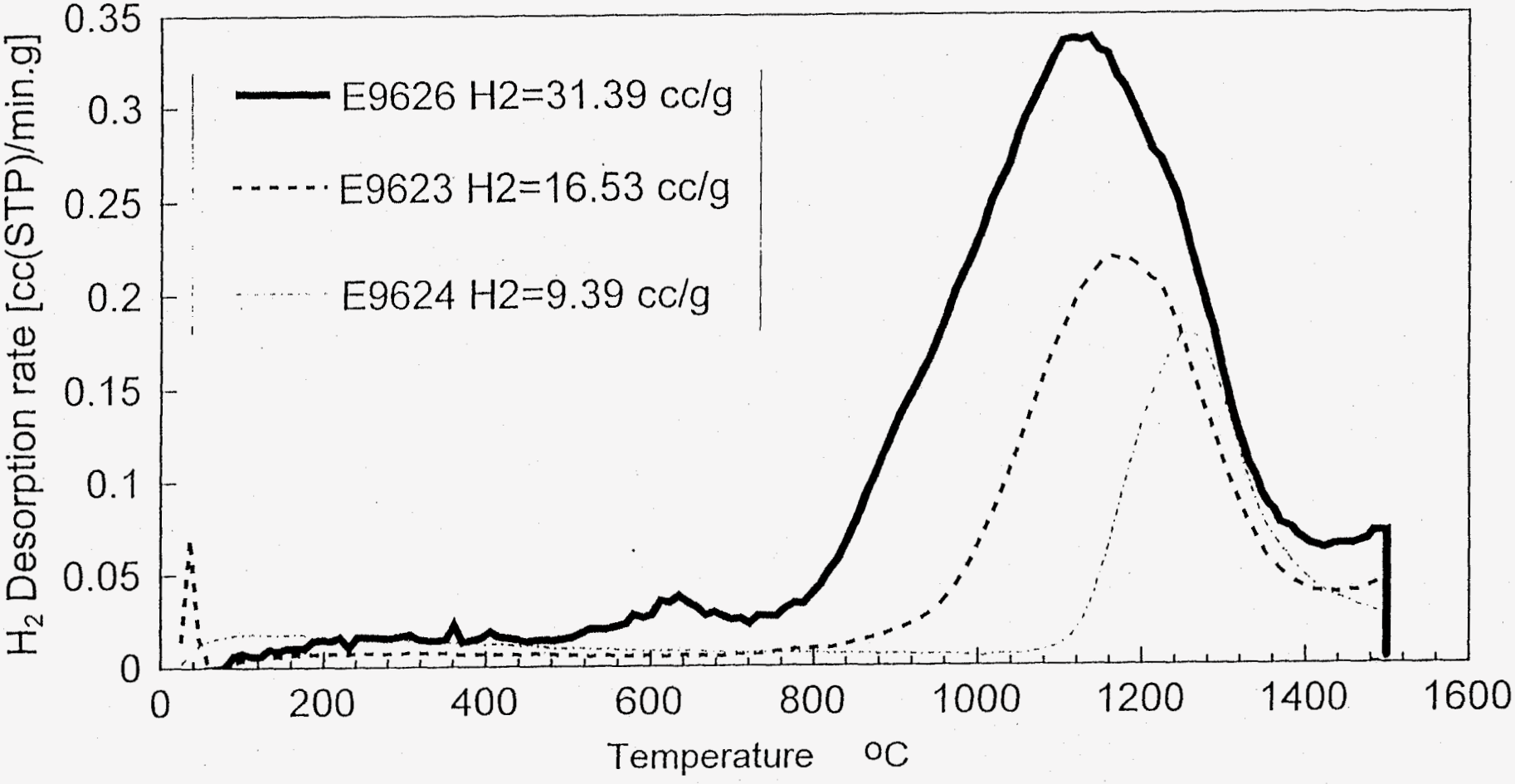

Figure 2: Temperature programmed desorption of H2 following gasification and oxidation

E9626 Gasification in 3.0 MPa H2 at 850 °C for 4 hr.

E9623 Gasification in 3.0 MPa H2 at 850 °C for 4 hr followed by oxidation in 5% O 2 in Argon,455 °C for 2.5 hr.

E9624 Gasification in 3.0 MPa H2 at 850 °C for 4 hr followed by oxidation in 10 % O 2 in Argon, 475 °C for 1.7 hr.

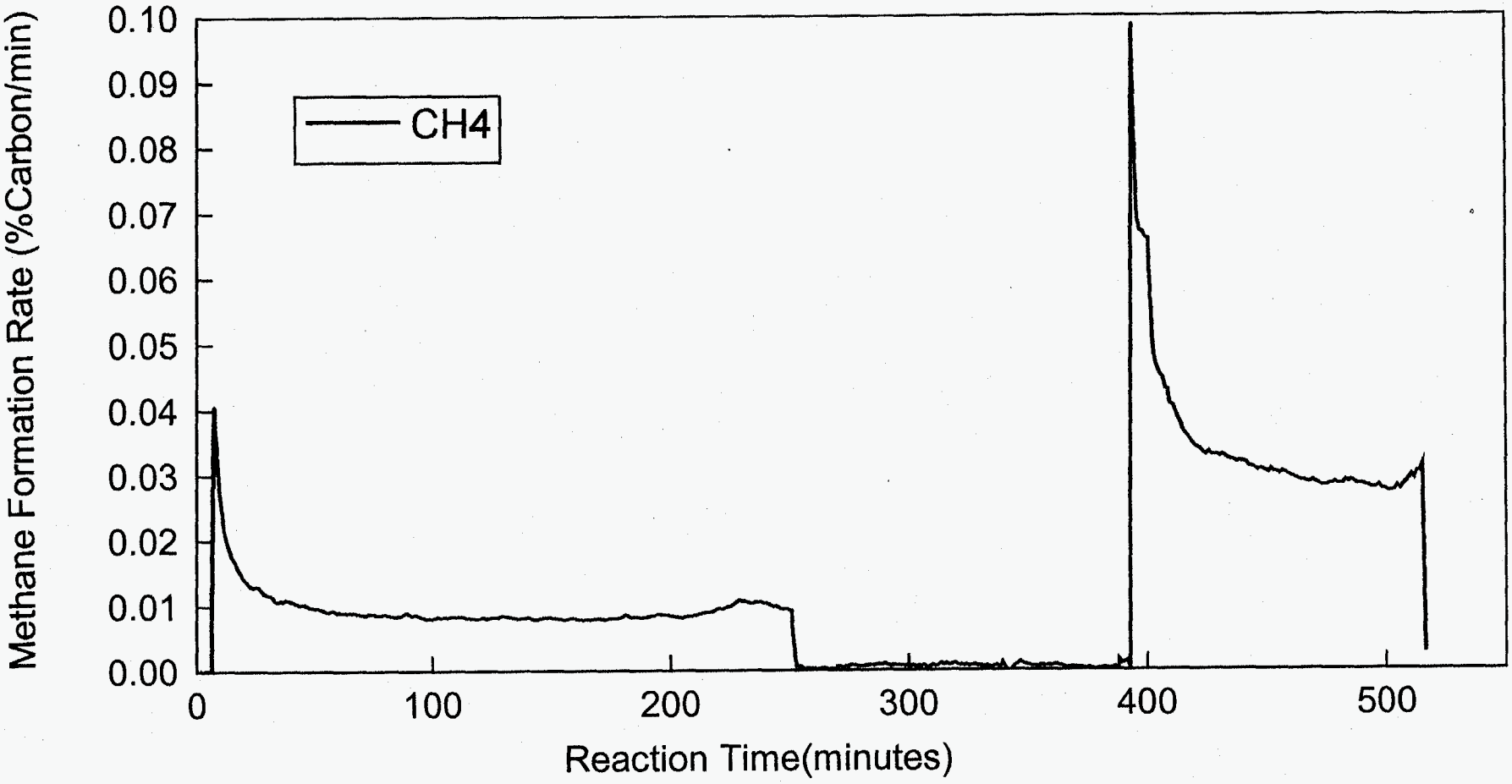

Figure 3. Rate enhancement of hydrogengasification rate (850 °C, 3.1 MPa) of annealed Saran Char by oxidation in molecular oxygen (120 min in 10% O_2 in Ar at 450 °C)

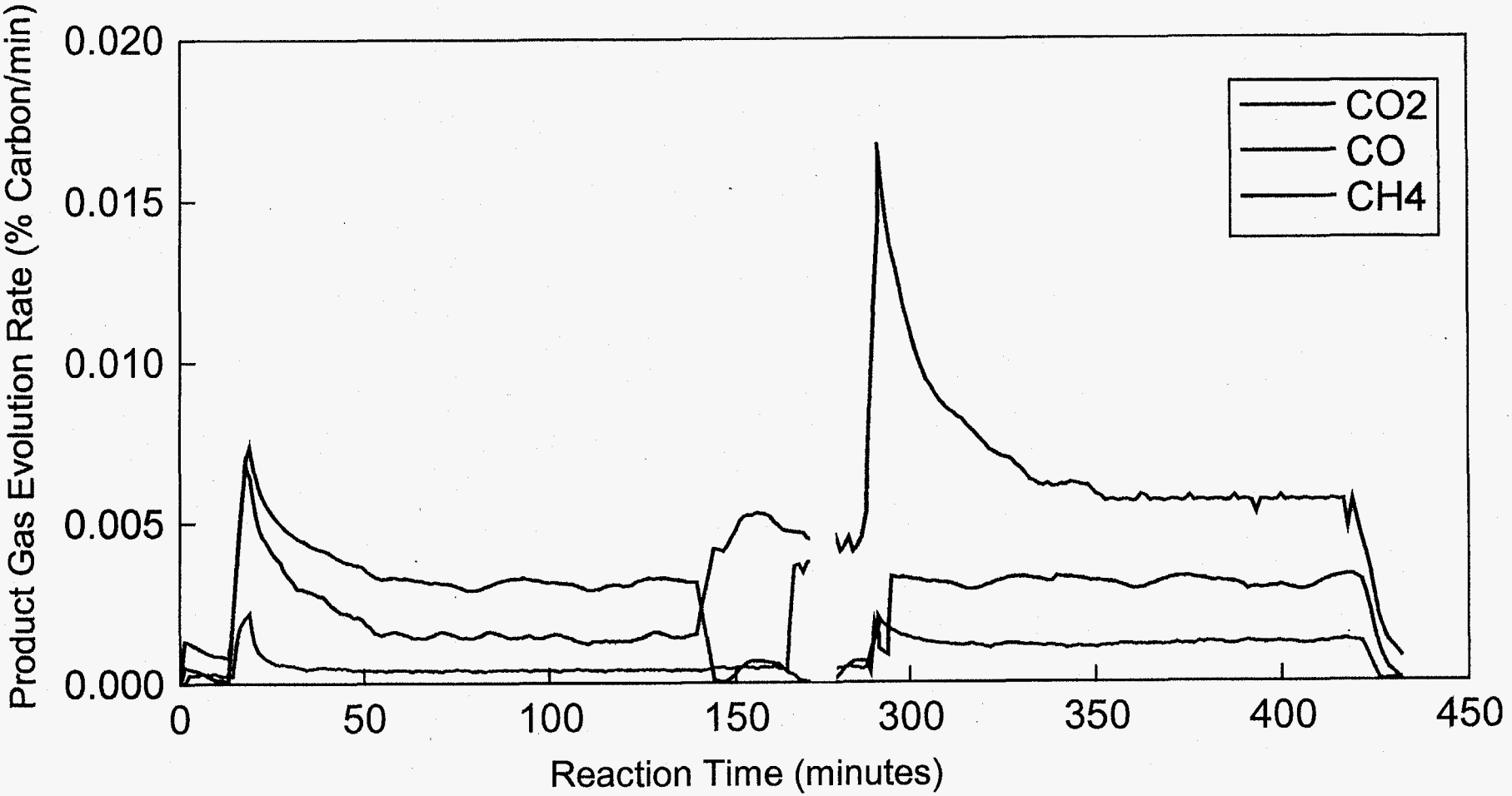

Figure 4. Rate enhancement of steam gasification rate (725 °C, 3.1MPa) of annealed Saran char by oxidation in molecular oxygen (120 min in 10% O_2 in Ar at 450 °C)