

# Effect of Reactant Penetration on Inhibition of Coal Char Gasification

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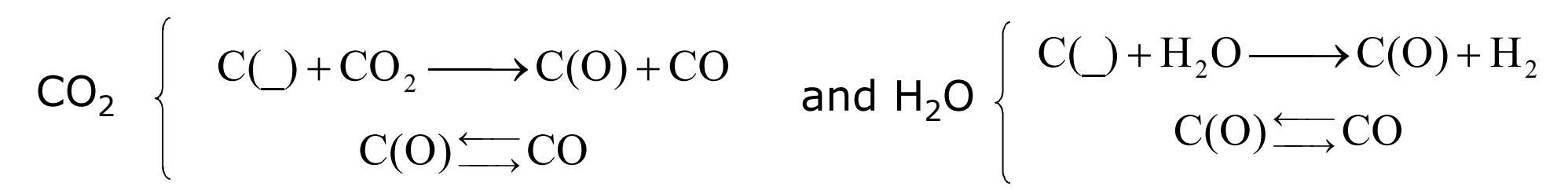
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## Introduction

- H<sub>2</sub> and CO are products and inhibitors of the gasification of char by:



- The mechanism of inhibition has been constantly studied leading to Langmuir-Hinshelwood expressions to represent the kinetics of the gasification reaction

- Recent computational tools allow a more detailed analysis of the system that considers penetration of reactants inside the particle as well as distribution of surface site complexes

- The poster describes a modeling exercise that (1) identifies conditions in which the current reactivity data is not adequate to predict the char gasification reaction and (2) proposes experimental measurements aimed to correct this lack of available information

## Inhibition by H<sub>2</sub>

Three mechanisms have been proposed:

- Dissociative hydrogen adsorption:*  $\text{C}(\_) + \frac{1}{2} \text{H}_2 \rightleftharpoons \text{C}(\text{H})$
- Reverse oxygen exchange:*  $\text{C}(\text{O}) + \text{H}_2 \rightleftharpoons \text{C}(\_) + \text{H}_2\text{O}$
- Associative hydrogen adsorption:*  $\text{C}(\_) + \text{H}_2 \rightleftharpoons \text{C}(\text{H}_2)$

- It is believed that mechanism (1) is responsible for saturating surface sites with hydrogen at temperatures below 1600 K
- Once the char surface reaches steady state, mechanism (2) has the highest contribution to inhibition

## Inhibition by CO

Inhibition by CO occurs by the reverse reaction for CO

desorption:  $\text{C}(\text{O}) \rightleftharpoons \text{CO}$

This reaction has been widely studied since it is part of the char/O<sub>2</sub> reaction

Montoya et al. (2004) report a kinetic expression for the desorption of C(O) sites found by ab initio calculations

## Modeling

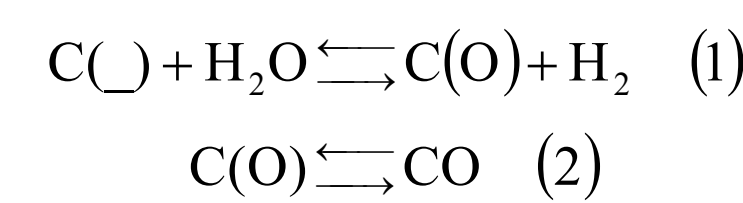
- Modeling was performed with the University of Sydney's Skippy (Surface Kinetics in Porous Particles) computer program

- Skippy calculates steady-state species and temperature profiles for the reaction of a porous solid in a reacting gaseous environment and predicts species concentrations and temperature within the char pores, at the outer char surface, and within the boundary layer surrounding the particle

- For homogeneous mechanism, GRI-3.0 MECH was used. However, the effect of the homogenous mechanism was found negligible in the temperature range studied and most simulations were performed without homogeneous chemistry to increase speed

## Heterogeneous mechanism

- The heterogeneous mechanism considered a reversible step of H<sub>2</sub>O/char reaction and the desorption of CO<sub>2</sub>:



- Char gasification by CO<sub>2</sub> was not considered in this first approximation

- H<sub>2</sub> inhibition was assumed as occurring by oxygen reverse exchange. Although dissociative hydrogen adsorption should be important under the conditions of this study, it was assumed that the effect of a reduction of reactivity because of active site saturation by H<sub>2</sub> could be represented by the reverse reaction (1)

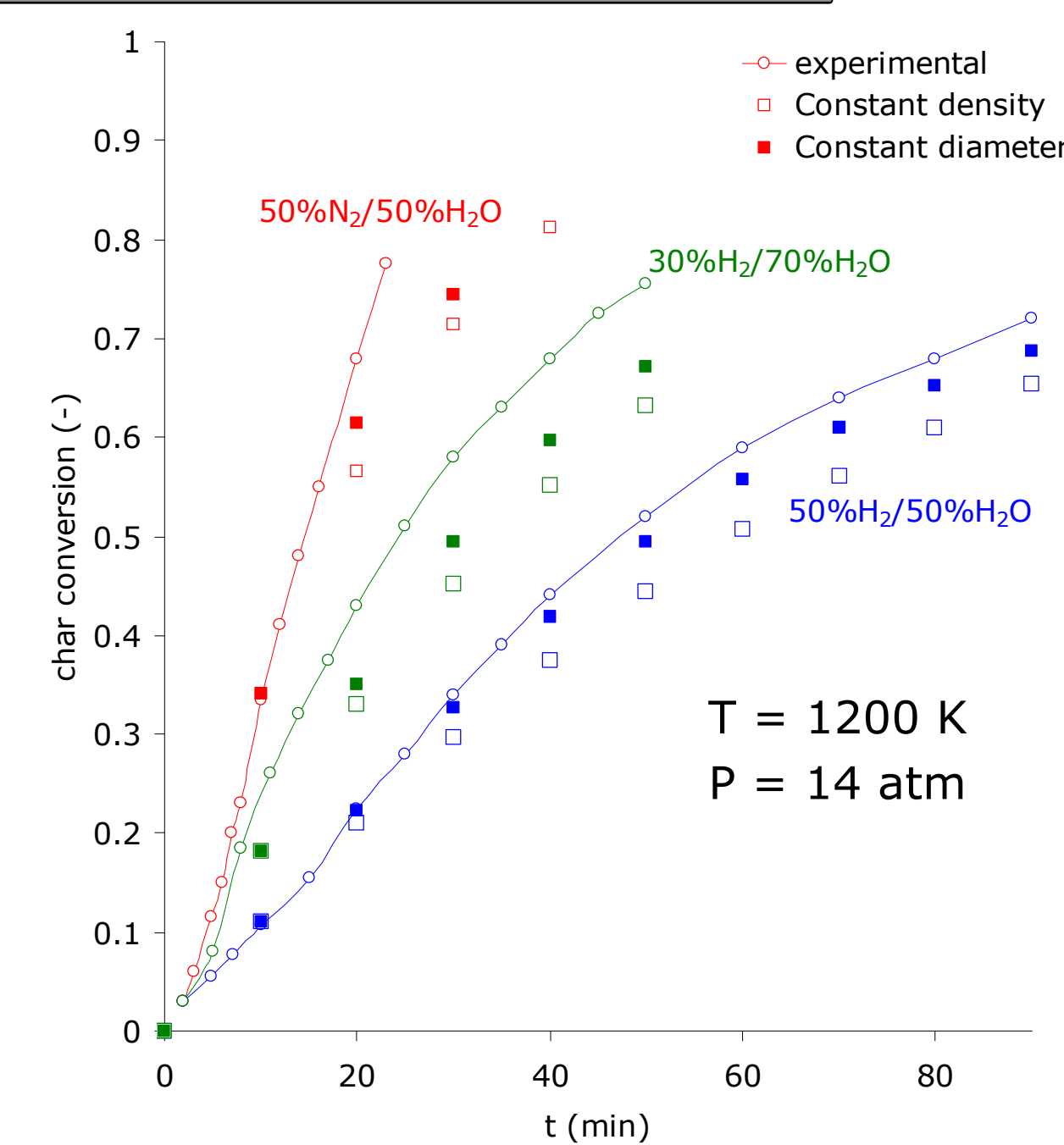
- Original rate expressions were taken from Yang and Yang (1985) and Montoya et al. (2004) for reaction (1) and (2). The model was calibrated according to the experimental data of Goyal et al. (1989)

## Mechanism calibration

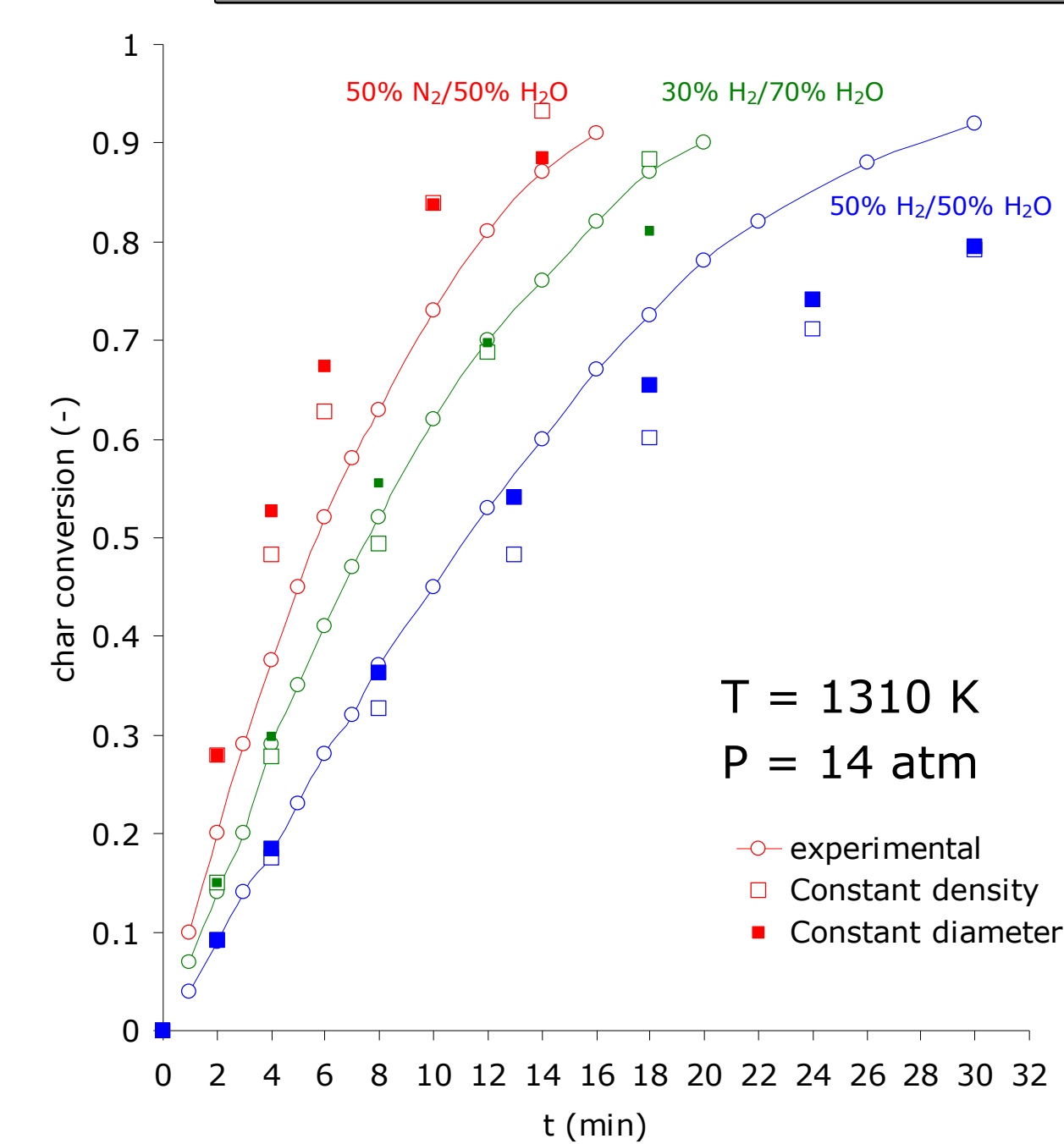
- Experimental results are from Goyal et al. (1989) for char collected from a pilot gasification plant working with Kentucky bituminous coal with a typical size of 0.032 cm

- Simulations performed following constant density and constant diameter cases

- Heterogeneous mechanism was the same in all cases



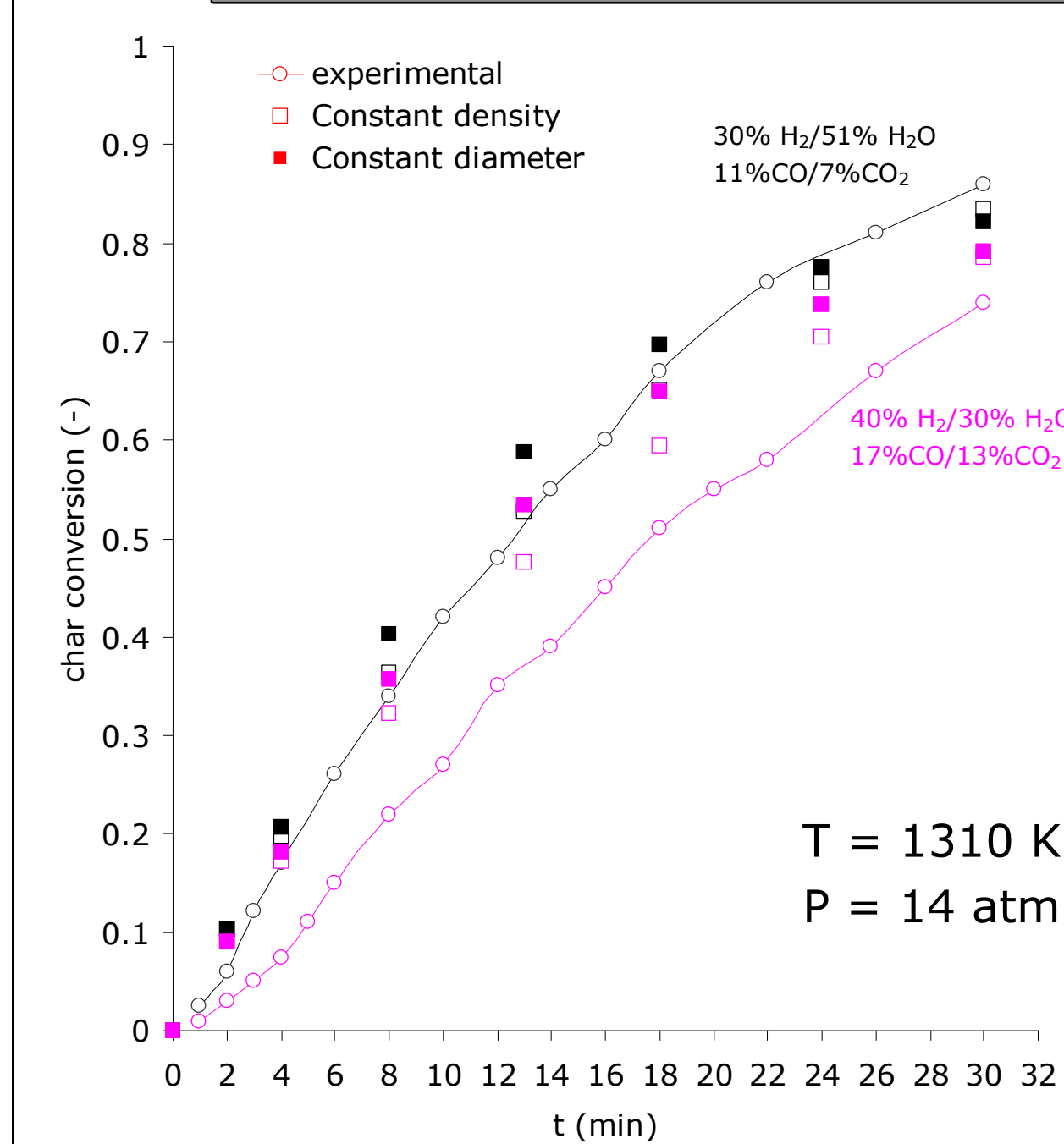
## Mechanism calibration (2)



- Although not perfect, the simulations agree with experimental data collected for the different temperatures and gas compositions

- Major differences between simulations and experimental data observed at high conversion levels

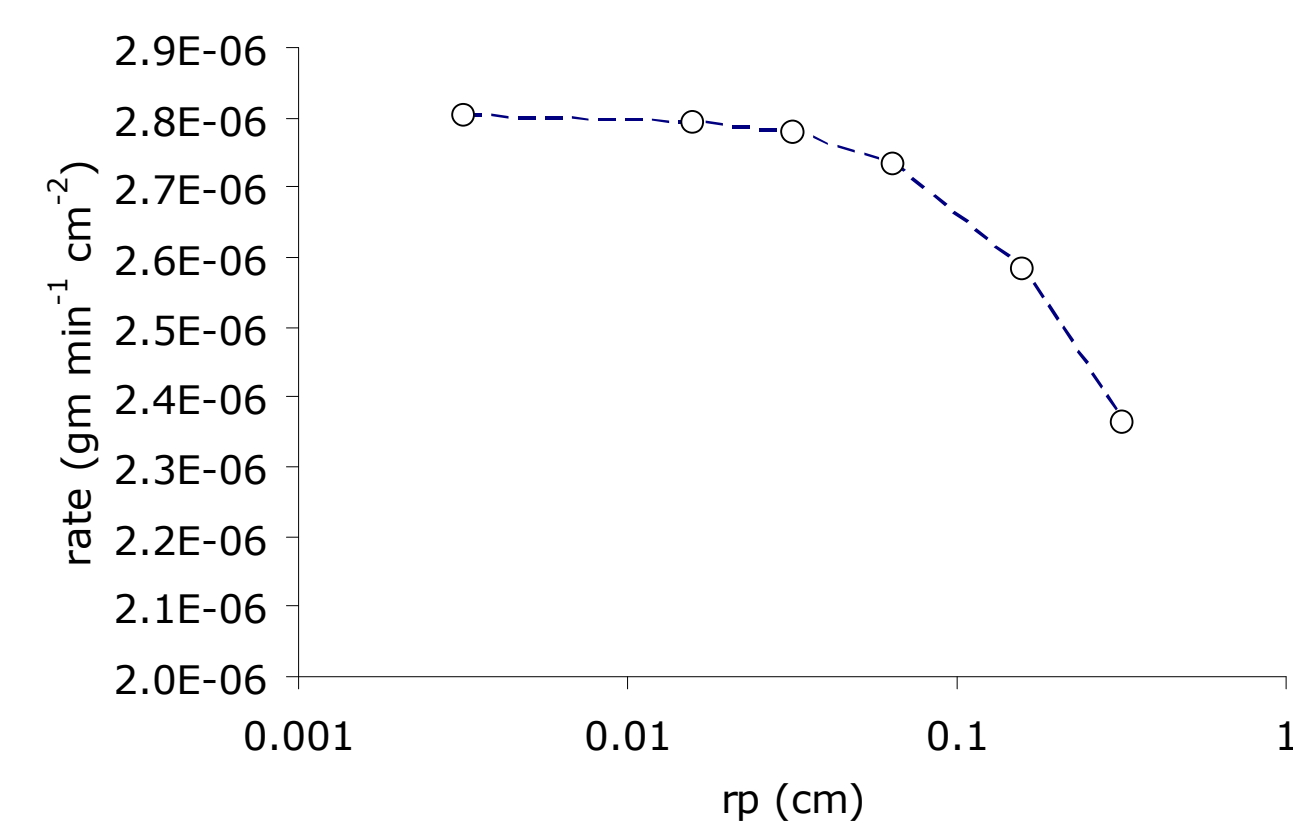
## Mechanism calibration (3)



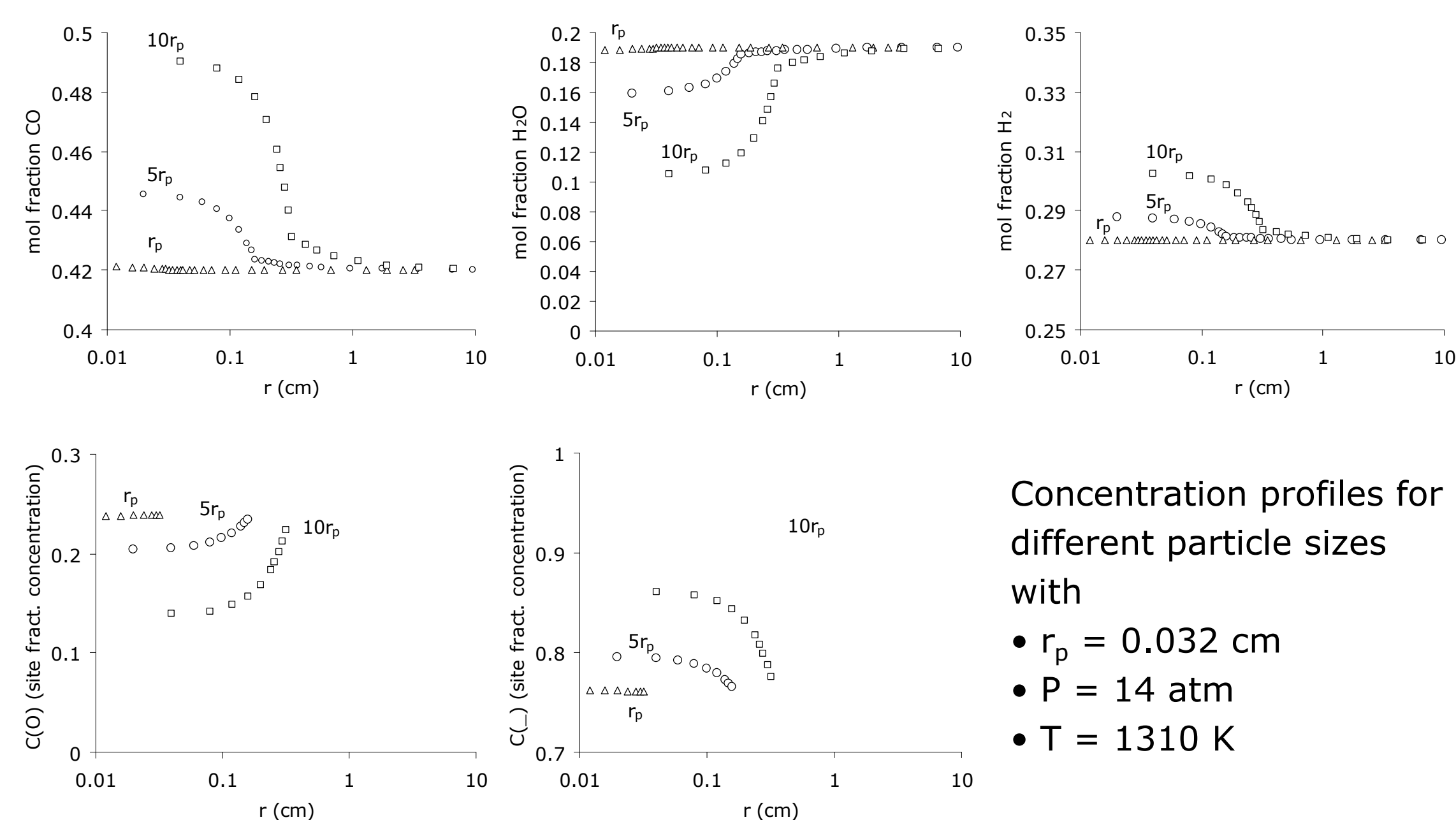
- Agreement between experiments and simulation was slightly better for the constant diameter model than for constant density model

## Effect of particle size on gasification rate

- Validated mechanism used to predict initial gasification rate for a gas with composition 42% CO, 28% H<sub>2</sub>, 19% H<sub>2</sub>O, 9% CO<sub>2</sub> and 2% N<sub>2</sub> (gas synthesis for typical oxy-blown gasification synthesis gas); T= 1310 K, P = 14 atm.
- Results show a decrease in reaction rate as particle size increases



## Concentration profiles (1)



- Concentration profiles for different particle sizes with
- r<sub>p</sub> = 0.032 cm
  - P = 14 atm
  - T = 1310 K

## Concentration profiles (2)

- Variation in concentration profiles with particle size suggest that the predicted reduction in reaction rate as particle size increases is caused by either:
  - Higher concentration of inhibitors (H<sub>2</sub> and CO) inside the particle
  - Lower concentration of reactant (H<sub>2</sub>O)

- Analysis of the concentration of surface sites suggests that for the mechanism used in this simulations, a lower H<sub>2</sub>O concentration has a higher effect on decreasing the gasification than the higher inhibitor concentration.

- For the typical particle size of 0.032 cm, the variation of concentration inside the particle is minimal, suggesting that the reaction occurs mostly through a constant diameter mechanism at the conditions of the simulation

## Conclusions

- The information available in the open literature for the gasification reactions, particularly for the inhibition by CO and H<sub>2</sub>, is scarce and dominated by Langmuir-Hinshelwood expressions that are difficult to translate to detailed heterogeneous systems.
- When the available kinetic expressions are calibrated with existent experimental data, the resulting model captures the trends of reduction in reaction rate by inhibitors.
- Major discrepancies between models and experiments occur at higher char conversion, possibly because of the crude system used to model the changes in physical properties.
- As the particle size increases, the model predicts a reduction in the reaction rate that is caused by a lower concentration of H<sub>2</sub>O inside the particle. This effect is more important than the higher inhibitor concentration inside the reactor.
- Future research on char gasification at high pressure should study the effect of inhibitor penetration inside the particle and determine kinetic expressions suitable for the use in detailed heterogeneous models