

KINETICS OF THE HOMOGENEOUS REVERSE WATER-GAS SHIFT REACTION AT HIGH TEMPERATURE

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ABSTRACT

The high-temperature rate of reaction of the homogeneous, reverse water-gas shift reaction, rWGSR, has been evaluated in quartz reactors with rapid feed pre-heating at low-pressure and high-pressure conditions. The form of the power-law rate expression was consistent with the Bradford mechanism. The Arrhenius expressions for the reaction rate constant corresponding to the empty reactor were in very good agreement with the low-pressure results of Graven and Long, but yielded rate constants roughly four times greater than those obtained in our packed reactor and those reported by Kochubei and Moin and by Tingey. Reactor geometry was not responsible for these differences because CFD simulations revealed similar residence time distributions and comparable conversions when the same kinetic expression was used to model the rWGS reaction in each reactor. The empty NETL reactor and the Graven and Long reactor may not have attained an invariant value of the concentration of the chain carrier (H) at low reaction times, however, which led to an overestimation of the rate constant. Conversions attained in an Inconel® 600 reactor operating at comparable conditions were approximately two orders-of-magnitude greater than those realized in the quartz reactor. This dramatic increase in conversion suggests that the Inconel® 600 surfaces, which were depleted of nickel during the reaction, catalyzed the rWGSR.

INTRODUCTION

The Water-Gas Shift Reaction

The water-gas shift reaction, Equation 1, is important as a method for further enhancing the yield of hydrogen from industrial processes such as the steam reforming of natural gas or the gasification of heavy carbonaceous materials. Syngas mixtures containing mostly hydrogen and carbon monoxide are typically generated at elevated temperatures via the combustion of natural gas, coal, bio-mass, petroleum and organic wastes (Wender, 1996). Steam is then added to the CO – H₂ feed mixture prior to being introduced to water-gas shift, WGS, reactors to convert the CO to CO₂ and additional H₂. However, thermodynamic equilibrium favors high conversion of CO and steam to hydrogen and carbon dioxide at low temperatures. Therefore, the water-gas shift reaction is commonly conducted at low temperature in the presence of catalysts that enhance the reaction rate.



The water-gas shift reaction is reversible, and several correlations for the equilibrium constant have been published (Moe, 1962; Benson, 1981; Babieri and DiMaio, 1997; Singh and Saraf, 1977). A simple temperature-dependent correlation (Moe, 1962) was used to estimate K_{eq} in this study.

$$K_{eq} = \exp \left\{ -4.33 + \frac{4577.8}{T(\text{K})} \right\} \quad (2)$$

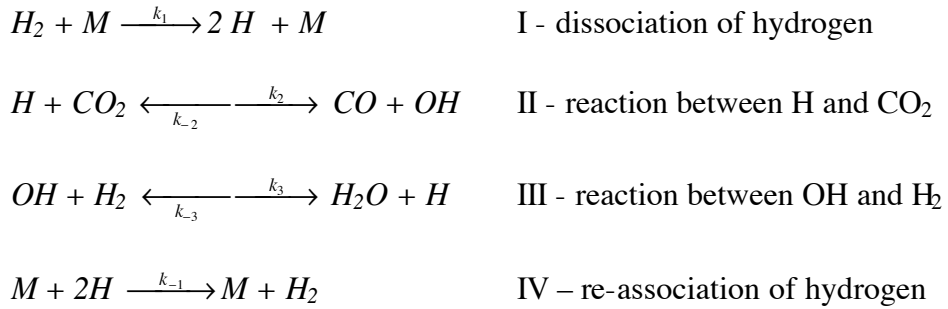
There are numerous kinetic studies of the catalyzed forward water-gas shift reaction at temperatures up to 873 K (Newsome, 1980). Kinetic studies of the forward or reverse water-gas shift reaction at elevated temperatures (>873 K) are uncommon, however. This scarcity of data is probably attributable to the low equilibrium conversions of CO that can be achieved in conventional reactors operating in this temperature range. High conversions at elevated temperature can be achieved in a hydrogen-permeable membrane reactor, however (Enick et al., 2000). Further, extreme temperatures could enhance the kinetics to the extent that the reaction would proceed rapidly in the absence of heterogeneous catalysts. Therefore, an understanding of the forward and reverse reaction rates would be useful in the design of high temperature, hydrogen-permeable membrane reactors. The *reverse* water-gas shift reaction, rWGSR, is the focus of this investigation.

The Reverse Water-Gas Shift Reaction

Several investigations of the high temperature (>1148 K), low pressure (< 0.101 MPa), homogeneous, uncatalyzed rWGSR have been conducted. Power law correlations that comply with the Bradford mechanism (Bradford, 1933), a simple gas-phase chain-reaction model, have been used to model the rate of reaction. Although models based on a more comprehensive network of elementary steps, such as a model for the oxidation of H₂ and CO in sub- and supercritical water (Holgate and Tester, 1994), could be used to describe the reaction, we have found that such a network yields results nearly identical to

the Bradford mechanism. Therefore the Bradford mechanism was considered to be an adequate representation of the rWGSR under the conditions studied.

The Bradford mechanism, provided below, employs M as any gas phase molecule:



It has been shown (Graven and Long, 1954; Tingey, 1966) that under the conditions of low conversions (i.e. negligible effect of the opposing reaction) and the assumption of stationary state for the concentrations of the intermediates (H and OH concentrations do not change significantly with respect to time) leads to the following rate expression, Equation 3,

$$r = \frac{d[CO]}{dt} = \left[\frac{k_1}{k_{-1}} \right]^{0.5} k_2 [H_2]^{0.5} [CO_2] \quad (3)$$

Accordingly, the rate constant for the rWGSR may be expressed as shown in Equation 4.

$$k = \left[\frac{k_1}{k_{-1}} \right]^{0.5} k_2 \quad (4)$$

Therefore, the expression for the rate of reaction in terms of k becomes,

$$r = \frac{d[CO]}{dt} = k[H_2]^{0.5}[CO_2] \quad (5)$$

The temperature-dependence of the rate constant, k , is described by the Arrhenius equation

$$k = k_0 e^{-E_a/RT} \quad (6)$$

Most prior investigations of the homogeneous rWGSR at elevated temperature have employed power law models that are consistent with Equations 5 and 6. The activation energy and pre-exponential constant associated with each of these studies are summarized in Table 1. Graven and Long (1954) studied the rWGSR in the temperature range 1148-1323 K. CO₂ and H₂ were introduced to the reactor along with the N₂ diluent gas to control partial pressures. Their cylindrical quartz reactor (3.4 cm diameter, 6.4 cm length) featured tangential feed and withdrawal lines (1.5 mm ID). They reported that the reaction occurred rapidly in the gas phase without any heterogeneous contribution from the quartz surfaces. Tingey's reactor (Tingey, 1966) consisted of a cylindrical quartz tube (3.3 cm ID, 27.1 cm length) that contained a co-axial quartz insert (2.2 cm ID, 21.0 cm length), resulting in a long annular flow section that was preceded and followed by short cylindrical sections (3.3 cm ID, 6.1 cm combined length). Coaxial capillary tubing served

as feed and effluent channels for the reactor. Kochubei and Moin (1969) designed empty quartz reactors (ID ranging from 0.6 – 6.5 cm) that employed a static mixer to mix the pre-heated hydrogen and carbon dioxide. The effluent gases were withdrawn from a capillary tube (1.5 mm ID) extending in the same axial direction as the cylinder, but located along the outside edge of the reactor. Tingey (1966) and Kochubei and Moin (1969) published results that were in very good agreement, with both obtaining lower values for the rate of reaction than Graven and Long (1954). Tingey suggested that the higher reaction rate reported by Graven and Long (1954) may have been caused by traces of oxygen in their feed stream that acted as a homogeneous catalyst, but was unable to substantiate this claim.

The values of the rate constant, k , for the low-pressure rWGSR are presented as a function of inverse absolute temperature over the 1123 – 1223 K in Figure 1. The pre-exponential constant and activation energy of each correlation is listed in Table 1. The prediction of Karim and Mohindra (1974) model of the water-gas shift reaction as twelve, simple, reversible, intermediate reaction steps involving nine species at temperatures up to 2500 K which used kinetic data available at the time is also presented. Given the disagreement among these reported values, our first objective was to investigate the rWGSR kinetics at low-pressure conditions in quartz reactors. The rWGSR kinetics were then determined in a pressure-equilibrated quartz reactor that enabled the reaction to be conducted at elevated pressures similar to those attained in a gasifier. Finally, the rWGSR was conducted in an Inconel® 600 vessel at low- and high-pressure conditions in order to assess the catalytic influence of the metal reactor wall on the reaction rate. The reactors were designed to be analogous to the industrial application: rapid heating of a hydrogen

and carbon dioxide gas mixture followed by introduction to the quartz or Inconel reactor. In all cases, only the reacting gases, CO₂ and H₂, were introduced to the reactor. Gas phase partial pressures were adjusted by varying both total pressure and feed composition.

EXPERIMENTAL

rWGSR Apparatus

The Hydrogen Membrane Test Unit Number 1, HMT-1, at the US DOE National Energy Technology Laboratory, NETL, was designed to attain high-pressure (up to 3.0 MPa), high-temperature (up to 1198 K) conditions in Inconel® 600 or Quartz reactors, Figure 2. The reaction pressure was controlled with a stainless steel Badger Research pressure control valve (PCV) employing a control loop with a pressure indicator (PI). The reaction temperature was controlled with a ceramic heater using a control loop with a coaxially mounted type-K thermocouple (TI), which was placed approximately 3 mm from the reactor. An Iconic Genesis process control program provided the process control for the unit. It was not possible to place a thermocouple inside the reactor to monitor the outlet temperature due to the catalytic effect of the metal. The existence of a temperature profile, however, was verified with hydrogen or carbon dioxide flowing through the system. Under typical low-pressure experimental conditions, the temperature within the reaction zone was varied by 15 K along its length, and the average temperature was used in the evaluation of the data.

Reactor Feed

The flow rates of the feed gases, H₂ and CO₂ (99.999%) were controlled with Brooks mass flow controllers (FCVs) and verified with a soapfilm flow meter. Kinetic studies were conducted using either an equimolar feed mixture introduced to the reactor over a range of flow rates or for feed mixtures in which the concentration of one reactant was held constant while the concentration of the other was varied. Partial pressures were established by adjusting feed gas composition and total pressure; no inert diluent gases were employed. An oxygen trap was located before the reactor to eliminate the pronounced catalytic influence of O₂ on the reaction. Concentrations of oxygen in the feed remained below the gas chromatograph detection limit of 1 ppm.

The reactants were premixed and then fed to the quartz reactor through quartz tubing and a narrow annulus with a volume of 0.2 cm³, approximately one tenth that of the reaction zone volume. The gases were rapidly heated from 873 K to the reaction temperature as they passed through the annulus (annular gap = 0.13 mm). Control experiments indicated that no conversion of the CO₂ in the quartz reactor was detectable for reaction temperatures below 873 K.

Reaction Zone A pressure-equilibrated quartz reactor or Inconel® 600 reactor was accommodated in the HMT-1 unit. The geometry of these reactors is illustrated in Figure 3, and the dimensions of the reaction zone are provided in Table 2. When the quartz reactor was operated at elevated pressure, an overburden fluid, CO₂, was maintained at the same pressure as the reacting gases within the reactor to prevent stresses across the

reactor walls. The pre-heated feed gases entered the reaction zone and flowed upward toward the top of the narrow inner tube that led to the reaction zone exit. Residence times of 0.3 - 0.5 s were chosen for the reactions conducted in the quartz reactor at low pressure. This yielded conversions of 0.1 - 0.8 %, which were great enough to assure accurate measurements of conversion. Residence times of 2-10 s were realized at high-pressure conditions because of the increased gas density. Comparable residence times were selected when the Inconel® 600 reactor was used.

The reacting gases then flowed downward through the inner tube and exited the reaction zone. The reaction products were rapidly cooled to 873 K as they flowed toward the reactor effluent line. The temperature of the tubing was maintained at 573 - 673 K, which was hot enough to prevent condensation of water produced by the rWGSR but cold enough to prevent further conversion of the reactants.

Effluent Gas Stream The effluent of the reactor was analyzed with a gas chromatograph equipped with a TCD detector. Argon was used as carrier gas. The GC column, HayeSep® D (porous polymer), allowed the quantification of H₂, CO, CO₂ and H₂O in the range of concentrations of interest. Concentrations of oxygen in the product remained below the detection limit of 1 ppm. Reaction rates were evaluated from the CO₂ conversion, CO₂ concentration and residence time. Once the CO₂ and H₂ concentration exponents of the rate expression were elucidated, the rate constant was calculated from the rate value by using the integrated form of a PFR reactor design equation (Fogler, 1999).

Computational Fluid Dynamics Numerical Simulations

The steady-state flow of the gases through the empty quartz reactor used in this study was modeled using Computational Fluid Dynamics (CFD). Similar computations were also performed for the reactors described by Graven and Long (1954), Tingey (1966), and Kochubei and Moin (1969). The objective of these computations was to determine whether the reactor geometry could have influenced the kinetic results. Mixing within the reactor was assessed using residence time distribution plots that were determined by simulating the effluent concentration of a gas (hydrogen) that was pulsed into the feed stream (nitrogen). Additionally, the rWGSR was modeled in each reactor under the same conditions of temperature, pressure, residence time, and rate constant expression to elucidate the effect of the non-ideal flow on the kinetic results.

Flow Field The geometries were generated and meshed by using Gambit2.0 software (Fluent). Axisymmetric two dimension geometries that incorporated a mesh of quads were used for the NETL quartz reactor and the Tingey (1966) reactor. Three-dimensional geometries that incorporated a mesh of hexahedral/tetrahedral hybrid grids were used for the Graven and Long (1954) reactor and the Kochubei and Moin (1969) reactor. Finer grids were applied at the reactor inlet, reactor outlet and near the reactor walls in all cases.

The governing equations that were solved in order to describe the flow of gas through the isothermal reactors consisted of the continuity equation and the Navier-Stokes equations. The continuity equation can be expressed in the following form:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (7)$$

where ρ is the density, t is time, and \vec{v} is the velocity vector. The conservation of momentum equation is described as:

$$\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \nabla \cdot (\bar{\tau}) \quad (8)$$

where p is the pressure and $\bar{\tau}$ is the stress tensor given by

$$\bar{\tau} = \left[(\nabla \vec{v} + \nabla \vec{v}^T) - \frac{2}{3} \nabla \cdot \vec{v} I \right] \quad (9)$$

where μ is the molecular viscosity, I is the unit tensor, the superscript T means transposed matrix, and the second term on the right hand side is the effect of volume dilation. Because the flow is laminar in the reactors, no turbulence model has been included.

For steady-state calculations, the time derivative terms vanished. The governing equations were discretized by using a control-volume technique in which the algebraic equations were integrated on each control volume, yielding discrete equations that conserved each quantity on a control-volume basis. Second order upwind schemes were used for spacial discretizations. The solutions were converged quickly and the residuals were kept under 1.0E-06.

Simulation of a Tracer Input This simulation is an unsteady-state calculation, therefore time derivative terms were included. A first order implicit method was applied to discretize the governing equations. In this simulation, the species transport scalar equations were solved in order to trace the evolution of the species. The species transport scalar equation can be written in the following form:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \quad (10)$$

where Y_i is the local mass fraction of species i , \vec{J}_i is the diffusion flux of species i , R_i is the net rate of production of species i by chemical reaction, and S_i is the rate of reaction by addition from the dispersed phase plus any user-defined source.

The diffusion flux of species i was formulated as:

$$\vec{J}_i = \rho D_{i,m} \nabla Y_i \quad (11)$$

where $D_{i,m}$ is the diffusion coefficient for species i .

The two components used in the tracer simulation were non-reactive, therefore the last two terms in the species transport equation, Equation 10, were neglected. The flow rate at the inlet of the reactor was calculated corresponding to a residence time of 0.5 s. The inlet conditions were specified as to simulate a pulse of hydrogen into a stream of nitrogen flowing to the reactor:

$t \leq 0$ s and $t > 0.01$ s, only N_2 flows into the reactor.

$0 < t \leq 0.01$ s, a pulse of dilute H_2 (mole fraction = 0.01) is introduced.

Simulation of the conversions inside the reactor When reactions are involved, the net source of chemical species i due to reaction R_i in the species transport scalar equation can be computed as the sum of the reaction source over the N_R reactions that the species participate in:

$$R_i = M_{w,i} \sum_{r=1}^{N_R} \hat{R}_{i,r} \quad (12)$$

where $M_{w,i}$ is the molecular weight of species i , N_R is the number of the reactions, and

$\hat{R}_{i,r}$ is the molar rate of creation/destruction of species i in reaction.

The molar rate of creation/destruction of species i in reaction r is given by

$$\hat{R}_{i,r} = (v_{i,r}'' - v_{i,r}') (k_{f,r} \prod_{j=1}^{N_r} [C_{j,r}]^{\eta_{j,r}'} - k_{b,r} \prod_{j=1}^{N_r} [C_{j,r}]^{\eta_{j,r}''}) \quad (13)$$

where

$v_{i,r}'$ = stoichiometric coefficient for reactant i in reaction r

$v_{i,r}''$ = stoichiometric coefficient for product i in reaction r

N_r = number of chemical species in reaction r

$C_{j,r}$ = molar concentration of reactant and product species j in reaction r (kgmol/m³)

$\eta_{j,r}'$ = forward rate exponent for each reactant and product species j in reaction r

$\eta_{j,r}''$ = backward rate exponent for each reactant and product species j in reaction r

For the low conversions observed in our study, the rate of reaction can be expressed as Equation 5. The parameters for the rate constant, Equation 6, were evaluated by determining the temperature dependence of Equation 4 using values available from the up-dated and comprehensive kinetic GRI database (GRI) for each of the elementary reaction. The resultant parameters were $k_0 = 3.52\text{E}+11 \text{ (m}^3/\text{mol)}^{0.5} \text{ s}^{-1}$ and $E_a = 3.27294\text{E}+05 \text{ (J/mol)}$. The residence time was set at 0.5 second for a stoichiometric feed of hydrogen and carbon dioxide.

RESULTS AND DISCUSSION

Low-pressure rWGS in a quartz reactor

Equimolar feeds of CO₂ and H₂ were introduced at a total pressure of 0.101 MPa to the empty NETL quartz reactor that is illustrated in Figure 3. The power law exponents of the H₂ and CO₂ were assumed to be 0.5 and 1.0, respectively. The Arrhenius representation of the reaction rate data for this low-pressure rWGS over the 1148 – 1198 K temperature range is found in Figure 4. Table 1 provides the corresponding activation energy and pre-exponential constant.

The NETL rWGS reaction rate constant was approximately **25% greater** than that reported by Graven and Long (1954) as illustrated in Figure 4. The activation energy of 46.1 ± 0.8 kcal/mol [196.6 ± 3.3 kJ/mol] was slightly less than the value of 56 kcal/mol [234.3 kJ/mol] reported by Graven and Long. The measured reaction rate constant values were roughly **four** times greater than those reported by Tingey (1966) and Kochubei and Moin(1969), however, as shown in Figures 1 and 4 and Table 1. Therefore our low-pressure results for the empty reactor exhibited closest agreement with the results of Graven and Long (1954).

High-pressure rWGS in a quartz reactor

Equimolar feeds of CO₂ and H₂ were introduced at a total pressure of 1.6 MPa to the NETL empty quartz reactor. A separate stream of an overburden fluid, CO₂, was also maintained at 1.6 MPa in the space between the outer surface of the quartz reactor and the inner wall of the Inconel® 600 pressure vessel. The power law exponents of the H₂ and CO₂ were determined to 0.5 and 1.0, respectively (see Figure 5 and 6). The results are summarized in Figure 4 and Table 1. The activation energy of 45.3 ± 1.1 kcal/mol

[217.6 ± 4.6 kJ/mol] was slightly smaller than the low-pressure result of 46.1 ± 0.8 kcal/mol [196.6 kJ/mol], and the reaction rate constant slightly less than that reported by Graven and Long. Therefore, our high-pressure results for the empty reactor were also in good agreement with the Graven and Long (1954) finding.

Effect of reactor geometry on quartz reactor results

An attempt was made to determine the cause of the differences between the low-pressure rate constant correlations illustrated in Figures 1 and 4. Tingey (1966) suggested the relatively high reaction rate constant values reported by Graven and Long (1954) may have been caused by oxygen in their feed stream, but our rate constants derived from the empty quartz reactor were comparable to those of Graven and Long and no detectable amounts of O₂ were found in the CO₂ or H₂ feed streams or the pre-mixed feed stream. Therefore CFD calculations were performed to determine if the reactor geometry could have influenced the kinetic results. Comparisons of the flow patterns of a non-reacting gas, the residence time distributions of a non-reacting mixture, and the conversion of the rWGSR under identical conditions were made for the NETL empty quartz reactor and the Graven and Long (1954), Kochubei and Moin (1969), and Tingey (1966) reactors.

Flow Patterns and Residence Time Distributions In each representation of the flow patterns within the reactor, Figures 7 – 10, the length of the vector is proportional to the velocity of the particle at the origin of the vector. The direction of the vector indicates the direction in which the fluid located at the origin of the vector is moving. In some cases, as noted in the figure legends, portions of the reactor in which the fluid is moving at

extremely high velocity are represented by a white field (rather than a group of extremely long vectors) to avoid cluttering the figure.

The NETL Quartz Reactor was characterized by upward flow through the large annular gap within the reaction zone, followed by a flow reversal at the top of the reactor. The gas then flowed vertically downward through the inner tube. There is a very small stagnant zone above the exiting port. This is manifested in the tailing of the Residence Time Distribution, RTD, plot, Figure 11, which exhibits a distribution broader than the expected for a laminar flow reactor with axial dispersion (Fogler, 1999).

The tangential feed and withdrawal of the Graven and Long reactor induced circular flow that formed vortices within the reactor, as shown by the velocity vectors along the edge of the two xy planes in Figure 8. The performance of this reactor is very similar to an ideal CSTR, as the RTD shows (Figure 12).

The Tingey reactor also had very high sweep efficiency, Figure 9. Small recirculation zones formed at the entrance of the annular section of the reactor, but the majority of the reactor volume was retained in this annular section, where the reactor performed like a tubular laminar flow reactor. The flow of gases out of the annulus and toward the product port had small stagnant zones along the surfaces and no re-circulation zones. The RTD plot, Figure 11, is representative of a laminar flow reactor with dispersion, being very close to the ideal PFR behavior.

The flow field of the Kochubei and Moin reactor, Figure 10, was similar to a laminar flow reactor. It exhibited high sweep efficiency and had no significant recirculation or stagnant zones, Figure 10. However, the broader RTD and its displacement towards lower times (Figure 11), confirms the channeling observed in the flow field at the bottom part of the reactor (Figure 10). There is a small effect of the stagnant zone as well, observed in the tailing of the RTD. It was assumed that the static mixer on the left-hand side of the reaction zone mixed the CO₂ and H₂ feed streams perfectly and instantly as they entered the reactor zone.

Despite the almost ideal behavior observed in the reactors used by Graven and Long (1954) and Tingey (1966), there was a four-fold difference in the reaction rate constants reported for these investigators, suggesting that the discrepancy was not related to the geometry of the reactor.

Conversions of the rWGS The influence of reactor geometry on the kinetics results was also determined by modeling the rWGS reaction in each reactor. The rate of reaction was determined from Equation 5. The rate constant was obtained from Equation 4 using the values reported in the GRI database (GRI). The reaction conditions were 900C, 1 atm, equimolar feed of CO₂ and H₂ and a residence time of 0.5 seconds. The results, shown in Table 3, indicate that the outlet concentrations were within 7% of one another, confirming that the reactor geometry was not responsible for the differences observed in the reported reaction rate expressions.

Effect of pressure on the quartz reactor results

Because all prior studies had been confined to ambient pressure conditions and there was a slight difference between the NETL low-pressure and high-pressure results, the effect of elevated pressure conditions employed in this study on the reaction kinetics was considered. The low-pressure experimental results of Tingey (1966) and Kochubei and Moin (1969) are in excellent agreement with the value obtained from the Bradford mechanism by using the values for the rate constant of the elementary steps reported in the GRI database (GRI) in Equation 4: k_1 , k_{-1} and k_2 , the rate constants of the initiation (I) step, termination (IV) step, and forward reaction of step II, respectively. Although Reaction II is known to display pressure-dependence (Bierman et al, 1978; Fulle et al, 1996; Troe, 1998), with the rate constant being proportional to the total pressure, the pressure dependence is very weak (less than 10%) under the temperature range of interest of this study. Therefore, the very small difference between our low-pressure and high-pressure results was probably due to experimental uncertainties rather than changes in the reaction mechanism. Further, the difference of the NETL results and the Kochubei and Moin (1969) and Tingey (1967) results cannot be attributed to the pressure difference.

Effect of H and OH Not Being at Stationary State Conditions within the Reactor

The concentration of H and OH radicals within the reactor may not have been invariant, as was assumed in the derivation of the expression for the overall rate constant, Equation 4. This effect was addressed to some extent in the prior investigations of the low-pressure rWGSR. Graven and Long (1954) noted an induction period for the rWGSR, a common feature in chain-reaction chemistry. Kochubei and Moin (1969) kept

the H₂ stream at the reaction temperature for a time long enough (15 - 1000 s) to achieve a stationary state concentration of H (i.e., the equilibrium concentration from the H₂ dissociation (steps I and IV)) before mixing it with CO₂ at the reactor inlet. Tingey (1966) stated that the geometry of the reactor was changed to minimize the observed induction period, which was attributed to heating and cooling times, as well as the time to achieve invariant concentrations of H and OH radicals within the reactor.

The possibility of changing concentrations of [H] and [OH] under our experimental conditions of rapid feed heating and mixing at the reactor entrance was studied using ChemKin®. The NETL empty quartz reactor, Figure 7, was modeled with a tubular laminar flow reactor of comparable dimensions (1 cm diameter, 1.6 cm long). The residence time of the simulations was maintained at values similar to the observed in the experiments by adjusting the volumetric flowrate. The elementary steps of the Bradford gas-phase mechanism were used as the input for ChemKin® and rate constant values were taken from the GRI database. Figure 13 shows the molar fraction of H as a function of the distance along the reactor. These simulation results indicate that NETL results may have been influenced by the non-stationary state concentration of H, which would vary significantly along the first fourth (0 - 0.4 cm) of the NETL reactor (1.6 cm total length). In the temperature range corresponding to our experiments, 1148 - 1198 K, the steady-state concentration of H was attained only at the latter section of the reactor, confirming that the initial transient period of [H] and [OH] values must be accounted for in determining the actual rate parameters of the reaction.

The Bradford mechanism was solved numerically to determine whether this induction period might have a significant effect on the overall reaction at low conversions. Stiff integrators (ODE23s from MatLab®) were used to solve the concentration-time profiles for each one of the six species involved in the reaction mechanism. This simulation describes the reaction as it would take place in an ideal isobaric and isothermal (i.e. constant density) batch reactor. Values of the individual rate constants were taken from the GRI database. Figure 14 shows the concentration profile of H as a function of reaction time at 1250 K and 16 atm, confirming the results from the ChemKin® simulation. The simulation was run until a H₂ conversion of 10% was obtained, which was low enough to minimize the effect of the opposite reaction. There was a continuous increase in [H] until the stationary state value was achieved at time greater than 0.5 s (conversion at t = 0.5 s is 1.86 %), suggesting that the period during which [H] changes plays a significant role in the gas-phase kinetics, especially for low reaction times/conversions.

The reaction rate expression derived from the Bradford mechanism is:

$$r = \frac{d[CO]}{dt} = k_2[CO_2][H] - k_{-2}[CO][OH] \quad (14)$$

Equation 14 reduces to Equation 3 under steady-state concentrations of H and OH. The second term on the right hand side can be neglected for the early stages of the reaction because the concentration of [CO] is close to zero, k_2 and k_{-2} are of the same order of

magnitude, and [OH] is several orders of magnitude smaller than [H]. The reaction rate can therefore be simplified to the expression below, Equation 15.

$$r = \frac{d[CO]}{dt} = k_2[CO_2][H] \quad (15)$$

From Equation 15 and Figure 14, it can be concluded that as the reaction commences, the rate of reaction *increases* (rather than decreases) with residence time because the increase in [H] is more significant than the decrease in [CO₂]. Once an invariant concentration of [H] is attained, however, the rate of reaction decreases with residence time as CO₂ is depleted.

If the reaction rate data is collected during this initial period and analyzed using Equation 5, (the rate expression obtained under the assumption of stationary [H]) the rate constant will be given by Equation 16 (obtaining from combining Equations 5 and 15). This rate constant will be an *apparent* rate constant rather than the *effective* rate constant of the rWGSR (Equation 5).

$$k = k_2 \frac{[H]}{[H_2]^{1/2}} \quad (16)$$

The effect of the changing concentrations of H and OH on the magnitude of the reaction rate constant was determined for conditions of 1250 K and 1 atm **to provide an indication of the significance of this non stationary state conditions on the interpretation of the results.** The reaction rate constant was determined using (a) Equation 16 and [H]

and $[H_2]$ values from the simulation during the initial non-stationary period (e.g., $t < 0.5$ s in Figure 14) (b) results directly from the simulation of the Bradford mechanism where the simulation is allowed to run long enough for both the non-stationary state and stationary state regimes to be manifest, until stationary-state is achieved (the rate constant was determined by linear regression from runs varying the inlet $[H_2]$ and $[CO_2]$), (c) NETL experimental correlation for the rate constant obtained by analyzing our experimental rate data with Equation 5, (d) the GRI data in Equation 4, (e) the correlation of Tingey (1966), and (f) the correlation of Kochubei and Moin (1969). Results are presented in Table 4. The simulation results that account for the changing concentrations of H and OH, entry (b), are of the same order of magnitude that our experimental results, entry (c), suggesting that if $[H]$ varies during an experiment but this change is not accounted for (i.e. equation 5 is used to solve for k), then the k values will overestimate the effective rate constant. This is a likely cause for the discrepancies between the data reported in this study and that of Tingey (1966) and Kochubei and Moin (1969). The presence of the non stationary period where $[H]$ has not yet attained its equilibrium value might also explain the results of Graven and Long whose rate constant values lie between our correlation and the predicted value from the steady-state Bradford expression, Equation 4.

An attempt to further verify that the presence of a non-stationary state regime at the reactor inlet caused an overestimation of the reaction rate constant was then made. It is well known that quartz surfaces act as radical quenchers for reactions involving H radicals. This would cause an increase in the rate of the chain termination, via the

additional wall reaction. Simulations of the intrinsic kinetics (MatLab®) suggested that such an increase would bring the [H] to a stationary state earlier during the reaction. However, the value of the stationary [H] is lower than the predicted from the purely gas-phase reaction. This should render an energy of activation similar to the Bradford value, but with a smaller pre-exponential value. Such a possibility was studied using simulations (ChemKin®) and an experiment with a quartz-packed reactor. The temperatures were chosen in the interval where surface reactions appear to have some effect on the rWGSR, i.e. 1073 - 1123 K (Kochubei and Moin, 1969; Tingey, 1966).

We attempted to tract the radical quenching effect by adding the surface reactions suggested in the work of Aghalayam (Aghalayam et al., 1998). However, the kinetic parameters available, i.e. the sticking coefficient, only provide an upper bound for the effect of radical quenching. Consequently, the simulation predicted a large inhibition in the rate of reaction even at high temperature (>1148 K) where such inhibition has not been observed experimentally (Graven and Long, 1954; Kochubei and Moin, 1969). Therefore, no reliable estimation could be obtained from these calculations.

Figure 15 presents the experimental results from the quartz reactor packed with small cylinders of quartz, Table 2, that increased the reactor surface area by a factor of two. Our correlation was extrapolated to the 1123 - 1223 K temperature range to facilitate the comparison with our previous empty reactor results. CFD simulations of this packed reactor, in which the packing was modeled as porous media, yielded flow patterns nearly identical to those shown in Figure 7. The rate constant for the packed quartz reactor was

similar to the results of Tingey (1966) and Kochubei and Moin (1969), and the corresponding values of the pre-exponential constant and the energy of activation are reported in Table 1. This observation appears to corroborate the hypothesis that the suppression or minimization of the period of the reaction where $[H]$ increases considerably, brought by the radical-quenching effect of the quartz surface at moderate temperature, prevents an over-estimation of the rate constant. However, we could not reconcile the observation of Kochubei and Moin (1969) of small enhancement in the reaction rate brought by the addition of quartz packing. The high inlet $[H]$ in the work of Kochubei and Moin would reduce the impact of the radical quenching, however. Further, the removal of H radicals from the gas-phase could eventually drive the chain initiation step towards the production of H, decreasing the concentration of H_2 .

Low-pressure rWGS in an Inconel reactor.

Rates of reactions in quartz vessels provide an understanding of the intrinsic kinetics of the reverse WGS reaction. Industrial application of this technology will occur in vessels where the reacting gases will be exposed to the metal surfaces within the reactor. Therefore, the catalytic wall effects on the rate of reaction were evaluated for empty and packed Inconel reactors at 1173 K and 0.1 MPa using an equimolar feed of CO_2 and H_2 . Conversions were very high (10-40%), given the short residence time (< 0.5 s) and the equilibrium limitation of 55%, as shown in Figure 16. These levels of conversion were approximately two orders of magnitude greater than those observed using the quartz reactor, which were less than 0.1% under the same experimental conditions. This result

implied that the metal walls of the Inconel reactor catalyzed the reaction. An increase in the Inconel surface area was achieved by packing the reactor with Inconel rings. As shown in Figure 16, the conversions were twice that observed with the empty Inconel reactor.

High-pressure reverse water gas shift reaction in an Inconel reactor.

The rWGSR was also conducted at high-pressure conditions in an Inconel reactor over a wide temperature range using equimolar feeds of CO₂ and H₂. Longer residence times were employed (8-10 sec) because of the increase in gas density and limitations on the maximum flow rate of the reactor effluent. The high-pressure results from the Inconel reactor experiments are presented in Figure 17 along with experimental results obtained using the empty quartz reactor. The rate of reaction in the Inconel reactor was significantly greater than that obtained in the quartz reactor, especially at low temperature. Near-equilibrium conversions were attained at temperatures greater than 873 K in the Inconel reactor. These results confirm the observations obtained at low-pressure conditions, Figure 16; Inconel 600 surfaces catalyze the rWGSR. Levels of conversion were so high that accurate kinetic expressions could not be derived for the reverse WGS reaction in an Inconel reactor. Although a residence time of 10 s was used in this study, the residence time needed to achieve this level of conversion may have been substantially less, especially at higher temperature.

Both the low-pressure and high-pressure results indicated that the Inconel 600 catalyzed the rWGSR. Two rings of the Inconel 600 packing (72% Ni, 17% Cr, and 10%

Fe) were analyzed using SEM-EDS before and after their use in the low-pressure reactor, Figures 18 (a) and 18 (b), respectively. Significant loss of Ni and/or enrichment of Cr occurred in the Inconel surface after exposure of the Inconel to the rWGSR environment. (The Al, Si, and Ti detected in the rings reflect the composition of the Inconel 600; the source of the Ca is not known but could be due to surface contamination.) A likely cause of Ni loss is the so-called “metal dusting”. This type of corrosion is characterized by mass loss due to the formation of carbon deposits in H₂-CO-H₂O environments in the temperature range 400-800°C. The carbon diffuses into the metal and the Nickel migrates to the surface forming small pure-metal particles. Inconel 600 has been reported to be susceptible to this kind of attack (Klower et al., 1998). Evidence to this effect was gathered in our experiments: a considerable amount of coke was removed from the reactor and SEM-EDS analysis confirmed the presence of small Ni particles dispersed in the coke. The formation of carbon deposits may be attributable to the Boudouard reaction (17), due to the somewhat large CO concentrations present in the system; this reaction is known to occur in the temperature range 673 - 1173 K.



Although the mass loss in Inconel® 600 associated with “metal dusting” is more considerable than for other high-Ni alloys, the damage appears to be more superficial (Baker et al., 2002). However, other materials should be considered for the long-term operation of the moderate-high temperature, high-pressure WGSR.

Another side reaction, formation of methane, was observed in the Inconel reactor. The concentration of methane at the outlet of the reactor exhibited temperature

dependence reaching a maximum value at 1023 K, as shown in Figure 19. Methane formation in a CO-CO₂-H₂-H₂O system is possible via reactions 18 – 21. With our experimental data is not possible to determine which one of those reactions is the main contributor to the formation of methane. However, the fact that the CO/H₂O ratio decreases and the CO₂/H₂ ratio increases noticeably at 1023 K suggests that Reaction 18 and/or 20 are playing an important role in the process. Removal of H₂ from the system led to complete suppression of methane formation.



Conclusions

The rate of reaction of the homogeneous, reverse water-gas shift reaction has been evaluated in an **empty** quartz reactor at elevated temperature (1148-1198 K), low pressure (0.1 MPa) conditions in the absence of a diluent gas. The power-law rate expression employed exponent values of 1.0 and 0.5 for CO₂ and H₂, respectively. The reaction rate was characterized by an activation energy of 47 kcal/mol [196.6 kJ/mol] and a pre-exponential constant of $8.32 \times 10^7 \text{ L}^{0.5} \text{ mol}^{0.5} \text{ s}^{-1}$. This result was consistent with the previously published, low-pressure rate expression of Graven and Long, but the yielded rates were roughly four times greater than reaction rates obtained **in our quartz-packed**

reactor (FELIPE PUT ko AND Ea for the packed reactor here) and rates reported by Tingey and by Kochubei and Moin. CFD simulation results indicated that differences in reactor geometry were not responsible for these differences. Further, oxygen, which is known to catalyze the reverse WGS reaction, was maintained at a concentration of less than 1 ppm in our reactor. The importance of an initial induction period in which the concentration of the chain carriers increases steadily with time was confirmed and the discrepancies between the different studies could be related to this effect. The simple gas-phase mechanism proposed by Bradford was found to satisfactorily describe the reaction. Felipe add a sentence how/why the quartz packing also reduced the rate

A pressure-equilibrated quartz reactor was also used to study the homogeneous rate of reaction for the first time at high temperature, high-pressure conditions (up to 1.6 MPa). The results yielded an activation energy of 53.1 kcal/mol [222.2 kJ/mol] and a pre-exponential constant of $8.69 \times 10^8 \text{ L}^{0.5} \text{ mol}^{0.5} \text{ s}^{-1}$. The rate constant correlated by the low-pressure and high-pressure Arrhenius expressions were in good agreement over the 1148 – 1198 K temperature range, indicating there was no significant effect of elevated pressure on the rate constant.

Conversions attained in an Inconel® 600 reactor at 1173 K and 0.101 MPa were approximately two orders-of-magnitude greater than those attained in the quartz reactor for residence times of 0.1 – 0.5 seconds. A dramatic increase in the reaction rate was also observed when the Inconel® 600 reactor was operated at high pressure, with near-equilibrium conversions realized at temperatures as low as 873 K for residence times of

8-10 s. This increase in conversion suggested that the Inconel® 600 surfaces catalyzed the rWGS. Therefore, the use of intrinsic kinetic results based on quartz reactors in the design of a reverse WGS Inconel® 600 reactor will lead to overestimates of the volume required to attain a specified level of conversion. Further, the depletion of nickel from the Inconel® 600 reactor surfaces indicates that **metal dusting is an issue that needs to be addressed in an Inconel® 600 reactor for the moderate-high temperature rWGS,**

Acknowledgements

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Table 1. Kinetic expressions for the rWGS in quartz reactors.

$$r = k[\text{H}_2]^\alpha[\text{CO}_2]^\beta = k_0 \exp(-E/RT)[\text{H}_2]^\alpha[\text{CO}_2]^\beta, R = 8.3145 \times 10^{-3} \text{ kJ/mol} \cdot \text{K};$$

QT= quartz reactor with inner quartz tube, FS = flame study

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Reference	Mat.	T K	P MPa	α	β	E kJ/mol	k_0 (L/mol) $^{\alpha+\beta-1}$ s $^{-1}$
Graven and Long (1954)	Q	1148-1323	0.1	0.5	1.0	234.3	2.9×10^9
Kochubei and Moin (1969)	Q	1023-1523	0.1	0.5	1.0	326.4	6.4×10^{12}
Tingey (1966)	Q	1073-1323	0.1	0.5	1.0	318.0	1.2×10^{13}
Tingey (1966)	Q	673-1073	0.1	0.333	1.0	164.2	7.6×10^4
Karim and Mohindra (1974)	FS	<2400	0.1	0.5	1.0	397.5	2.3×10^{16}
NETL empty reactor (This work)	QT	1148-1198	0.1	0.5	1.0	192.9 \pm 3. 3	(2.17 \pm 0.69) $\times 10^7$
NETL empty reactor (This work)	QT	1148-1198	1.6	0.5	1.0	189.5 \pm 4. 6	(1.22 \pm 0.65) $\times 10^8$
NETL packed reactor (This work)							

Table 2. Dimensions of the reaction zone of the NETL Quartz and Inconel® 600 reactors.

FELIPE<PUT IN A FOOTNOTE THE DIMENSIONS OF A TYPICAL QUARTZ PACKING

	Quartz with Tube	Inconel With Tube
Reactor Height (cm)	1.9	2.54
Reactor ID (cm)	1.1	1.35
Inner Tube Height (cm)	1.4	1.91
Inner Tube ID (mm)	1.85	2.87
Inner Tube OD (mm)	3.85	4.14
Annular Gap, reactor (mm)	3.57	4.66
Volume (cm ³)	1.81	3.38

Table 3. CFD conversions of the four reactors assuming identical operating conditions and rate of reaction. Conditions: 1173 K, 0.1 MPa, residence time 5 s, inlet molar fractions of CO₂ and H₂ are 0.5.

Reactor	CO ₂ conversion, %
Graven and Long (1954)	0.0990
Tingey (1967)	0.1017
Kochubei and Moin (1969)	0.0990
NETL (This work)	0.1053

Table 4. Estimation of k Values at 1250 K and atmospheric pressure

Conditions		$k@1250K$ cm^3,s,mol
a	Non-stationary [H]	325
b	Mixed, non- and stationary [H]	79
c	NETL	44
d	GRI, stationary [H]	7.3
e	Tingey (1967)	9.1
f	Kochubei and Moin (1969)	9.0

Note: If inlet [H] is constrained to its stationary value, the simulation result (7.1) is in

excellent agreement with the value (d). **FELIPE >>>EITHER GET RID OF THIS NOTE**

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Figure 1. Arrhenius representations of rate constant expressions for the reverse WGS reaction obtained using quartz reactor, $r = [\text{CO}_2][\text{H}_2]^{0.5}$, $k [\text{L}^{0.5}\text{mol}^{0.5}\text{s}^{-1}]$; results of previously published literature.

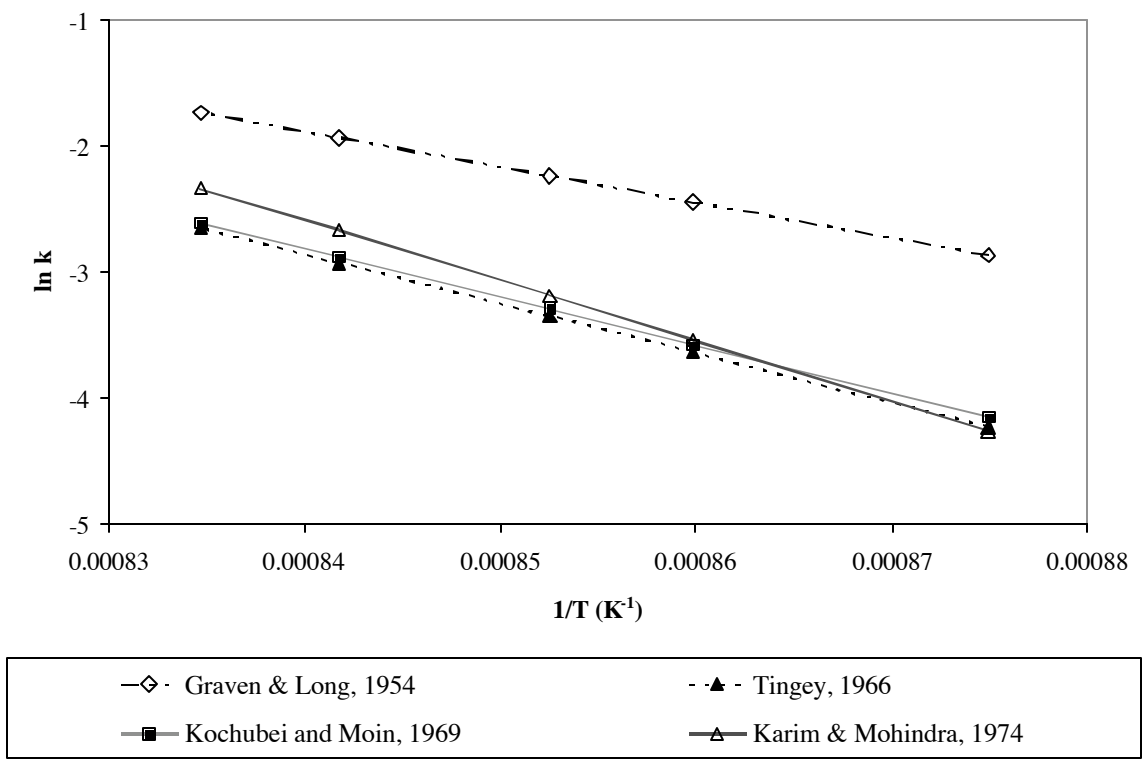


Figure 2. Schematic of HMT-1 unit. FCV – Flow Control Valve. PCV – Pressure Control Valve. PI – Pressure Indicator. GC - Gas Chromatograph. TI – Temperature Indicator.

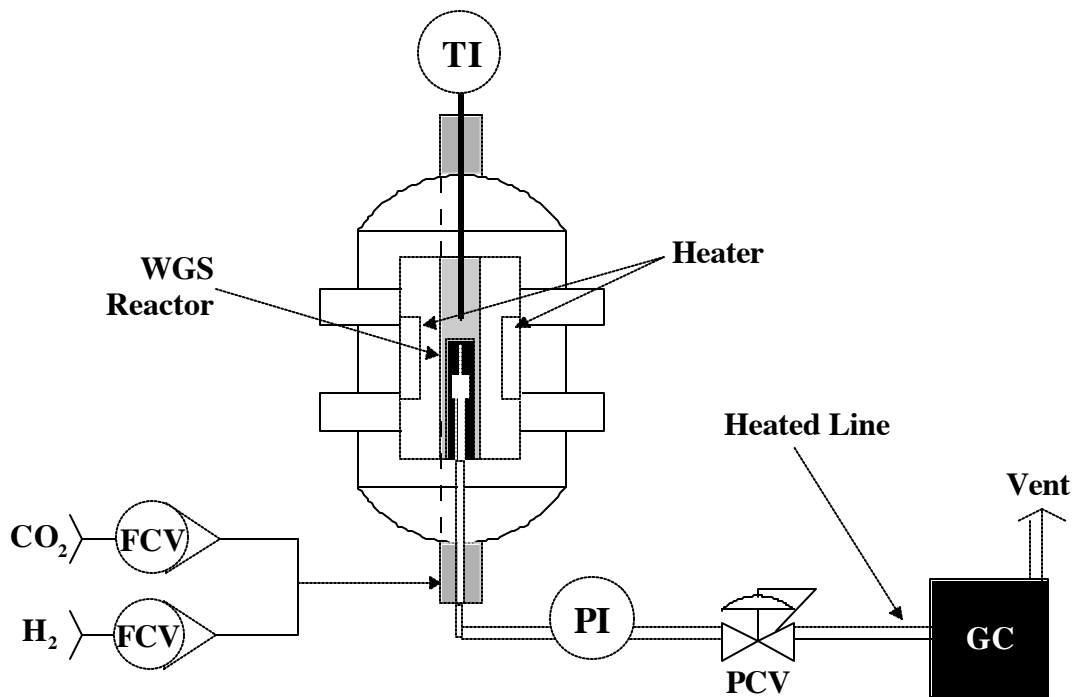


Figure 3. Details of the quartz (a) and Inconel® 600 (b) reactors.

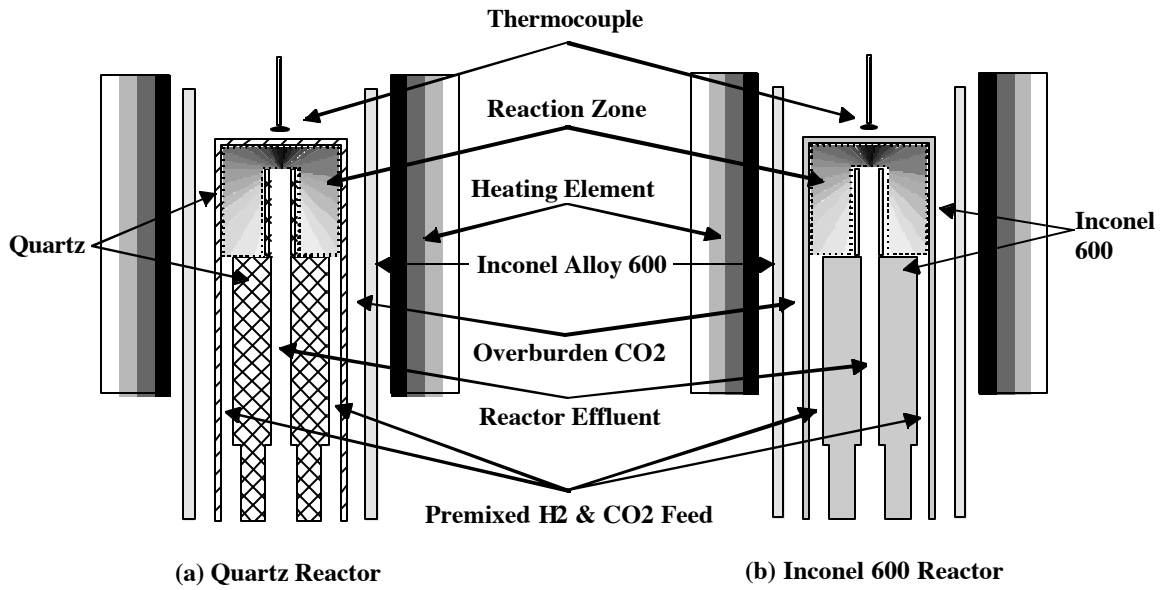


Figure 4. Arrhenius representations of rate constant expressions for the reverse WGS reaction obtained at NETL using the quartz reactor, $r = [\text{CO}_2][\text{H}_2]^{0.5}$, $k [\text{L}^{0.5}\text{mol}^{0.5}\text{s}^{-1}]$. Low-pressure results (\bullet), high-pressure results (\blacksquare). Graven and Long low pressure correlation (Graven and Long, 1954) -dotted line- provided for reference.

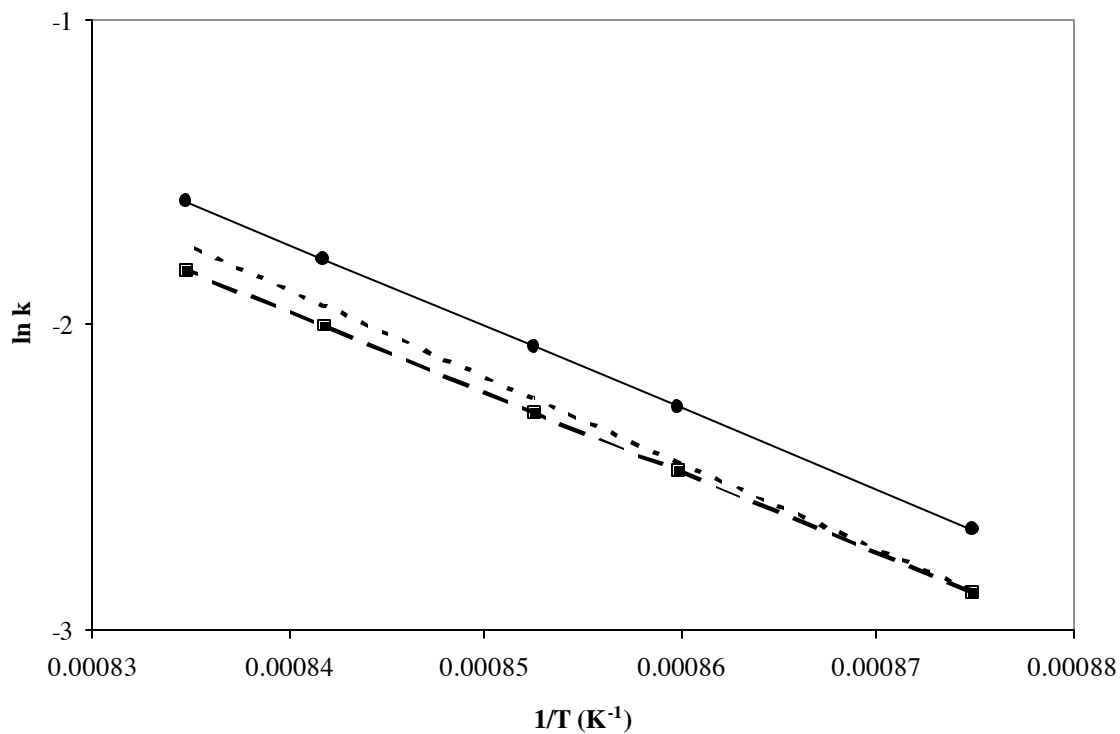


Figure 5. Dependence of the rate on the concentration of CO₂. Partial pressure of H₂ was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = 1.92 ± 0.15 s based on swept volume

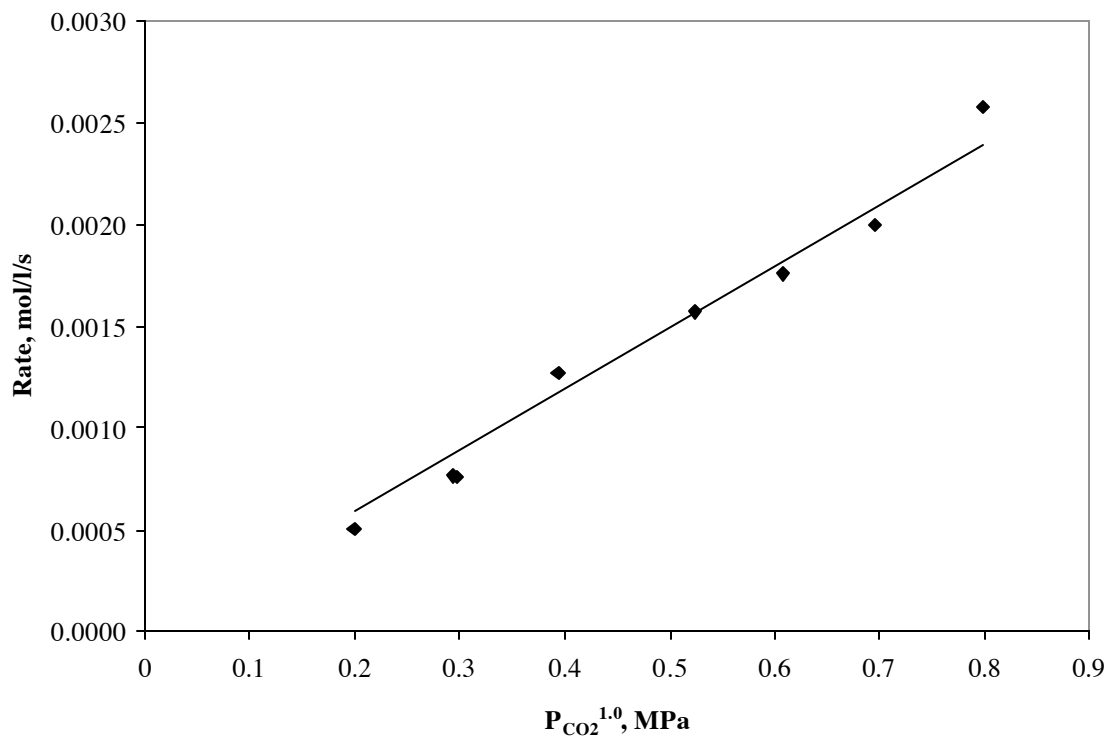


Figure 6. Dependence of the rate on the concentration of H_2 . Partial pressure of CO_2 was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = 1.85 ± 0.08 s based on swept volume.

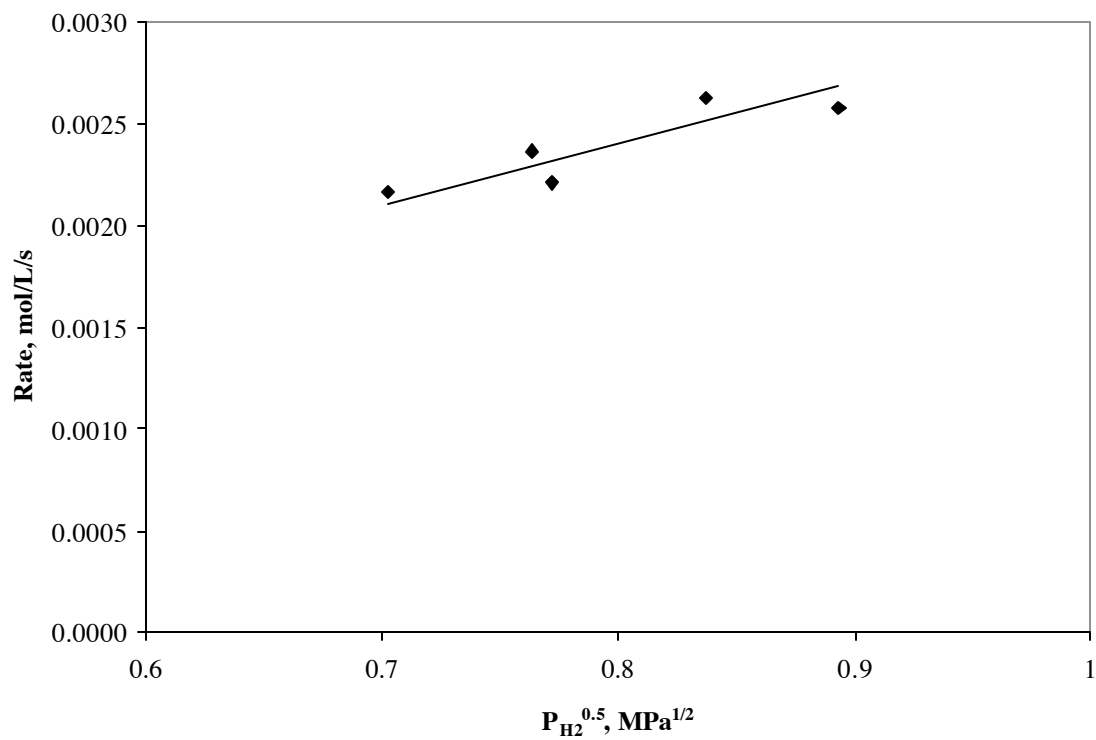


Figure 7. Flow field in NETL quartz reactors; axisymmetric; feed from narrow annulus along the perimeter of the bottom of the reactor; reactor with product withdrawal from the co-axial tube.

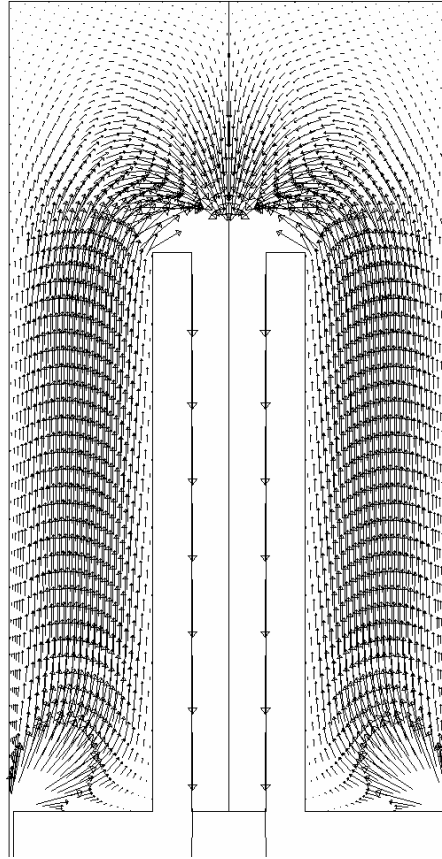


Figure 8. Graven and Long; non-axisymmetric cylindrical reactor; tangential feed entering at the top, right hand corner of the xz plane; tangential withdrawal of products through narrow tube at the bottom left hand corner of the xz plane; the 2 circular xy cross-sections are $1/3$ and $2/3$ of the way up the reactor in the z -direction.

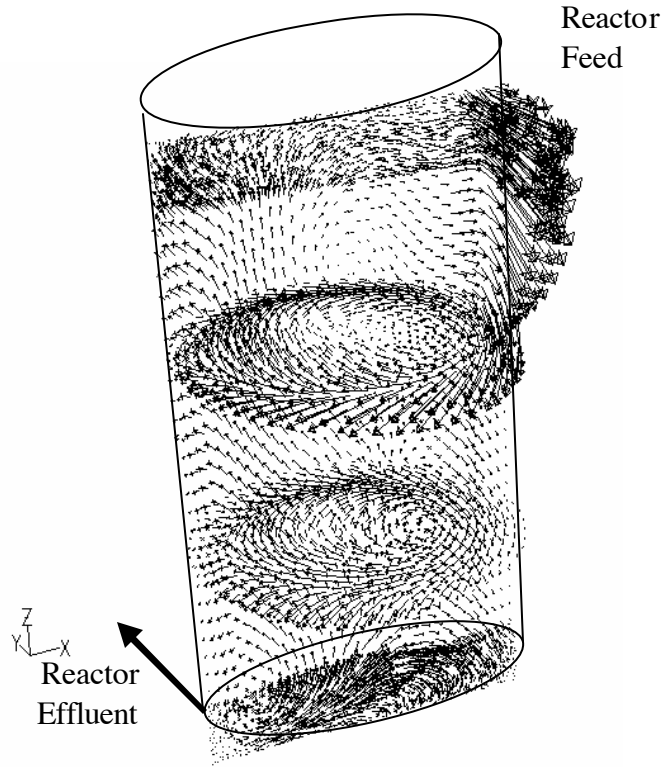
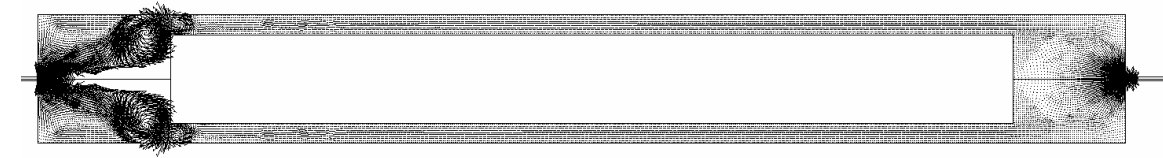


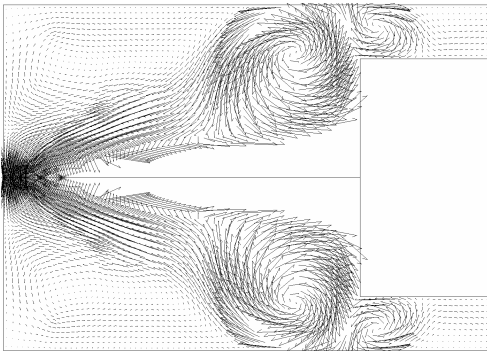
Figure 9. Tingey reactor; axisymmetric; enlargement of feed and product sections provided; white rectangle is a solid quartz cylinder; white flow field in feed section is high velocity flow field.



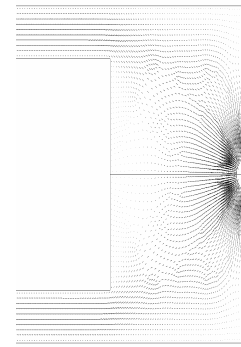
feed zone

annular section

product zone



feed zone detail



product zone detail

Figure 10. Kochubei and Moin; non-axisymmetric cylindrical reactor; axial feed along entire cross-section on the left-hand side of the reactor; product withdrawn through a narrow tube at the bottom right corner of the xz plane; white field in the center of the xz plane is a thermocouple; velocity vectors on a xy circular plane normal near the right-hand side of the reactor also shown; white field in this plane near the bottom corresponds to high fluid velocity near the exit tube.

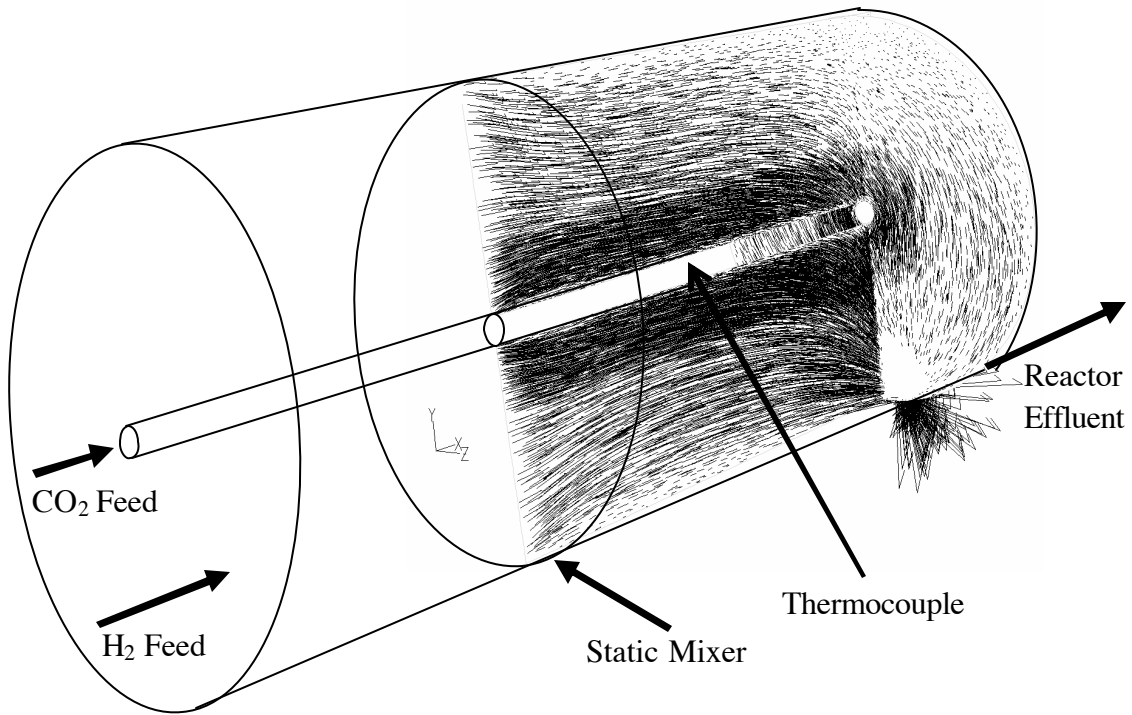


Figure 11. Residence Time Distribution plots for the (a) Tingey (1967), (b) Kochubei and Moin (1969) and (c) NETL reactors. Nominal residence time is 0.5 s. Ideal case (PFR) reactor is included as comparison.

FELIPE...I BELIEVE YOUR Y AXIS LABEL IS WRONG...IS IT NOT A NORMALIZED MOLE FRACTION (WE ONLY INJECTED A 1% PULSE, HOW COULD IT REACH A MOLE FRACTION OF 1?

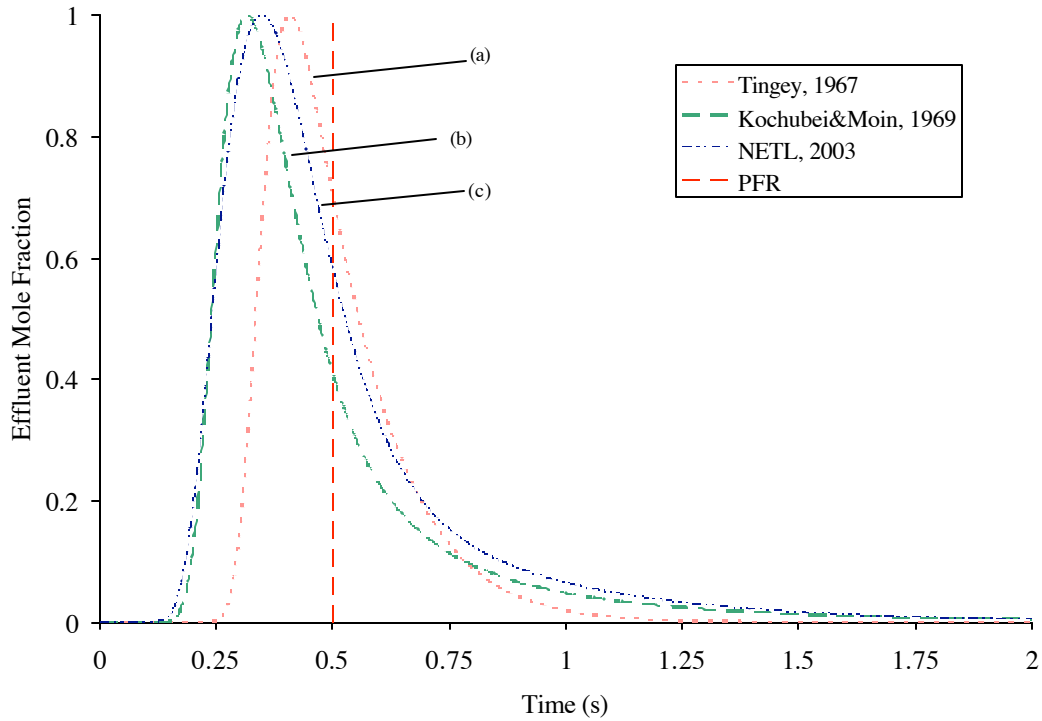


Figure 12. Residence Time Distribution Plots. Graven and Long (1954) reactor.

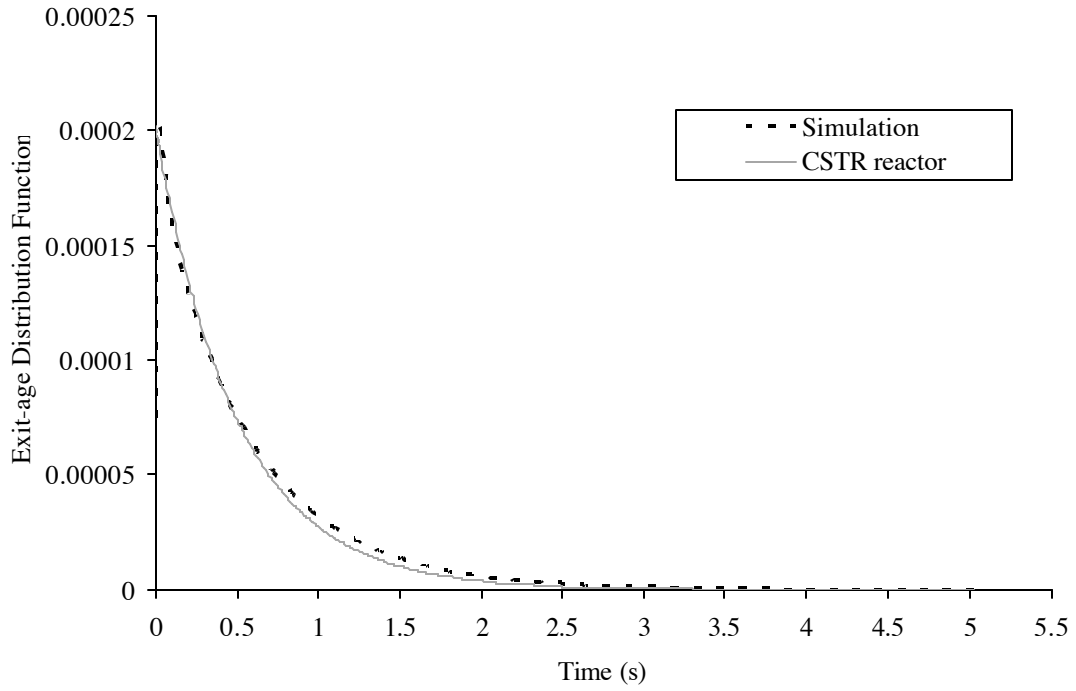


Figure 13. ChemKin® simulation of the rWGS in a tubular reactor. Inlet molar flowrates: CO₂ = H₂ = 50 sccm.

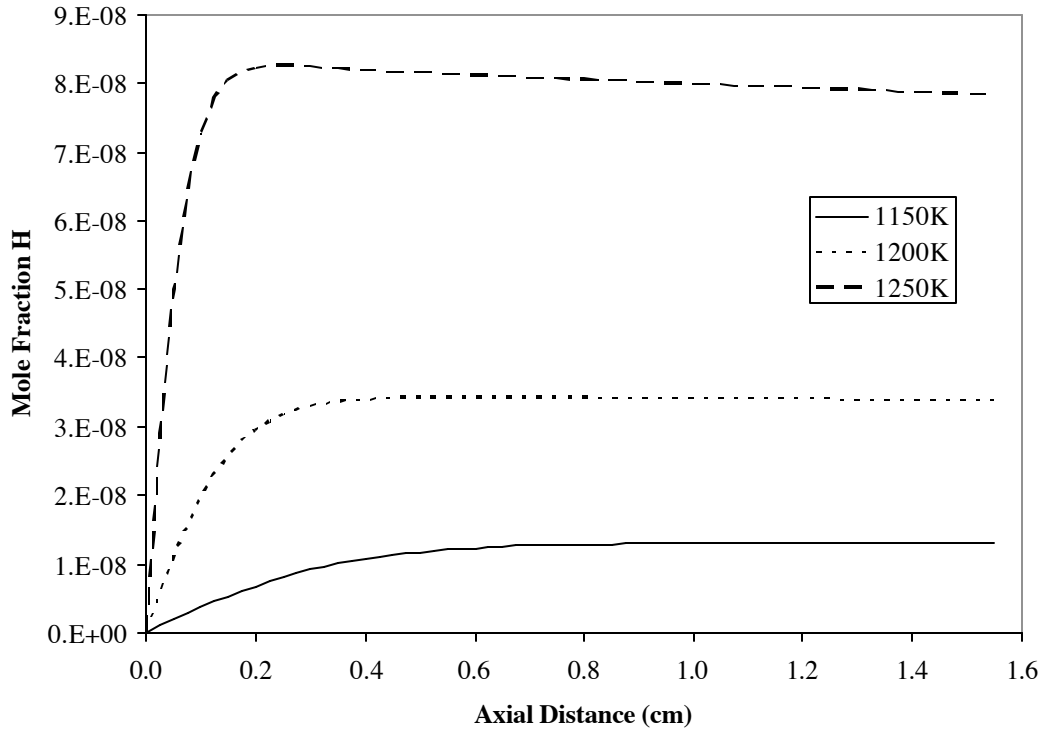


Figure 14. Concentration – time profile for [H]. $[\text{CO}_2]_0=[\text{H}_2]_0$, $[\text{CO}]_0=[\text{H}_2\text{O}]_0 = 0$, 1250 K, 16 atm, final conversion is 10%.

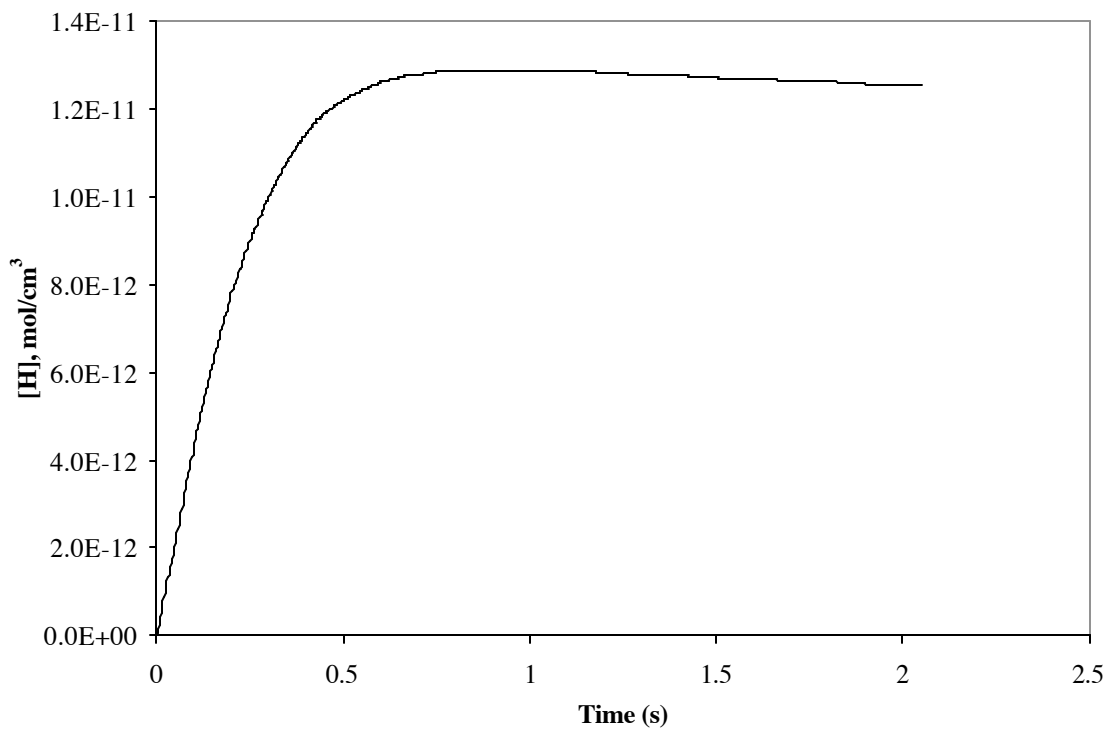


Figure 15. Packed Reactor *this plot may change a little bit (empty results) !!!*

MAKE SURE YOU change the legend titles from QUARTZ&NIPPLE to EMPTY QUARTZ and change “QUARTZ REACTOR QUARTZ PACKING” to “NETL Low P Quartz Packing”

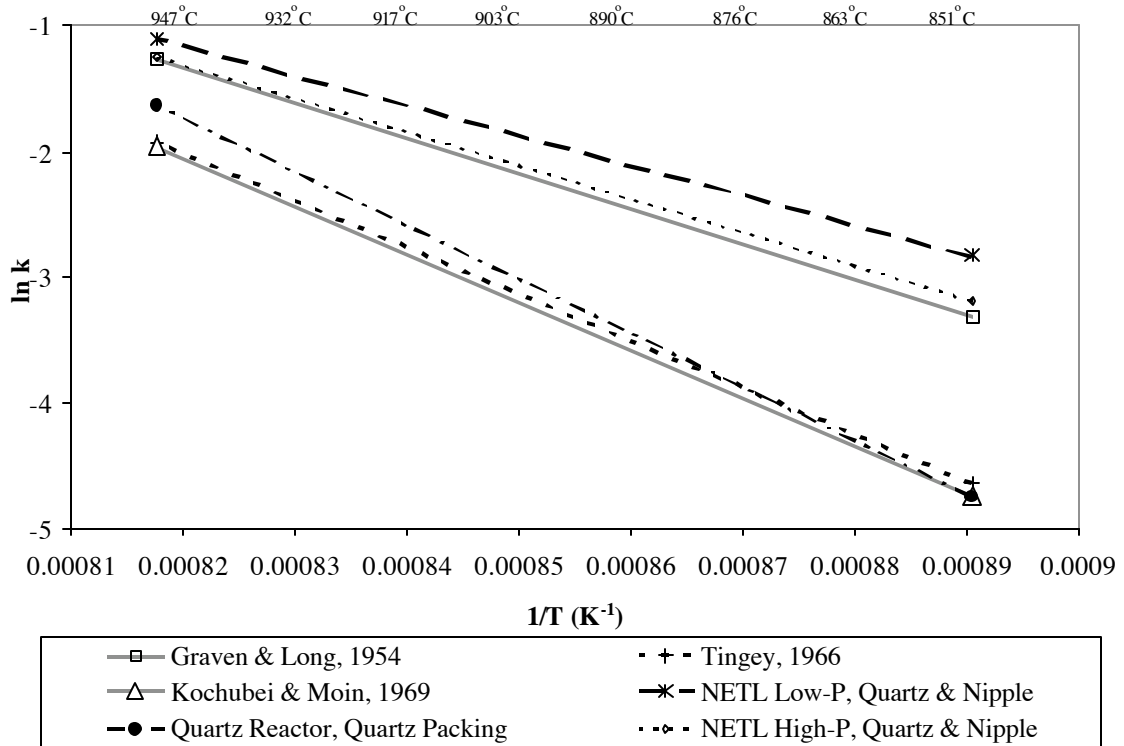


Figure 16. Reverse Water-Gas Shift Reaction in an Inconel® 600 reactor. 1173 K, 0.101 MPa, $[H_2]_o=[CO_2]_o$. Equilibrium conversion at these conditions is 55%.

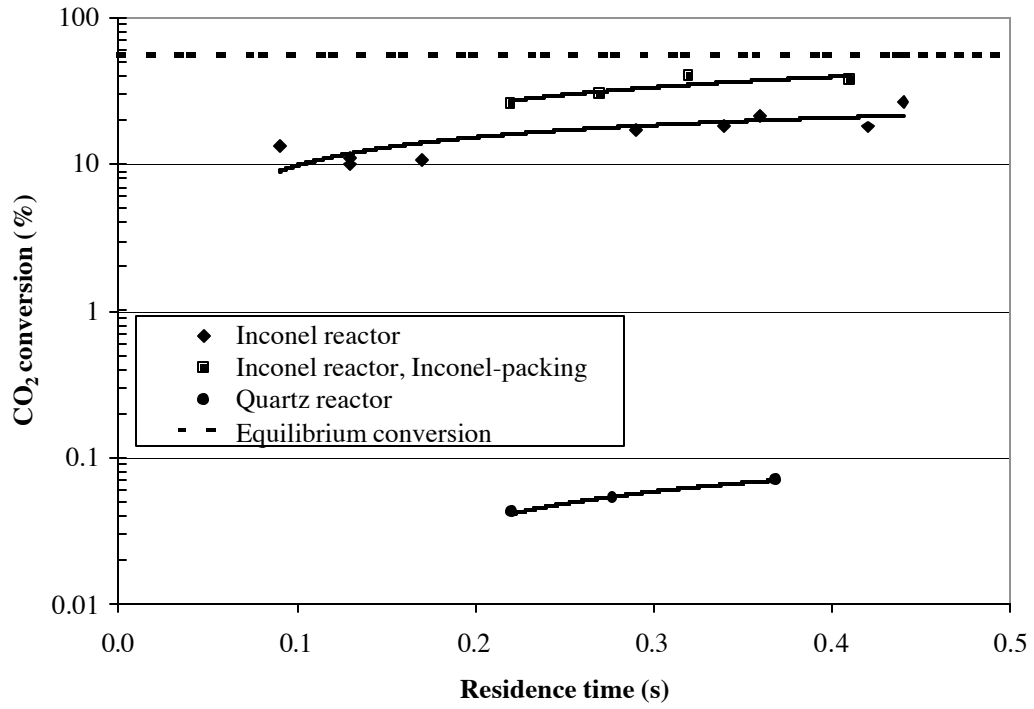


Figure 17. Reverse Water-Gas Shift Reaction in an Inconel® 600 reactor. 1.6 MPa, $[H_2]_0=[CO_2]_0$. Conversions in the quartz reactor were estimated with our high-pressure kinetic results. Residence times were 8-10 s.

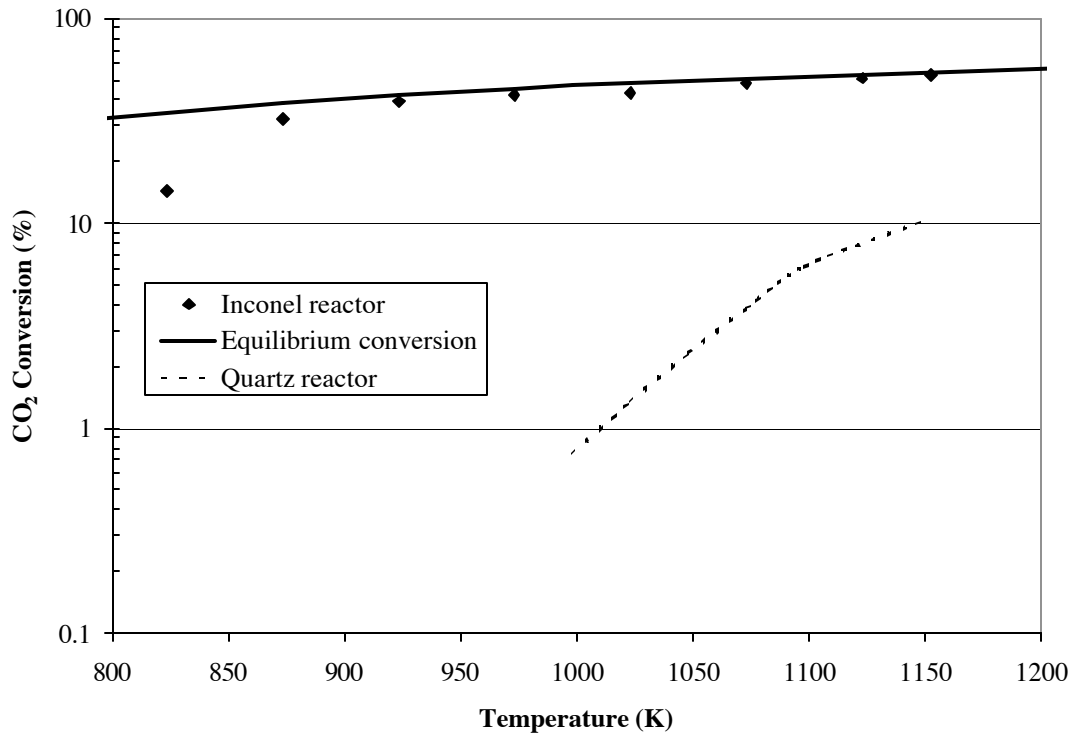


Figure 18. SEM-EDS for Inconel® 600 rings before (a) and after (b) exposure to reverse WGSR environment.

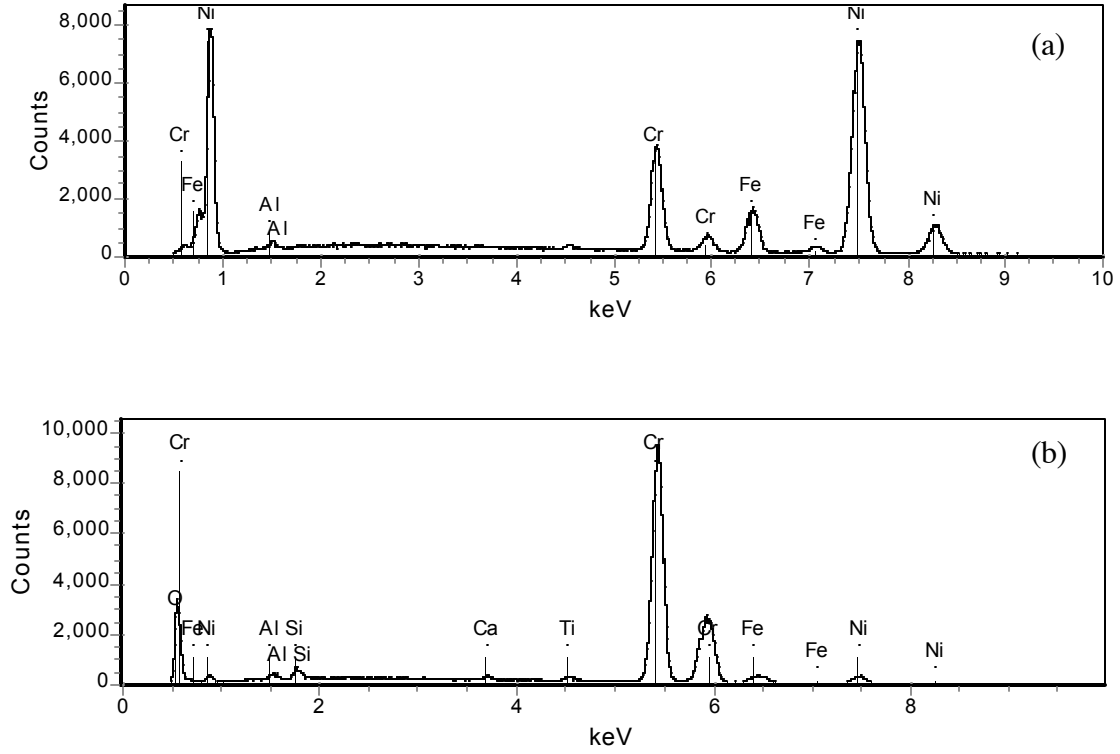


Figure 19. Side reactions in the WGS in an Inconel 600 reactor.

