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**CHAR REACTIVITY IN GAS MIXTURES: TOWARDS AN
UNDERSTANDING OF THE C-CO-CO₂ REACTION SYSTEM**

TECHNICAL NOTE 35

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EXECUTIVE SUMMARY

This report is a milestone report of recent activities in Task 2 of CCSD Project 3.1 – Entrained Flow Gasification. It is a summary of a portion of the work undertaken during the financial year 06/07 and represents the achievement of milestones to the level planned in the current scope of work.

Following on from previous work in this Task this report presents new reaction rate and char surface area data for the CO inhibition of the char–CO₂ gasification reaction. Previous work in this area demonstrated that Langmuir-Hinshelwood (LH) kinetics could be used successfully as the basis for the development of a ‘CO inhibition factor’ to estimate the inhibiting effect of CO on the rate of the char–CO₂ reaction. The current work presents new data and further analysis of the reaction system in terms of a LH reaction scheme. This continues a recent line of work, in which a LH kinetic model (generally used for atmospheric pressure applications) is tested for its applicability at high pressures.

The new data presented in this work show some deviation from the accepted atmospheric pressure form of the LH reaction scheme. This is an unexpected result, given the success with which the scheme has been hitherto applied to gasification reaction systems. This work also shows that the surface area development during reaction is affected by the partial pressure of CO₂, consistent with similar work previously reported. However, the partial pressure of CO is also shown to be significant, and in some cases more so than CO₂ on the development of surface area. Since a key term in the LH rate equation is the number of total active sites which, in the equation, is treated as a constant, it follows that the deviation from ‘ideal’ LH behaviour at high pressures with CO may be related to the unusual effect of CO on the development of char surface area, and not a failure of the LH reaction scheme at a more fundamental level.

Further work in this area must explore the development of char surface area during gasification at high pressures in order to appropriately understand the phenomenon. Similar measurements should be made for the char–H₂O system. Application of these results (and the results on which these new data build) to more realistic gasification temperatures will be undertaken as part of associated research activities.

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1. INTRODUCTION

1.1. Background

A focus of the recent experimental work in the area of char gasification kinetics has been investigations of the mechanisms and kinetics of char gasification reactions in complex gas mixtures. This has included mixtures of reactants (CO₂ and H₂O) as well as mixtures containing reaction products (CO and H₂) which are known to inhibit the gasification rates [1-3].

That work provided important and novel insights into the kinetics of the char gasification system. It showed, for the first time, how CO₂ and H₂O compete for active surface on a reacting char particle [1], and demonstrated how a kinetic model based entirely on a LH reaction scheme was able to describe this competition. This new finding has significant implications for how gasification reactivity data are used as assessment tools, both in their own right and through process models. Other, related work provided high pressure rate data for the inhibition of the gasification reaction rates by CO and H₂ [2, 3] and showed how, in general, the data can be described using a model based on the Langmuir-Hinshelwood (LH) reaction scheme.

This report presents new data and analysis for CO inhibition of the char–CO₂ reaction, extending the previously-reported data to higher temperatures, and providing data which allow a more complete analysis using a LH kinetic scheme.

1.2. The C–CO–CO₂ Reaction System

Previous work studying CO inhibition of the char–CO₂ reaction used a Langmuir-Hinshelwood (LH) reaction scheme to describe reaction kinetics. A LH reaction scheme is based on the dissociative adsorption of a CO₂ molecule on an active site on the char surface. This produces a molecule of CO and a surface complex as a reaction intermediate. Desorption of the surface complex produces another molecule of CO and in doing so ‘gasifies’ some of the solid carbon. This is commonly represented by the following:



In this representation, k_1 and k_2 are the rate constants for the forward and back equilibrium reaction respectively, and k_3 is the rate constant for the surface complex

desorption. C_f represents a free active site, and $C(O)$ a surface-bound reaction intermediate.

In this reaction scheme, the presence of CO inhibits the overall rate of reaction via the reverse equilibrium in the first step, which effectively decreases the concentration of surface complexes.

The overall rate of reaction can be related to the total number of available active sites and the concentrations of CO and CO₂ using a rate equation derived from the above reaction scheme (see [4, 5]):

$$\rho_{CO_2} = \frac{[C_t]k_1P_{CO_2}}{1 + \frac{k_2}{k_3}P_{CO} + \frac{k_1}{k_3}P_{CO_2}} \quad (2)$$

The $[C_t]$ term in this reaction scheme represents the *total* concentration of active sites on the char. This differs from the concentration of *available* active sites at any one time (the C_f term in Equation 1 represents one of these available active sites). For a fresh, unreacted char, no sites are occupied and $[C_f] = [C_t]$. Once reaction has begun, there will be some adsorption of CO₂ and formation of surface complexes, therefore $[C_f] < [C_t]$.

It is implicit in this reaction scheme that the $[C_t]$ term is constant for all temperatures and gas partial pressures. It is likely, however, that the total number of active sites on the char surface ($[C_t]$) changes during reaction: pores are opened, active sites are removed by reaction and total surface area eventually decreases. For this reason, analyses of reaction systems in the manner reported here are usually performed at a constant level of carbon conversion.

There have been many analyses of the kinetics of the C–CO–CO₂ reaction system, due largely to its importance to the blast furnace, and more recently its significance to the coal gasification system (see, for example, [6-9], and the numerous references therein). The operation of the blast furnace at (close to) atmospheric pressure has meant that most of the reported investigations are performed at atmospheric pressure. Atmospheric pressure analyses of the C–CO₂ reaction are performed either using the *n*th order rate equation (e.g. [10, 11]) or the LH rate equation described above (e.g. [6, 8, 9]). The *n*th order rate equation is useful for describing reaction systems over a limited range of temperatures and pressures, and in the absence of inhibiting effects of CO, but its limitations become apparent when significant concentrations of CO are introduced into the system, and when the pressure range of CO₂ becomes wider [2, 12].

Some recent work by the authors [12] demonstrated the ability of the LH reaction scheme to describe the kinetics of char gasification with CO₂ and H₂O at high pressures, both separately and as mixtures. This work was performed in the absence of inhibition by CO and H₂. More recent work in this area [2] showed how the inhibition of the C–CO₂ reaction was independent of CO₂ partial pressure and coal type when reported on a ‘relative rate’ basis¹, and that the relative rate could be represented mathematically using an operator derived from the Langmuir-Hinshelwood rate equation.

This ‘relative rate’ operator provided a useful means of incorporating CO-inhibited C–CO₂ kinetics into overall descriptions of a high pressure char gasification system, using a technique broadly based on the accepted reaction mechanism. Whilst it is based fundamentally on LH kinetics, that work did not test the ability of the LH equation in its entire form to describe the C–CO–CO₂ reaction system. This is important information, as for any CO inhibition factor to be relevant to a wide range of gasification conditions a complete understanding of the reaction system is required.

This report, therefore, presents new specific and intrinsic reaction rate data for the C–CO–CO₂ reaction system, obtained in a manner that allows them to be directly interpreted using the LH reaction scheme. These data are used to assess the suitability of the use of the LH rate equation (Equation 2) at high pressures more directly, leading to a better understanding of the processes on which the ‘CO inhibition factor’ are based.

2. EXPERIMENTAL SYSTEM

Reaction rates were determined in this work using a high pressure thermogravimetric analyser (TGA). This apparatus has been used extensively in CCSD research activities to measure high-pressure reaction rates of chars with pure reactant gases. Some modifications to the apparatus and the laboratory were performed to allow safe experimentation with CO in the reactant stream.

This facility and the procedures used have been extensively documented already [13-15] and only a brief summary of the experimental procedure is given here. A dried char sample (~100 mg) was loaded into the TGA sample holder which was continuously purged with dry inert gas (N₂). The system was brought to reaction pressure and temperature with the reactant gas stream flowing through the hot

¹ That is, the rate in a CO₂/CO mixture relative to the rate, under the same conditions of temperature and P_{CO₂}, in the absence of CO.

zone². The sample was lowered into the reaction zone to initiate reaction. The mass of the sample was monitored and used to calculate a reaction rate using established techniques.

Experiments presented in this work were designed to generate rate data as a function of CO₂ partial pressure at three constant CO:CO₂ ratios. This is the usual approach when attempting to interpret the results using the LH reaction scheme. A rearrangement of the LH rate equation for the C–CO₂ reaction (Equation 2) is:

$$\frac{1}{\rho_{CO_2}} = \frac{1}{k_1[C_t]P_{CO_2}} + \frac{k_2}{k_1k_3[C_t]} \cdot \frac{P_{CO}}{P_{CO_2}} + \frac{1}{k_3[C_t]} \quad (3)$$

Using this equation (and assuming all rate constants and the [C_t] term are constant as partial pressures and temperatures change), a chart of 1/ρ_{CO₂} vs 1/P_{CO₂} at a constant CO:CO₂ ratio should give a straight line, with a slope equal to 1/k₃[C_t] and an intercept a combination of rate constants and [C_t]. Table 1 shows the nominal experimental plan for the work presented in this report.

Char used in these experiments was made from two CCSD reference coals, prepared to a size range of -1.0+0.6 mm. These coals were chosen to, where possible, be consistent with previous reactivity work in this laboratory. Table 2 lists these coals and their proximate analyses.

Chars were produced in a laboratory tube furnace at atmospheric pressure. Coals were heated under flowing nitrogen at 10°C/min to 1100°C, and held there for 3 hours to ensure complete devolatilisation. This is a technique used extensively in this laboratory for preparation of large volumes of char under consistent, well-defined conditions. Whilst the physical structure of chars produced in this manner is known to differ from those produced at higher pressures and heating rates, the chemical reactivity of the resultant char is not significantly affected [16]. This means that such a char preparation technique is well-suited for detailed investigations into so-called ‘intrinsic’ reactivities of chars.

Surface areas of chars were determined prior to and after reaction to 10% conversion. These were measured using CO₂ adsorption, with the resulting isotherm analysed using the Dubinin-Radushkevich equation [17].

² Gas flowrates through the reaction zone were in the range 1–3 L_N min⁻¹ and were adjusted according to system total pressure to maintain a minimum gas velocity of 3 cm s⁻¹. Such a velocity is required to minimise effects of bed diffusion and to ensure that a constant and known concentration of reactants are available to the entire sample.

| CO ₂ (bar) | CO (bar) | Total Press (bar) | CO/CO ₂ ratio |
|--------------------------|-------------|----------------------|-----------------------------|
| 5 | 0 | 5 | 0 |
| 10 | 0 | 10 | 0 |
| 15 | 0 | 15 | 0 |
| 20 | 0 | 20 | 0 |
| 5 | 0.5 | 5.5 | 0.1 |
| 10 | 1.0 | 10.1 | 0.1 |
| 15 | 1.5 | 16.5 | 0.1 |
| 20 | 2.0 | 22 | 0.1 |
| 5 | 1.0 | 6 | 0.2 |
| 10 | 2.0 | 12 | 0.2 |
| 15 | 3.0 | 18 | 0.2 |
| 20 | 4.0 | 24 | 0.2 |

Table 1: Nominal experimental program for CO inhibition experiments. This program was performed on two coal chars at 900°C and 950°C.

| Coal | Moist (%ad) | Ash (%ad) | VM (%ad) | FC (%ad) | MVR |
|--------|----------------|--------------|-------------|-------------|------|
| CRC272 | 2.8 | 13.5 | 34.3 | 49.4 | 0.70 |
| CRC252 | 6.7 | 12.1 | 40.2 | 41.0 | 0.44 |

Table 2: CCSD coals used to make chars for investigation in this work. MVR = mean vitrinite reflectance, an indicator of coal rank.

3. RESULTS: TESTING THE LH EQUATION AT HIGH PRESSURE

Specific reaction rate measurements (rates in units of $\text{g g}^{-1} \text{s}^{-1}$) for chars from both coals as a function of CO₂ partial pressure at three CO:CO₂ ratios are given in Figure 1 (900°C) and Figure 2 (950°C). Generation of rate data using these variables allows the applicability of the LH reaction scheme to be assessed: as discussed, each CO:CO₂ ratio should give a straight line, each being parallel with the other.

It is clear that the data are inconsistent with what might be expected if the system is in fact reacting according to atmospheric-pressure LH mechanisms. There is a large degree of deviation from linearity (in particular for the data at CO:CO₂ = 0.2) and

the datasets obtained at different CO:CO₂ ratios are clearly not parallel. The trends in the data obtained for both coals at both temperatures are similar, with the difference being only in the scale or magnitude of the data (arising from different ‘reactivities’ of the two samples).

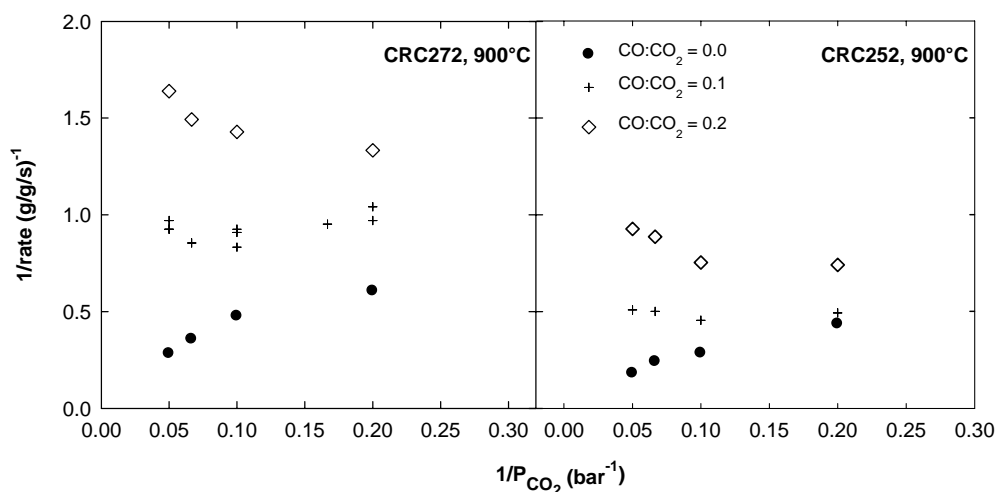


Figure 1: Specific reaction rate measurements at 900°C and three CO:CO₂ ratios as a function of CO₂ partial pressure. Rate data determined at ~10% conversion.

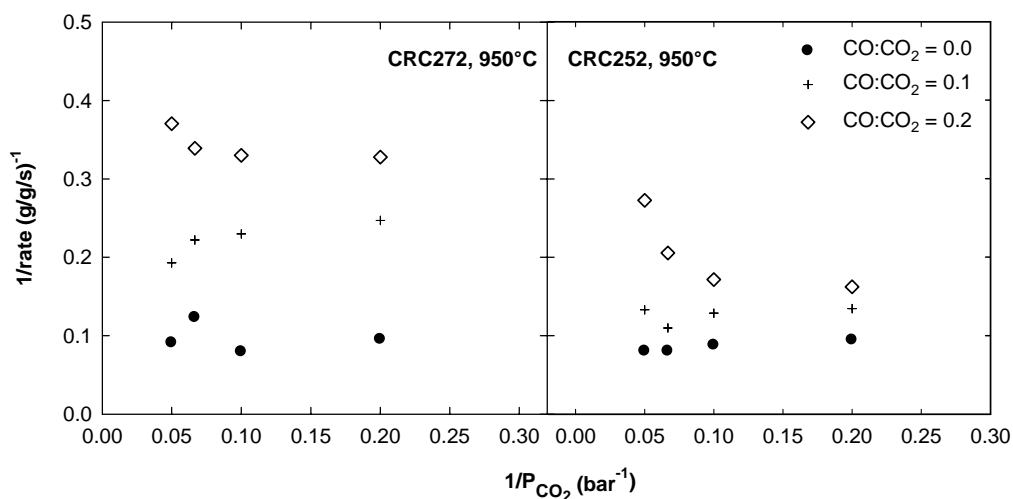


Figure 2: Specific reaction rate measurements at 950°C and three CO:CO₂ ratios as a function of CO₂ partial pressure. Rate data determined at ~10% conversion.

In the past, some authors have attributed any such divergence from ideal behaviour to the inability of the LH scheme to represent accurately the reaction system at high pressures. Solutions have included addition of extra reaction steps to the mechanism, e.g. [18, 19], in order to adequately describe the reported experimental results. Unfortunately, there has been little consensus as to the nature of these additional reaction steps, so there exists no commonly-accepted, high pressure set of reactions that are understood to be adequate in describing the high pressure char–CO–CO₂ reaction system.

The next section discusses the implications of these results in more detail.

4. IMPLICATIONS: IS SURFACE AREA DEVELOPMENT THE ISSUE?

The previous section presented new rate data of the char–CO–CO₂ reaction system, providing a LH analysis of the rate data over a wider pressure range than currently available in the literature. The results obtained do not seem to be consistent with the LH reaction scheme used at atmospheric pressure, due primarily to the lack of linearity in the LH transformations at higher partial pressures of CO and CO₂. There are several possibilities for this, and in the past such deviations have been attributed to extra reaction mechanisms occurring at the higher pressures used in the studies, e.g. [18, 19].

The current work investigates a different possibility, and considers the data presented here alongside findings from previous work [1, 2, 12]. In that work, the suitability of the LH reaction scheme for describing the kinetics of a system at high pressures *in the absence of product gas inhibition* for (separately) H₂O or CO₂ gasification [12], and also when these two reactants are reacting simultaneously and competing for active surface [1], was demonstrated. This was shown to be the case at pressures up to 30 bar. It has also been demonstrated that an analysis of the reaction system studied in this current report using LH-based mathematical operators describes well the product gas inhibition of the C–CO₂ reaction on a relative rate basis³ [2] at pressures up to 25 bar.

The last point above is perhaps the most important: CO inhibition of the C–CO₂ reaction can be described using a LH reaction scheme on a relative rate basis but, based on the data in this report, not on an absolute rate basis. The presentation of rate data on a relative rate basis effectively removes variables from the equations that are assumed to be independent of temperature or reactant pressure; in the current case, the [C_i] term (total number of active sites). The difference between the equations that are able to describe the measured kinetics (relative rates) and

³ That is, the rate in a CO₂/CO mixture relative to the rate, under the same conditions of temperature and P_{CO₂}, in the absence of CO.

those that are not (presented in this current work) is the presence of the $[C_i]$ term in the analysis.

Recent CCSD work has shown that reactant partial pressure can affect the development of char surface area. For example [20], it has been shown that increasing the partial pressure of CO_2 and H_2O increases the apparent (low-temperature) char–gas reaction rates. When these data are reported on an intrinsic basis, however, the effect of reactant partial pressure is much less. That is, the development of surface area is also affected by reactant pressure. More detailed investigations, as yet unreported, have shown how this effect depends strongly on coal char type and reactant, as well as reactant pressure.

New data demonstrating the variability in surface area developed following reaction at different CO_2 partial pressures, as well as the effects of CO partial pressure are shown for CRC252 chars in Figure 3 and CRC272 chars in Figure 4. For chars made from CRC252 reacting at $900^\circ C$, increasing CO partial pressure increases the surface area developed. This is the case at all pressures of CO_2 ; however the significance of the effect seems to be reduced as P_{CO_2} is increased. The data for CRC252 reacting at $950^\circ C$ are less clear.

The data for chars made from CRC272 are, broadly speaking, similar to those discussed above for chars made from CRC252. Increasing P_{CO} increases surface area for 5 bar CO_2 , and this effect is reduced as the partial pressure of CO_2 increases. This effect of CO_2 pressure is such that at 15 and 20 bar the effect of CO pressure is to, generally, decrease the surface area developed.

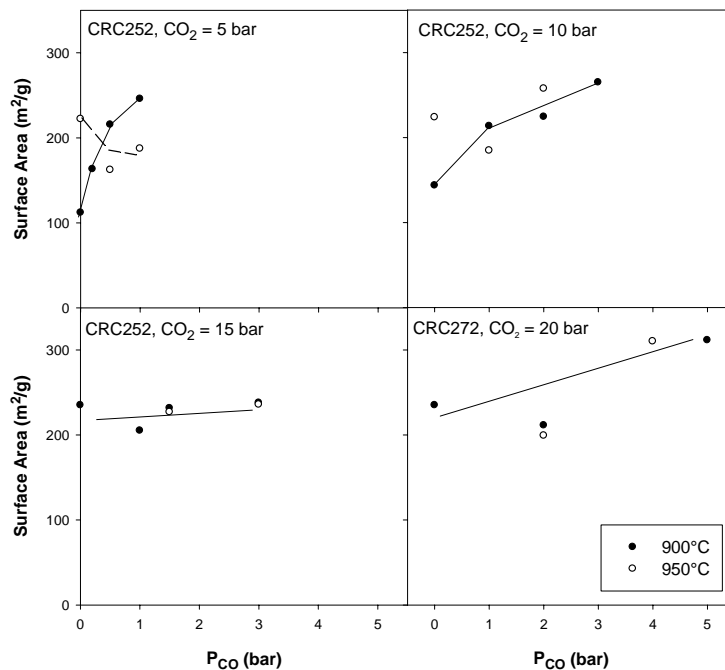


Figure 3: Effects of CO partial pressure on surface area developed at ~10% conversion for chars made from CRC252.

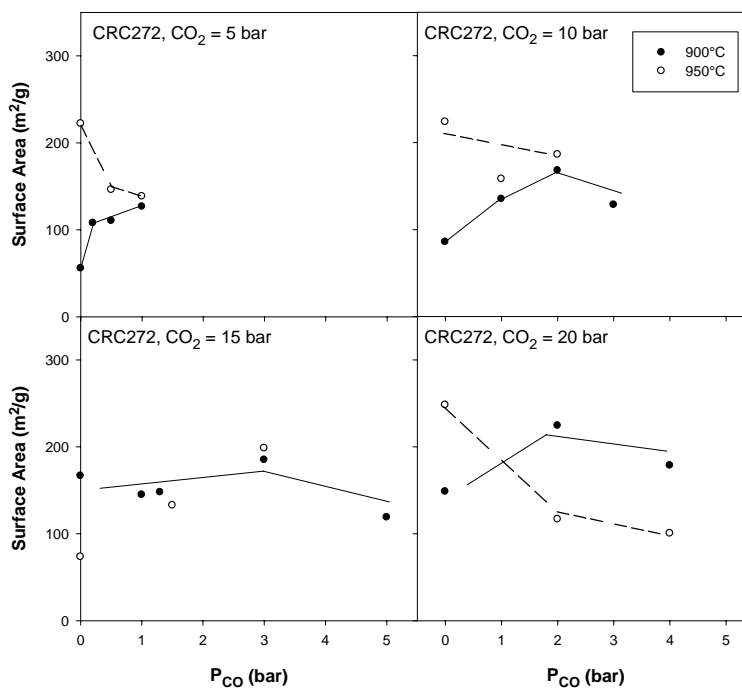


Figure 4: Effects of CO partial pressure on surface area developed at ~10% conversion for chars made from CRC272.

This is an interesting and important outcome. It confirms the suggestion that variations in CO₂ and CO partial pressures have the potential to change the way in which the surface area of char is developed. It also indicates that the nature of the effects is a complex issue, and varies considerably between samples.

There has not been any comprehensive program undertaken that provides an explanation of how CO₂ and CO partial pressures can influence the development of char surface area at a constant level of conversion. It is possible that there is a relationship between the number of sites reacting at a given set of partial pressures and the impact this has on the size of the developing pores. Without further investigation, however, this will remain open to speculation.

In any case, in terms of the current work, this observation can be used as the basis of an explanation of the apparent inability of the LH reaction scheme to describe the high pressure C–CO–CO₂ system. It is possible that the observed effects of pressure on char surface area development are indicative of a more fundamental effect of reactant (and product) pressure on the amount of active sites available. It is well-known that the measurement of surface area using CO₂ adsorption is not a technique suitable for determining the total available active surface of a char sample. Indeed, the debate in the literature regarding total, active, and reactive surface areas is extensive. Given, however, the strong and variable effect of reactant partial pressure on char surface area development, it seems unlikely that the assumption that $[C_t]$ is constant in Equations 2 and 3 is a valid one.

Kinetic analyses of gasification systems usually rely on measurements made at a constant level of conversion. This is due, largely, to the effect conversion is known to have on the development of surface area and, similarly, the active site concentration. If there is an effect of CO₂ and CO partial pressure on $[C_t]$, then it is a possible (and likely) reason for the inability of the ‘entire’ LH equation to describe char gasification kinetics over a wide pressure range with CO present.

The potential impact of surface area/active surface area (and the effect of reactant and product pressure on this impact) also explains why the use of relative rates to determine a CO inhibition factor based on the LH rate equation was successful in describing the data. Describing effects of CO on *relative rates* mathematically removes the $[C_t]$ term from the equations, effectively removing the effect described in this work from the calculations. The results presented here, therefore, reinforce the value of the use of ‘relative rates’ in kinetic analyses of gasification reaction rates, and demonstrate their foundation in a fundamental understanding of the reaction system.

5. FUTURE WORK

Much of the recent CCSD work in this area has been developing systems for the description and application of char gasification kinetics at high pressures. Significant progress has been made in the areas of pure-gas reaction kinetics, reaction kinetics in mixtures of reactants, and kinetics of the inhibition of the gasification reactions. This report represents completion of the planned program of work studying CO inhibition of the C–CO₂ reaction; however, it remains to assess the C–H₂O reaction (and its inhibition by H₂) in terms of the complete LH reaction mechanisms.

The completion of this work means that our knowledge of char gasification kinetics at a stage where they are ready for application to more realistic gasification systems. Investigations into high temperature and high pressure gasification reactions [21, 22] will require ‘Regime 1’ kinetics applied to temperatures of interest (up to 1400°C). Such applications of the kinetic systems described in this and previous work will be a test for the applicability of the low-temperature data to higher temperatures.

It is clear from the data presented here that char surface area continues to play a fundamentally-significant role in controlling the reactivity of chars to CO₂. It is also apparent that our understanding of how char surface area develops during reaction is insufficient. Future work in this area must lead to a better understanding of surface area development at high pressures. The impact of such work lies not only in direct studies of char reactivity, but also in the development and application of pore structure and surface area development models such as the random pore model (which currently contains no effect of pressure at all).

6. CONCLUSIONS

This report presents new data of the reaction kinetics of the char–CO₂ reaction at high pressures inhibited by CO. It extends previous work characterising the high pressure char–CO₂–H₂O reaction system using Langmuir-Hinshelwood reaction schemes by determining data at high pressures and in a form that allows them to be interpreted using LH reaction schemes accepted for use at atmospheric pressure.

These new data demonstrate some deviation from ideal behaviour, based on an atmospheric pressure LH reaction scheme. This deviation is unexpected based on results from previous investigations into this system. The data also demonstrate a strong effect of CO₂ and CO partial pressures on the development of surface area during reaction. This effect is believed to be the underlying reason for the deviation

from ‘ideal’ LH behaviour, as in a LH reaction scheme the total amount of active sites available for reaction is assumed constant.

These results do not suggest that the LH formulation is inappropriate for use to describe gasification kinetics; indeed, they reinforce previous CCSD work in which a ‘relative rate’ method was used to assess the inhibiting influence of CO. This relative rate method removes the effect of surface area, and in light of the new data presented here, is a potentially useful way of incorporating complex CO inhibition kinetics into models of the gasification reaction system.

The development of char surface area during gasification is emerging as a key aspect of understanding gasification science. Future work in this area will need to understand better the way surface area develops during gasification.

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