REACTION OF SYNTHESIS GAS (C+H$_2$O) UNDER SUPERCRITICAL CONDITIONS

F. Salvador, M.J. Sánchez-Montero, C. Izquierdo, J. Montero and A. Salvador
Dpto. Química Física. Plaza de la Merced s/n. 37008 Salamanca. Spain
salvador@usal.es

1. Introduction

The reaction of carbon with steam to form synthesis gas ($CO + H_2$) is the basis of many industrial processes, such as the gasification of coal, the steam reforming of natural gas or hydrocarbons, the regeneration of coked catalysts, the industrial manufacture of activated carbon, etc. It is an endothermic reaction that in the absence of catalysts requires temperatures of 800-1000 ºC for the gasification rate to be appreciable.

In the sixties, and especially in the United States, the interest aroused in the development of coal gasification technology led to a plethora of research projects in this field. A summary of such investigations was reported by Johnson [1].

The main mechanistic studies of the C/steam reaction were performed by Gadsby et al. [2], Long and Sykes [3], Strickland-Constable [4], Johnstone et al. [5], Wike and Rossberg [6], Binford and Eyring [7], and Ergun [8] and later compiled in Laurendeau [9]. Although this reaction has been addressed in many studies, only two relevant works have been conducted at high pressure: i.e., Blackwood and McGrory [10] (1-50 bar) and Klaus and Wolfgang[11] (1-10 bar). In those works the authors reported that the reactivity and reaction mechanism under these conditions differ from when gasification is carried out at atmospheric pressure.

In addition, although in recent years knowledge about and the use of supercritical fluids have increased considerably [12], the C/H$_2$O reaction under supercritical conditions has never been studied.

Here we undertook a comparative study of the reactivity and reaction mechanism of the C/H$_2$O reaction with supercritical water, SCW, and with steam, S, using two carbonized materials of different structure and porosity.

2. Experimental

The gasification experiments with supercritical water and steam were performed with the installation depicted in figure 1.
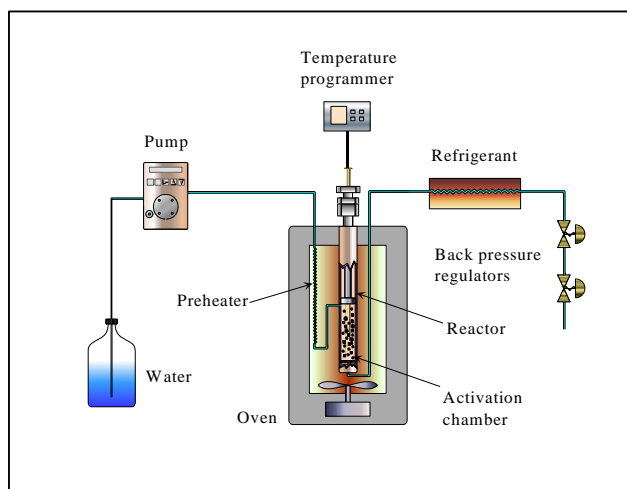

Figure 1. Experimental set-up.

The device is a tubular flow reactor that allows experiments to be performed with temperatures from 25 to 800º C and pressures of 1-400 bar. A wood char and another of anthracite were used in the different studies.

Samples of 4 g of char were gasified at a 4.0 g/min flow of water at atmospheric pressure and at 260 bar at different temperatures, 500-750 ºC. The time of activation was varied to obtain different burn-offs. Burn-off was determined from the loss of char weight and the ash content.

3. Results
3.1 Reactivity

The reaction kinetics of the gasification of a char can be determined globally from measurement of the reactivity R. At constant temperature and in the absence of catalysts, the reaction rate is a function of the concentration of the reactants. Assuming first order with respect to the carbon concentration and pseudo-zero order with respect to the concentration of the water (flow system with an excess of reagent), one has:

$$R = \frac{1}{1 - X_c} \frac{dX_c}{dt} = kC_c \tag{3.1}$$

where X_c is the conversion of the char at time t, k is the rate constant -which will depend on pressure if the rate is not of zero order with respect to the water-, and C_c is the concentration of active sites in the char.

The term dX_t/dt corresponds to the slope of the plot of conversion against time. Normally, $C_t = f(X_t)$. The nature of this function is unknown, but k can be calculated with equation (3.1) for the initial reaction conditions:

$$k = \frac{\left(\dfrac{dX_c}{dt}\right)_0}{C_{c,o}} = \frac{R_0}{C_{c,0}} \tag{3.2}$$

Bearing in mind the Arrhenius equation, it is possible to write the following expression:

$$\ln\left(\frac{dX_c}{dt}\right)_0 = \ln\left(C_{c,o} A\right) - \frac{E_a}{R} \frac{1}{T} \tag{3.3}$$

where A and E_a are the corresponding activation parameters.

Figures 2 and 3 represent the evolution of conversion with time in the activation of the two chars with SCW and with steam at different temperatures and were used to determine the initial reactivity, R_0.

Figure 4 shows the values of R_0 for the gasification of the two chars with SCW and with steam at the different temperatures.

For the same temperature, the reactivity of the wood char is much higher than that seen for the anthracite char with both activating agents. On comparing the two gasifying agents, the reactivity with SCW was much higher than that found with steam. Assuming that the mechanism of gasification with SCW is the same as with steam, the increase in reactivity with pressure could be due to: i) a greater degree of penetration of SCW into the pore structure of the char, allowing the agent to come into contact with a greater number of active sites, ii) modification of the reaction rate constant with pressure. The effect of pressure on the chemical reaction rate has mostly been described in the context of transition-state theory, used for interpreting the kinetics of elementary reactions. According to this theory, the magnitude and direction of the mole fraction-based rate constant k_x depends on the magnitude and sign of the activation volume $\Delta V^{\neq}$, which is defined as the difference between the partial molar volume of the activated complex and the sum of partial molar volumes of the reactants.

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_{T,x} = -\frac{\Delta V^{\neq}}{RT}$$

From this equation it emerges that a negative $\Delta V^{\neq}$ results in a rate acceleration with increasing P, whereas with a positive $\Delta V^{\neq}$ the reaction rate is retarded. Near the solvent's critical point, the values of $\Delta V^{\neq}$ are of the order of liters per mole, owing to the large negative partial molar volumes of the reactants and transition states.
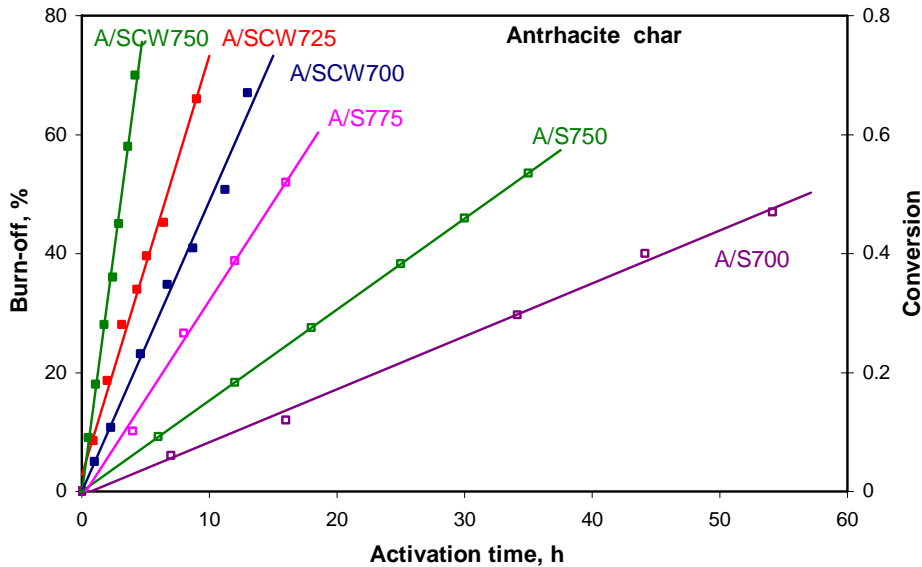

Figure 2. Burn-off and conversion *versus* time. Influence of temperature for gasification of the anthracite char.
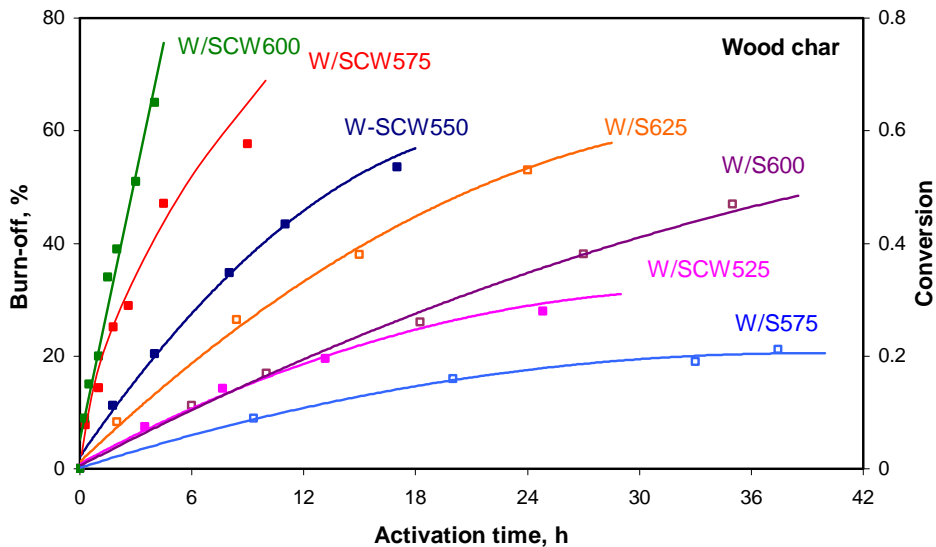

Figure 3. Burn-off and conversion *versus* time. Influence of temperature for gasification of the wood char.

Figures 2 and 3 show that in all series an increase in the gasification rate occurred with the rise in temperature. The dependence of reactivity on temperature was determined from the correlation of the experimental data with the Arrhenius equation (4), Figure 4. Table 1 shows the calculated values of the activation energies and the pre-exponential factors. As is well known, the experimental values of the activation energy will be low if the gasification is governed by diffusion in the pore and in the bulk, and they will be higher if the chemical reaction controls the process. The value of the activation energy, 186 kJ/mol, for the gasification with SCW of the anthracite char

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is lower than that of the oak char, 219 kJ/mol. These differences suggest that there could be some limitation to transport in the pores of the anthracite char because the porosity of this char involves narrower pores than those of the oak char. In addition, the factor, C_0A, of the wood char gasified with SCW is much higher than that of the other char. Taking into account that the pre-exponential factor is associated with the frequency of collision between the molecules of the activating agent and the active sites of the char, these differences could be related to the different porosities of the chars.

For both chars, the values of the activation energy and of the pre-exponential factor were always lower when gasification is carried out with steam. If it is assumed that the main mechanism involved in the reaction of the char with SCW and with steam is the same, these differences could again be explained in terms of the great difficulty with which steam is able to penetrate the pore structure of the char. Accordingly, the wood char will have higher values of this parameter since its pore structure is wider.
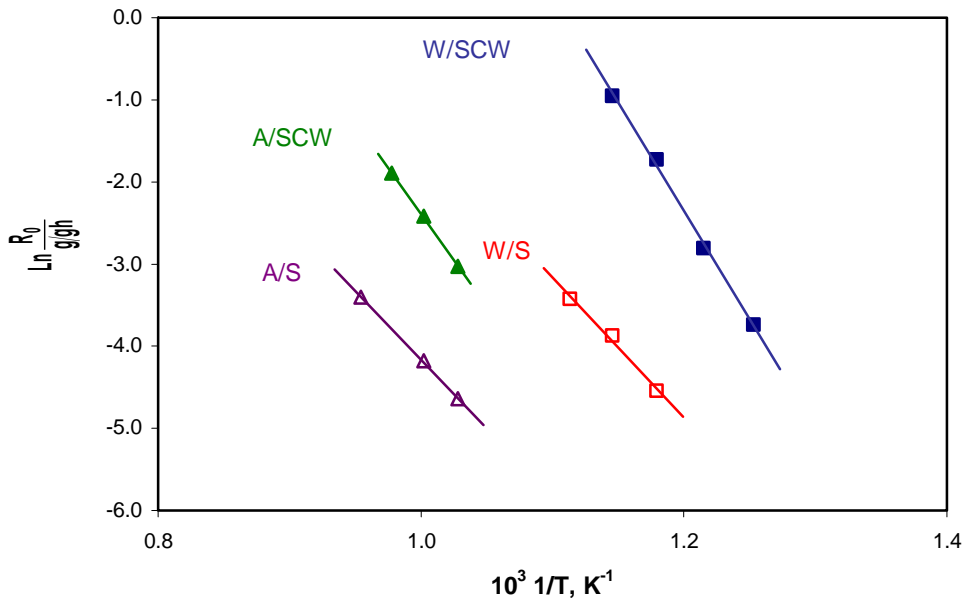

Figure 4. Arrhenius plot for the reaction rate of anthracite char and wood char with SCW and steam.

**Table 1.** Activation parameters values for SCW and steam gasification.

Sample	E_a (kJ/mol)	C_0A (g/gh)
Anthracite/SCW	186	$5.2 \; 10^8$
Anthracite/Steam	138	$2.7 \; 10^5$
Wood/SCW	219	$5.0 \; 10^{12}$
Wood/Steam	142	$6.5 \; 10^6$

3.2 Reaction mechanism

One of the most striking characteristics of supercritical fluids is the formation of a non-uniform spatial distribution of the solvent molecule around a solute molecule. This phenomenon, which has been termed local density enhancement, clustering, or molecular charisma, also occurs at supercritical fluid/solid interfaces as a consequence of the different interaction strengths (adsorption enthalpy) of the solute and solvent with the solid surface. The formation of a higher-density cluster around a solute in supercritical reaction mixtures can affect the rate of the chemical reaction through different mechanisms. For example, additional solvent molecules can become incorporated into the transition-state structure directly or may act in concert to stabilize that
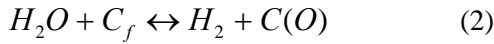
complex through solvent-like electrostatic forces. All this will introduce modifications in the reaction mechanism.

In the particular case of gasification with steam, the global reaction can be expressed thus:
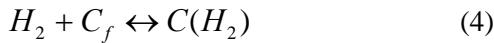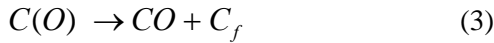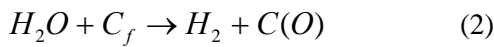
$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$
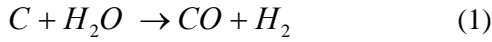
Two equivalent mechanisms have been proposed[11]:
I Oxygen Exchange Model:

$$H_2O + C_f \leftrightarrow H_2 + C(O) \qquad (2)$$

$$C(O) \rightarrow CO + C_f \quad (3)$$

II Hydrogen Inhibition Model:

$$H_2O + C_f \rightarrow H_2 + C(O) \qquad (2)$$
$$C(O) \rightarrow CO + C_f \qquad (3)$$
$$H_2 + C_f \leftrightarrow C(H_2) \qquad (4)$$

where C_f is a carbon-free active sites, $C(O)$ is the oxygen surface complex, and $C(H_2)$ is adsorbed hydrogen.

In terms of energy, the $C(O)$ complexes formed are more difficult to remove from the surface. According to Strickland-Constable [4],the rate-determining step in the mechanism is the slow desorption of CO from the surface: reaction (3).

Usually, during gasification with steam at atmospheric pressure the gases formed are H_2 and CO. However, sometimes small amounts of CO_2 and CH_4 appear. Most investigators assume that the CO_2 is not a primary product from the C/steam reaction but that it comes from the shift reaction:

$$H_2O + CO \leftrightarrow CO_2 + H_2 \qquad (5)$$
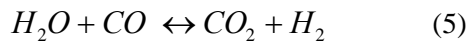
This equilibrium is shifted towards the formation of CO_2 only after very high temperatures have been reached (T>1200 ℃).

Very few studies using elevated pressures have been published: Blackwood and McGrory [10] (1-50 atm), Klaus and Wolfgang [11] (1-10 bar), Matsumura et al. [13] (25.5- 34.5 MPa (SCW). Under these conditions, the reactivity is greater than at atmospheric pressure and appreciable amounts of other reaction products, such as CO_2 ands CH_4, are produced, even when working at temperatures far below 1200 ℃.

In the present study, when gasification was performed with SCW the composition of the gas in all cases contained a large amount of H_2 and $CO_2$and a small amount of CH_4 and CO (64 % of H_2, 33 % of CO_2, 2% CH_4 and 1 % of CO), confirming that the water-gas shift reaction must be of great importance.

Melius et al. [14] investigated the mechanism of the water-gas shift reaction under supercritical conditions and proposed that the reaction would take place in two steps, with the formation of formic acid, which would later decompose into CO_2 and H_2O:

$$CO + (n+1)H_2O \rightarrow HCOOH + nH_2O \rightarrow CO_2 + H_2 + nH_2O$$
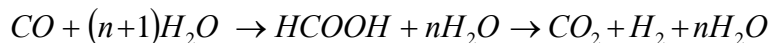
Quantum chemistry calculations carried out by those authors suggest that water may act as a catalyst for the reaction by lowering the energies of activation. These catalytic water molecules are more likely to participate in the reaction if it is carried out in supercritical water because its high compressibility promotes the formation of solute-solvent clusters. These effects of the density of water in the water-gas shift reaction were also investigated by Stevens et al.[15] in a study of the reaction in SCW from 410 to 520 ℃ and 2.0-60 MPa. The results of this experimental work revealed a noticeable increase in the reaction rate with the increase in pressure. The data support the theoretical prediction of the existence of a polar transition-state complex, characterized by an

unusually large negative volume of activation that results from a dramatic change in the local density of the SCW.

Although supercritical conditions provide a large displacement in the equilibrium of the water-gas shift reaction towards the formation of CO_2 and an increase its rate, there are serious doubts as to whether all the CO given off from the surface of the carbon during the gasification, reaction (3), is converted into CO_2 in the short residence time in the flow-mode gasification reactor.

Accordingly, and taking into account the mechanism of the water-gas shift reaction propitiated by the supercritical conditions, this latter reaction could be considered an alternative to reaction (3) and would be responsible for the greater reactivity of the char in SCW:

$$C(O) + H_2O \rightarrow CO_2 + H_2 + C_f \quad (6)$$

This reaction would be favored by the formation of clusters or aggregates on the C(O) of the surface. According to this reaction, the CO_2 would be a primary product of the gasification process.

Owing to the absence of kinetic data concerning the gasification of carbon with SCW, further intense work should be carried out to confirm this hypothesis.

Conclusions

The rate of gasification of the two chars with SCW is much higher than in gasification with steam as a result of the better penetration of SCW into the pore structure of the chars. The wood char was more reactive than that of anthracite and required lower temperatures (525-600 ºC). The activation energies and the pre-exponential factors of the Arrhenius equation suggest that: i) the process of gasification of wood char with SCW is governed by the chemical reaction; ii) in the case of the anthracite char/SCW, the process could be partially controlled by transport and diffusion phenomena in the pores, since this char has a narrower pore structure, and iii) the gasification of both chars with steam is diffusion-controlled.

Although the results reported here do not confirm the idea that the mechanisms of reaction with SCW and with steam are necessarily different, there is evidence to suggest that such a change in mechanism would be possible as a result of the special properties of SCW (low polarity, high density, cluster formation, etc.).

Finally, when SCW is used the gasification process is accompanied by the extraction of mineral matter, such that purer activated carbons can be obtained.

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