# KINETIC AND MECHANISTIC STUDY OF THE REACTION OF A CARBON FIBER WITH SUPERCRITICAL CO$_2$

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## 1. Introduction

The gasification of carbon with CO$_2$ is an endothermic reaction which in the absence of catalysts requires temperatures close to 1000 ºC for the rate to be appreciable. The main mechanistic studies on the C/CO$_2$ reaction were performed by Gadsby et al.[1], Reif [2], Ergun [3], Menster and Ergun [4], Strange and Walker[5] and Biederman et al. [6], later compiled in Laurendeau [7]. Although many studies have addressed this reaction, only a few have been carried out at moderate pressure [8-10], and there have been no studies performed under supercritical conditions.

The use of supercritical CO$_2$ and water in the preparation of adsorbent carbonaceous materials was reported by Salvador et al. [11]. Since then, however, the number of papers published on the topic has been very low [12-14]. Li et al. [12] carried out a brief study of the preparation of a carbon fiber with supercritical water, reporting a small development in surface area and the creation of some mesoporosity.

In light of the foregoing, it seems necessary to further investigate the C/CO$_2$ reaction at high pressure with a view to understanding the behaviour of supercritical CO$_2$, SCCO$_2$, as an gasifying agent. Here we address a comparative kinetic and mechanistic study of the C/CO$_2$ reaction in the supercritical state and at atmospheric pressure, ATCO$_2$.

## 2. Experimental

All studied samples were prepared from a common precursor; in this case a phenolic fiber, Novoloid, supplied by Kynol. This fiber was carbonized in nitrogen (100 cm$^3$/min) (25 ºC; 1 bar) in a horizontal furnace at 5 ºC/min with a residence time of 90 min at 700 ºC.

Gasification of the carbon fiber with SCCO$_2$ and ATCO$_2$ was accomplished in a flow reactor placed inside an oven. Figure 1 shows a scheme of the set-up.
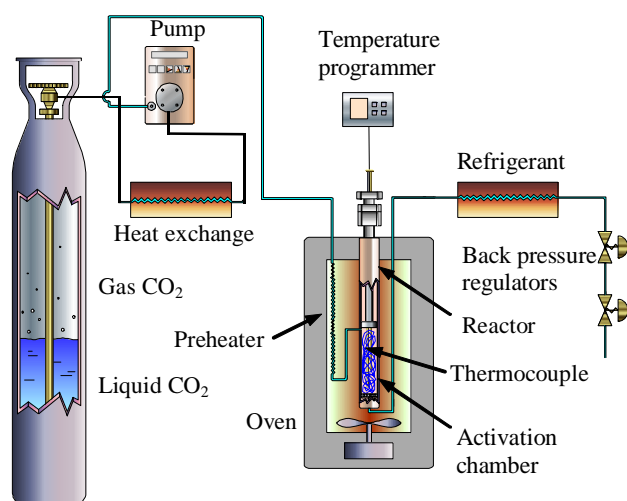


**Figure 1.** Experimental set-up.

The $CO_2$ is stored in a cylinder in the liquid state at a pressure of $50 \pm 2$ bar. It is impelled by a high pressure fluid pump (Thar P-50) such that it must previously be cooled to -2 ºC, to ensure the liquid state. In all experiments, flow rate was 1.5 cm$^3$ of liquid $CO_2$ per minute.

Samples of 2.5 g of carbonized fiber were placed in the gasification chamber and subjected to a stream of $N_2$ (100 cm$^3$/min) until the reactor had reached the working temperature. Once this temperature had been reached, the stream of $N_2$ was replaced by the $CO_2$ stream at the working pressure and temperature.

The gasification experiments were performed at 110 bar and at atmospheric pressure at different temperatures: 750, 775 and 800 ºC, maintaining these temperatures for the appropriate time in order to obtain gasification within the range of 8-67%.

## 3. Results and discussion

### 3.1. Kinetic studies

The reactivity, $r$, of the global gasification process is usually measured as the number of grams of carbon transformed per hour and per gram of carbon (g/gh). Often, this reactivity does not coincide with the rate of the chemical reaction, mainly because of diffusional limitations imposed by the microporous structure of the carbonized material. However, it is well known that the experimental values of the activation energy will be low if the gasification is controlled by diffusion in the pores and in the bulk, and that they will be higher if the process is controlled by the chemical reaction [15].

At constant temperature, and in the absence of catalysts and diffusional limitations, the global intrinsic reactivity (chemical reactivity) will be a function of both the concentration of active sites, $C_t$, present at the surface of the carbonized material and of the partial pressure of the activating agent.

Assuming first order with respect to the concentration of active sites, and pseudo-zero order with respect to the activating agent (flow-mode gasification system, with a large excess of activating agent), the intrinsic activity can be expressed as follows:

$$r = k\,C_t \qquad\qquad (1)$$

Normally, $C_t$ is a function of the degree of gasification. The nature of this function is unknown, such that it is not possible to integrate the previous equation to obtain the rate constant $k$. Despite this, the equation can be particularized for the first moments of the gasification:

$$r_0 = kC_0 \qquad\qquad (2)$$

where $r_0$ is the initial gasification rate and $C_0$ is the initial concentration of active sites; $r_0$ can readily be measured from the burnoff/time curve.

The effect of temperature on the gasification rate can now be calculated using the Arrhenius equation:

$$r_0 = C_0\,A\,exp\left(E_a/RT\right) \qquad\qquad (3)$$

where $A$ is the pre-exponential factor and $E_a$ is the activation energy.

In the present work, the kinetic study was conducted at temperatures of 750, 775 and 800 ºC. A series of runs was made at each of these temperatures using $SCCO_2$ and $ATCO_2$, in a gasification range of 8-67%. The results are shown in figure 2 and indicate that the gasification rate for each series can be considered constant between 0% and low burnoff values. Nevertheless, this rate decline for high burnoffs, especially when $ATCO_2$ is employed.

For the same temperature, the gasification rate of the fiber with $SCCO_2$ is significantly greater than with $ATCO_2$, revealing a clear dependence of the gasification rate on pressure. Global reactivity, $r_0$, at each temperature can be calculated from the slopes of the initial sections.
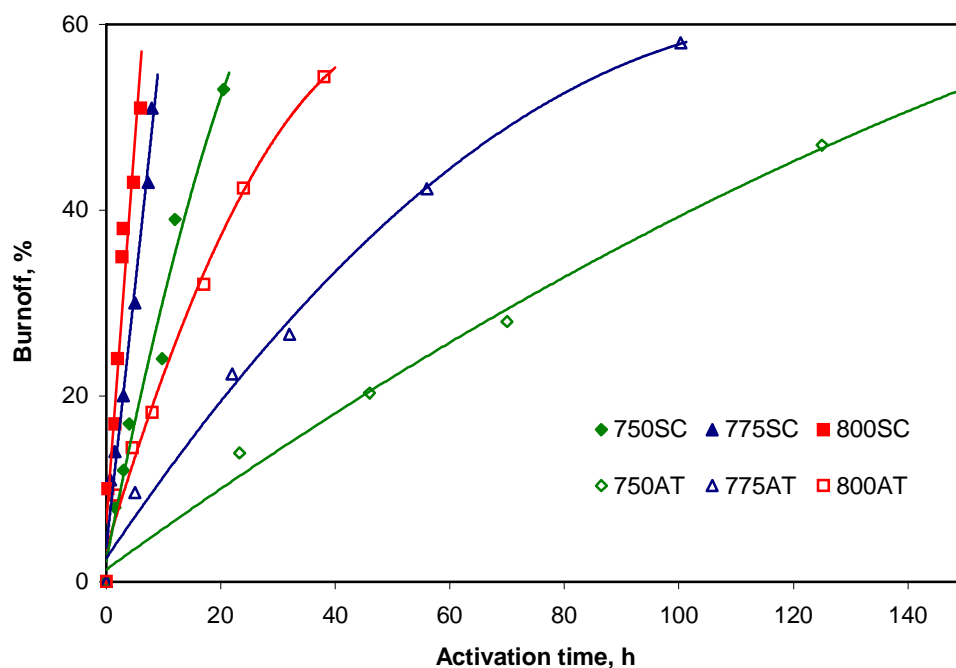
**Figure 2.** Effect of temperature and the activating agent on the gasification of a carbonized fiber.

The dependence of $kC_0$ on temperature is shown in Arrhenius plot in figure 3 for both activating agents. The lines through the experimental points were determined using the least squares method. The slopes of those lines provide the value of the activation energy, $E_a$, and the intercepts give the value of $C_0A$ (table 1). Evidently, the high values found confirm that they correspond to the intrinsic global kinetic parameters for $CO_2$ gasification.
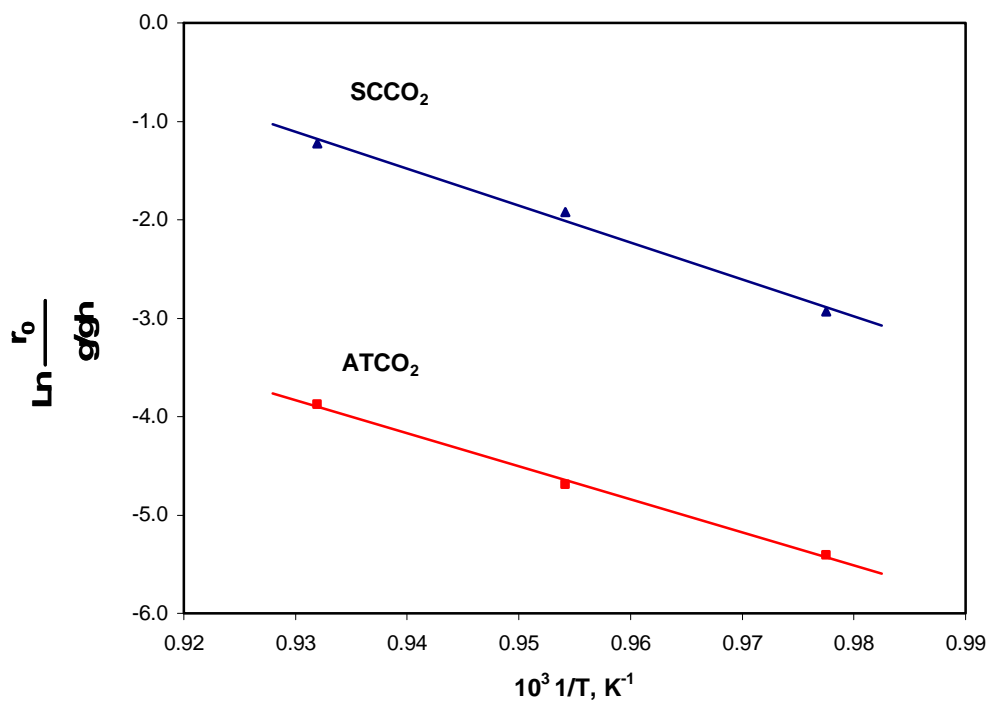


**Figure 3.** Arrhenius plot for the reaction of carbonized fiber with $SCCO_2$ and $ATCO_2$.

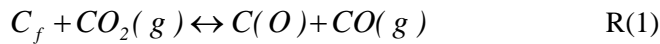**Table 1.** Values of the activation parameters for the gasification of the carbon fiber with $SCCO_2$ and $ATCO_2$.

| Sample | $E_a$ (kJ/mol) | $C_0A$ (g/gh) |
|---|---|---|
| Carbonized fiber/$SCCO_2$ | 312 | $4.8 \ 10^{14}$ |
| Carbonized fiber/$ATCO_2$ | 279 | $8.4 \ 10^{11}$ |

Few values of these parameters are available in the literature. For the gasification of different chars with $CO_2$, the true activation energy lies between 230 and 370 kJ/mol and the kinetic order of the reaction with respect to $CO_2$ is between 1 and 0. 1 for pressures lower than 1 atm and 0 for pressures above 15 atm [7].

The activation energy of 312 kJ/mol found in the present study for gasification with $SCCO_2$ is very high and approaches the activation energies found for the gasification of ultra-pure carbons (370 kJ/mol) [7, 16]. Moreover, the activation energy of 279 kJ/mol for the gasification with $ATCO_2$ is also high, suggesting that the gasification is not diffusion-controlled. These different activation energies obtained for the two activating agents suggest that the gasification could occur through different mechanisms. Additionally, the values of $C_0A$ are different, being greater for the gasification accomplished with $SCCO_2$. This would account for the greater reactivity observed with this activating agent. Bearing in mind that factor $A$ is associated with the frequency of collisions between the molecules of the activating gas and the active sites, the difference in the value of $C_0A$ could be due to the fact that the active sites involved in the gasification with $SCCO_2$ would be different and more numerous than those involved in the gasification with $ATCO_2$, also suggesting a change in the reaction mechanism at high pressure.

Two equivalent mechanisms have been proposed to explain the $C/CO_2$ reaction at atmospheric and subatmospheric pressure: an oxygen-exchange mechanism and a mechanism of inhibition by CO adsorption. Although both mechanisms lead to the same rate equation, there is strong evidence in favour of the first one [4].

Oxigen-exchange mechanism [3]:

$$C_f + CO_2(\,g\,) \leftrightarrow C(\,O\,) + CO(\,g\,) \qquad\qquad R(1)$$

$$C(\,O\,) \rightarrow CO(\,g\,) + C_f \qquad\qquad R(2)$$

where $C_f$ represents the number of free active sites and C(O) the sites occupied by an atom of oxygen.

The rate-determining step is the slow desorption of CO from the surface (eq. 2), and it leads to the following rate equation:
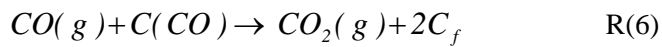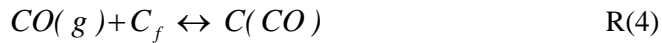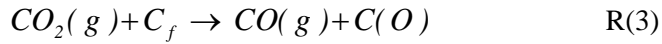
$$r = \frac{a \ p_{CO_2}}{p_{CO_2} + bp_{CO} + c}$$

where $a = C_t k_2;\ b = k_{-1}/k_1\ y\ c = k_3/k_1.$

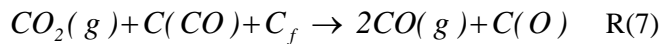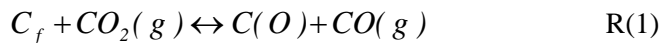This expression affords a kinetic reaction order of 1 for low pressures and 0 for high ones.

Although the oxygen-exchange mechanism allows one to predict the 0 order observed for high pressures, Blackwood and Ingeme [7] have reported that at between 4 and 40 atm the reactivity is greater than that attributed by the oxygen-exchange mechanism. These authors propose an expression for the reactivity thus:

$$r = \frac{a' \, p_{CO_2} + b' \, p_{CO_2}^2}{1 + c' \, p_{CO} + d' \, p_{CO_2}}$$

with a second-order dependence with respect to the pressure of $CO_2$, suggesting the following mechanism:

$$CO_2(g) + C_f \rightarrow CO(g) + C(O) \qquad \text{R(3)}$$

$$C(O) \rightarrow CO(g) + C_f \qquad \text{R(2)}$$

$$CO(g) + C_f \leftrightarrow C(CO) \qquad \text{R(4)}$$

$$CO_2(g) + C(CO) \rightarrow 2CO(g) + C(O) \qquad \text{R(5)}$$

$$CO(g) + C(CO) \rightarrow CO_2(g) + 2C_f \qquad \text{R(6)}$$

The mechanistic work of Blackwood and Ingeme [8] is the only one that has been carried out in an attempt to explain the increase in reactivity with pressure. However, more recently a simple and more realistic mechanism consistent with the oxygen-exchange mechanism has been suggested [17]:

$$C_f + CO_2(g) \leftrightarrow C(O) + CO(g) \qquad \text{R(1)}$$

$$C(O) \rightarrow CO(g) + C_f \qquad \text{R(2)}$$

$$CO_2(g) + C(CO) + C_f \rightarrow 2CO(g) + C(O) \qquad \text{R(7)}$$

In reaction R(7), a molecule of $CO_2$ reacts with an oxygenated complex at the surface, which decomposes to release a molecule of CO. At the same time, the $CO_2$ is reduced, giving rise to a second molecule of CO and forming a new oxygenated surface complex. With this mechanism the gasification rate will now be determined by the contribution from reaction R(2) and reaction R(7), thereby explaining the increase in the reaction rate with the increase in pressure. Reaction R(7) would be favoured by the increase in pressure, above all when the $CO_2$ is under supercritical conditions. One of the most peculiar characteristics of supercritical fluids is the formation of higher-density clusters or aggregates around the molecules of a solute and in the fluid-solid supercritical interphase as a consequence of the different interaction strengths (adsorption enthalpy) of solute and solvent with the solid surface. The formation of such clusters may modify the reaction rate by acting on the transition complex, either stabilizing it through solvent-like electrostatic forces or by direct incorporation of solvent molecules into the complex.

A reaction equivalent to R(7) has been proposed by Salvador et al. [18] to explain the increase in the $C/H_2O$ reaction rate when carried out with supercritical water.

**Conclusions**

The present kinetic study shows that the rate of gasification of the fiber with $SCCO_2$ is significantly greater than that obtained with $ATCO_2$, with a clear dependence of the gasification rate on pressure.

The different values of the parameters of the Arrhenius plot, $E_a$ and $C_0A$, obtained in the gasification of the fiber with $SCCO_2$ and $ATCO_2$ suggest that it occurs through different reaction mechanisms.

Although the mechanism of Blackwood and Ingeme [8] is the only one that has been proposed to explain the increase in reactivity with pressure, another simpler mechanism, the oxygen-exchange mechanism, does seem plausible. In this new mechanism, the $CO_2$ would interact with the oxygenated

complexes of the surface of the carbonized fiber, facilitating its removal. This interaction would be favored by the formation of clusters or aggregates as a consequence of the high pressure.

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