Interaction Soot-SO$_2$. Experimental and Kinetic Analysis

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ABSTRACT

This study aims to evaluate the capability of SO$_2$ to interact with soot and to determine the kinetics of this reaction under conditions of interest for combustion. The conditions of the soot reactivity experiments were: 1% SO$_2$ with nitrogen to balance, around 10 mg of soot, and different reaction temperatures for each run: 1275, 1325, 1375, 1425, and 1475 K. Results demonstrate that SO$_2$ does interact with soot. The evaluation of the soot reactivity has been based on the calculation of the time for the complete conversion of carbon through the employment of the Shrinking Core Model equations for decreasing size particle with chemical reaction control. The reactivity of soot with SO$_2$ increased by a factor of about 3 when increasing the reaction temperature of the test from 1275 K to 1475 K. Kinetics in terms of Arrhenius parameters showed that the activation energy of the interaction of soot with SO$_2$ was around 82 kJ/mol.

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Introduction

Usually, sulfur is present in fossil fuels and even in biofuels and household wastes. The 20
combustion of these sulfur-containing fuels releases the sulfur to the gas-phase, principally
as sulfur dioxide (SO$_2$) (Cullis and Mulcahy, 1972; Glarborg, 2007; Johnsson and
Glarborg, 2000). When the flue gas recirculation (FGR) technique is applied in combustion processes, the SO$_2$ in the flue gas can be removed before or after the recirculation of
the gases, which in the latter case may affect the overall combustion scheme and/or the 25
fate of other pollutants, such as soot. The interactions between sulfur dioxide and soot can
be produced through indirect ways, by altering the radical pool (SO$_2$ has been reported to
act as a radical sink, e.g., Alzueta et al., 2001) or through direct reaction of SO$_2$ with the
soot and hydrocarbons involved in the soot formation processes (see, e.g., Abián et al.,
2015a; Gülder, 1993; Lawton, 1989). 30

The interaction of carbon with SO$_2$ has been studied for different carbon materials.
Humeres et al. (2002) studied the kinetics and product distribution under chemically
controlled steady-state conditions of the reactivity of SO$_2$ with various carbon materials
with different degrees of crystallinity. The authors found CO$_2$ and S$_2$, in the ratio 2:1, as
the main products for all of the carbon materials analyzed. The reaction sequence 35
suggested involved the adsorption of SO$_2$ on an active site of carbon to consecutively
lead to the main products CO$_2$ and S$_2$. Globally, the SO$_2$ + C ⌧ CO$_2$ + ½ S$_2$ reaction was

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proposed as the path for SO_2 reduction, as it is the only reaction whose stoichiometry corresponds to the ratio CO_2:S_2 equal to 2 (Humeres et al., 2002).

The reactivity of soot towards different oxidants has been studied under a variety of conditions. In the review presented by Stanmore et al. (2001) on the oxidation of soot, the oxidizing compounds considered are oxygen, carbon dioxide, water vapor, and nitrogen dioxide, but no mention is done to sulfur dioxide. To our knowledge, there is a lack of studies on the oxidation of soot with SO_2 under non-catalyzed combustion conditions. In this context, the objective of this work is to study, in terms of kinetic analysis, the reactivity of soot with SO_2 at high temperatures (1275–1475 K). To that end, a series of experiments was performed under chemically controlled conditions to further analyze the kinetics of the soot-SO_2 interaction and determine the activation energy of the reaction. Soot samples obtained in a laboratory facility, from the pyrolysis of ethylene (one of the main soot precursors) in a N_2 atmosphere at high temperature (1375 K) were selected for this study. This soot was characterized and used in a previous study regarding the oxidation of soot with O_2 and CO_2 (Abián et al., 2012).

Experimental installation and procedure

The soot samples were prepared in a quartz flow reactor from the pyrolysis of 30,000 ppm of ethylene in a N_2 atmosphere at 1375 K, following the methodology described in Abián et al. (2014). The experimental installation used for the formation of soot has been successfully used thus far in a number of earlier works by our group (e.g., Abián et al., 2015a; Esarte et al., 2009; Ruiz et al., 2007a).

The soot produced was collected in a quartz fiber thimble (mesh light lower than 1 μm) placed at the outlet of the reactor. Previously to the reactivity experiments, each soot sample is annealed by heating for 1 h in a nitrogen atmosphere at its formation temperature (1375 K), to remove adsorbed compounds on the surface of the particles. Afterwards, the soot sample is subjected to the reactivity experiments.

The interaction experiments of the soot samples with the reactant SO_2 were carried out in an experimental installation, which has been also used with success in a number of earlier works by our research group, addressing heterogeneous gas-carbon materials reactions (e.g., Arnal et al., 2012a; Guerrero et al., 2005).

In the reactivity experiments, the reaction takes place in a quartz tubular reactor with a 15-mm inside diameter and with a bottle neck in the middle where a quartz wool plug is placed. A mixture of around 10 mg of soot and 350 mg of silica is deposited over the plug resulting in a thin layer. Silica is used to facilitate the introduction of the sample in the reactor and prevent the agglomeration of soot particles. A given SO_2 concentration of 1% has been used for all of the experiments, whereas the influence of different reaction temperatures (specifically 1275, 1325, 1375, 1425, and 1475 K) has been analyzed. Gases are fed into the reaction system through mass flow controllers at a total flow rate of 1000 mL (STP)/min. N_2 has been used to balance. During the heating of the reaction system up to the reaction temperature, an inert flow of N_2 is fed. Once the desired temperature is reached, the reactant gaseous mixture is fed into the reactor.

In each experiment, the reaction products are cooled down at the reactor outlet up to room temperature by means of external air refrigeration and analyzed as a function of the reaction time. To measure the concentration of the product gases, a continuous infrared (IR) CO/CO_2 analyzer and a Fourier transform infrared (FTIR) analyzer calibrated to determine sulfur compounds have been used. The estimated uncertainties of the measurements are ±5% for
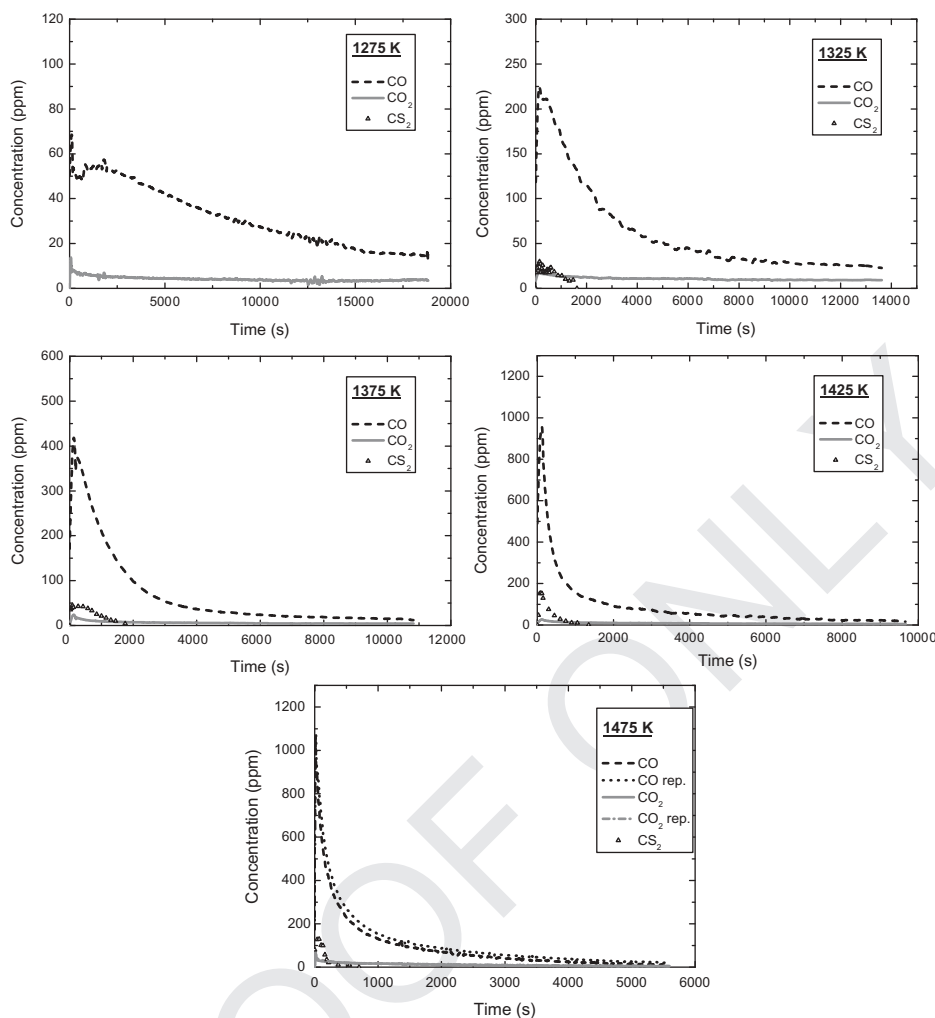
Figure 1. Evolution of CO, CO_2, and CS_2 concentrations as a function of time. Influence of reaction temperature on the soot interaction with 1% SO_2.

the continuous IR analyzer and ±10% for the FTIR, but not less than 10 ppm. The uncertainty in the experimental procedure was analyzed by performing repeatability experiments (an example is included in Figure 1). Considering the different experimental uncertainty sources, a general good response was obtained in the results, with an agreement within 20% in the subsequently 85 determined time for the complete conversion of carbon.

Results and discussion

Interaction soot-SO$_2$: experimental results and product distribution

In order to analyze the interaction of soot with 1% SO_2, several experiments were performed at different reaction temperatures (specifically at 1275, 1325, 1375, 1425, and 90 1475 K). Previous studies regarding the interaction of carbon materials with SO_2 show

that products from the reaction are mainly CO_2 and S_2, but also CO, COS, and CS_2, depending on the specific operating conditions the carbon sample considered and whether the reaction was diffusional or chemically controlled (Humeres et al., 2002). As previously mentioned in the present work, the outlet gas composition was analyzed by means of a continuous IR CO/CO_2 analyzer and a FTIR. In the present experiments, the formation of CO, CO_2, and CS_2 was experimentally observed. COS was not detected under any experimental condition analyzed. SO_2 concentration was quantified and results indicated that it was kept practically constant at 1% throughout the experiments; therefore, no more considerations are given in relation to the time evolution of this reactant.

Elemental analysis of the soot samples revealed the following composition: 97.77 wt% C, 1.01 wt% H, and 0 wt% N (Abián et al., 2012). Considering the resultant H/C ratio in weight (equal to 0.01), the composition of the reacting mixture (1% SO_2 in N_2), and the estimated uncertainty of the FTIR measurements, the formation of H_2S and of any other hydrogen-containing compound was directly disregarded.

Figure 1 shows the concentration results (in ppm) of CO, CO_2, and CS_2 obtained from the interaction soot-SO_2 at the different reaction temperatures. This figure also shows, as an example, repeatability experimental results obtained at 1475 K.

As it can be observed in Figure 1, for all of the temperatures studied, CO is the main product of the reaction. CO_2 concentrations are always around 25–30 ppm at the first stages of the reaction to further decrease to concentrations lower than 10–15 ppm, which can be considered as negligible. CS_2 was only detected at the very first stages of the reaction, and for temperatures higher than 1275 K. It is important to mention that the remaining carbon weight decreases as the reaction advances and, thus, for a given experiment the total amount of the different products is also expected to decrease with time up to insignificant concentrations when soot is fully consumed.

Considering the product distribution of the present experiments, the possible reaction paths of the reaction of soot with SO_2 are discussed as follows.

Humeres et al. (2002) proposed that the interaction of different carbon materials with SO_2 occurs through the adsorption of SO_2 on active sites leading to the formation of CO_2 and S_2 (r.1). Consecutively, insignificant amounts of CO are slowly formed by the Boudouard reaction (r.2). Once CO is formed, it reacts with sulfur complexed on active sites to form COS, and possibly CS_2 is produced from the same site active.

$$SO_2 + C \rightarrow CO_2 + \tfrac{1}{2}S_2 \tag{r.1}$$

$$CO_2 + C \leftrightarrow 2CO \tag{r.2}$$

Another path for CO formation could be the direct reaction of SO_2 with the carbonaceous compound to produce CO and COS (r.3):

$$SO_2 + 2C \rightarrow CO + COS \tag{r.3}$$

As previously mentioned, in our work CO is the main product detected under all conditions analyzed and CO_2 concentrations can be considered negligible (Figure 1). This fact indicates that in the case of reaction (r.1) as the main path, the CO_2 formed should quickly react through (r.2) to form CO. The Boudouard reaction (r.2) for CO formation is an endothermic reaction and it would be both thermodynamic and kinetically favored by temperature.

Taking into account these considerations, under the conditions of the present work, the interaction of soot with SO_2 could be initiated in a parallel process leading to CO formation through both the reaction sequence (r.1) and (r.2), and the direct CO formation (r.3).

Stoichiometry in reaction (r.3) shows a ratio CO:COS equal to 1. However, COS was not experimentally detected at any of the conditions studied. Therefore, COS must be regarded as an intermediate under the studied conditions. On the basis of the previous carbon-SO_2 interaction study (Humeres et al., 2002), the COS consumption could be described according to the global reactions (r.4) and/or (r.5); although, the main elemental reaction pathways involved in the decomposition of CO can be found in Abián et al. (2015b):

$$2COS \rightarrow 2CO + S_2 \tag{r.4}$$

$$2COS \rightarrow CO_2 + CS_2 \tag{r.5}$$

Reaction (r.5) produces CO_2 and CS_2 in the same proportion. However, as it can be observed in Figure 1, the amount of CO_2 and CS_2 are not the same for a given temperature and neither in the time. CS_2 is only present as a final product at the very first stages of the reaction and for specific temperatures (1325 K and above), whereas CO_2 always appears as a final product. Besides, when present, CS_2 concentrations are generally higher than the CO_2 ones. Therefore, if reaction (r.5) would occur, most of the CO_2 formed should be converted, for example, through reaction (r.2). On the basis of this discussion, both COS consumption paths [(r.4) and (r.5)] may happen.

Regarding the source of the little amount of CO_2 quantified, besides the SO_2 + C reaction (r.1) and the conversion of COS (r.5), the gas-phase reaction of CO with SO_2 can also produce CO_2 (r.6) (Alzueta et al., 2001; Giménez-López et al., 2011):

$$CO + SO_2 \leftrightarrow CO_2 + SO \tag{r.6}$$

In the case of CS_2 formation, besides reaction (r.5), two other possible reaction paths are proposed (Humeres et al., 2002):

$$C + S_2 \rightarrow CS_2 \tag{r.7}$$

$$C + 2COS \rightarrow CS_2 + 2CO \tag{r.8}$$

Taking into account the product distribution of the present work, the formation of CS_2 could be produced through any of these reactions [(r.5), (r.7), and (r.8)].

Considering all of the above, the overall reaction scheme of possible paths involving the interaction of soot with SO_2 (shown in Figure 2) seems to be more complicated than the mechanism for the interaction of carbon with SO_2 proposed by Humeres et al. (2002).

Kinetic study

The kinetics of the reactivity of soot towards SO_2 was obtained from the values of the remaining carbon weight (W_C) for different reaction times. The Shrinking Core Model for decreasing size particle with chemical reaction control (Levenspiel, 1999) was used. The
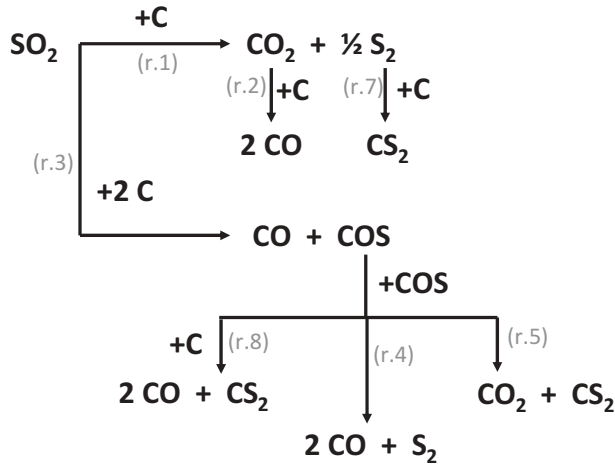
Figure 2. Global reaction scheme of possible paths involved in the reaction of soot with SO_2.

equations of the model have been applied successfully in similar previous studies (e.g., Arnal et al., 2012b; Ruiz et al., 2007b).   175

The remaining carbon weight in the reactor at any time (W_C) is calculated from the time variation concentrations of CO, CO_2, and CS_2 (as main reaction products) in the outlet gas. In this way, W_C can be calculated as:

$$W_C = W_{C_0} - M_C \cdot F_T \cdot 10^{-3} \int_0^t (C_{CO} + C_{CO_2} + C_{CS_2})dt \tag{1}$$

where W_{C_0} is the initial amount of carbon (in mg) in the reactor [Eq. (2)]; M_C is the   180
atomic weight of carbon; F_T is the exit flow in moles of total gas per second [Eq. (3)]; C_{CO}, C_{CO_2}, and C_{CS_2} are the concentrations in ppm of CO, CO_2, and CS_2, respectively, at time t.

$$W_{C_0} = M_C \cdot F_T \cdot 10^{-3} \int_0^\infty (C_{CO} + C_{CO_2} + C_{CS_2})dt \tag{2}$$

$$F_T = \frac{Q \cdot P}{R \cdot T} \tag{3}$$

In Eq. (3), Q is the total flow rate fed to the reactor (m^3/s); P is the reactor pressure (Pa); R 185
is the universal gas constant (Pa m^3/mol K); and T is the reactor temperature (K).

According to the Shrinking Core Model, the reaction rate can be referred to the external surface of the particle, and may be also described as a function of the remaining carbon weight during the reaction, W_C. The expressions for decreasing size particle with chemical reaction control are presented in Eqs. (4) and (5):   190

$$-\frac{1}{S_{ext}} \cdot \frac{dN_C}{dt} = bk_S C_{reactantgas}^n \tag{4}$$

$$-\frac{1}{W_C^{2/3}} \cdot \frac{dW_C}{dt} = Cbk_S C_{reactantgas}^n \qquad (5)$$

In these equations, N_C are the moles of carbon; b is the carbon stoichiometric coefficient according to the global reaction with t.e reactant gas, in this case SO_2; k_S is the rate constant; $C_{reactantgas}$ is the inlet gas reactant concentration (SO_2); n is the reaction order 195 with respect to the gas reactant; C is a constant equal to $(4\pi M_C)^{1/2} \cdot (3/\rho_C)^{2/3}$, considering spherical particles; and ρ_C is the molar density of the particles (moles of carbon/m^3).

The Shrinking Core Model equations with chemical reaction control must be applied in the carbon weight interval where $-\frac{1}{W_C^{2/3}} \cdot \frac{dW_C}{dt}$ is considered as constant. Figure 3 shows the results obtained at the different reaction temperatures when determining the carbon 200 weight interval where the equations of the model can be applied to analyze the reactivity of soot with SO_2.

It can be inferred from the results presented in Figure 3 that the equations of the Shrinking Core Model with chemical reaction control can be applied in the carbon weight interval covering the 20–90% of the soot conversion at any of the temperatures analyzed. 205

The employment of the equations of this model allows to calculate the time needed for the complete conversion of carbon, τ, by relating the reaction time, t, and the carbon conversion, X_c, all along the experime nt through the use of Eq. (6). The τ value is considered as indicative of the carbon reactivity.

$$\frac{t}{\tau} = 1 - (1 - X_c)^{1/3} \qquad (6)$$

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The conversion of carbon, X_c, at any time, t, is determined as the weight of carbon reacted in the experiment related to the initial weight of carbon:

$$X_C = \frac{W_{C_0} - W_c}{W_{C_0}} \qquad (7)$$

From the values of $1 - (1 - X_c)^{1/3}$ versus time (t), the time for the complete conversion of carbon (τ) for the different operating conditions can be obtained. The experimental 215
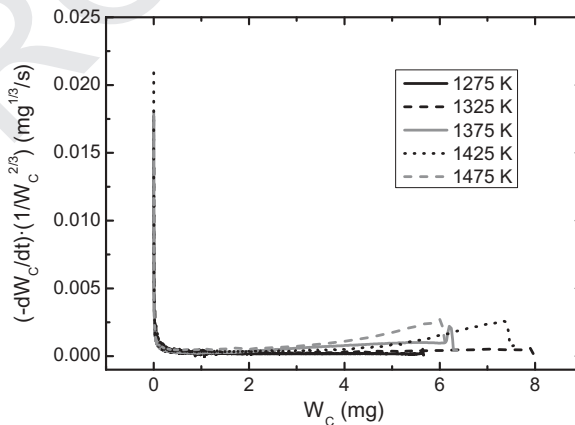

Figure 3. Carbon consumption rate expressed as a function of the remaining carbon weight, W_C, in the reaction of soot with 1% SO_2 at different temperatures (1275–1475 K).

Complete carbon conversion times, τ, obtained in the interaction of soot with 1% SO_2 at the different reaction temperatures (1275–1475 K). Linear regression coefficients result from the fitting of Eq. (6).

Temperature (K)	τ (s)	R^2
1275	28,904	0.998
1325	23,035	0.996
1375	16,254	0.962
1425	15,374	0.991
1475	9404	0.987

carbon conversion data used in Eq. (6) to determine the τ values are the ones corresponding to the carbon weight interval considered as constant in the analysis of results shown in Figure 3.

Table 1 summarizes the values of the time for complete conversion of carbon obtained in the soot-SO_2 reactivity experiments at different temperatures, along with the linear regression coefficient results for each condition.

As it can be observed in Table 1, the complete carbon conversion time, τ, decreases as the reaction temperature is increased, indicating the higher reactivity of soot towards SO_2 with temperature. In this way, the complete carbon conversion time is in general decreased by a factor of about 3 when increasing the reaction temperature 200 K (from 1275 K to 1475 K).

The results from the interaction soot-SO_2 obtained at different temperatures (1275–1475 K) allowed the calculation of the activation energy (E_a) value of the process. Considering that τ can be expressed through Eq. (8) (Levenspiel, 1999), and displaying the reaction rate as a function of the Arrhenius equation, the activation energy can be derived from the linearization of the Arrhenius equation rewritten as a function of τ (9):

$$\tau = \frac{\rho_C R_0}{b k_s C_{reactant\ gas}^n} \tag{8}$$

$$\ln \frac{1}{\tau} = ln \frac{b k_0 C_{reactant\ gas}^n}{\rho_C R_0} - \frac{E_a}{R} \frac{1000}{T} \tag{9}$$

In Eqs. (8) and (9), R_0 is the initial radius of the soot particle; k_0 is the pre-exponential factor; R is the gas constant (J/mol K); and T is the operating temperature (K).

Figure 4 shows the Arrhenius plot for the soot interaction with 1% SO_2 at the different temperatures analyzed, along with the linear regression coefficient value obtained. From this fitting, an activation energy of about 82 kJ/mol was obtained.

Comparing the reactivity of soot towards SO_2 and O_2 (as the main oxidant in combustion), it is worth noting that the activation energy of the soot-SO_2 interaction (about 82 kJ/mol, present work) is much lower than the activation energy of the soot oxidation process, which was about 152 kJ/mol for the same soot sample (Abián et al., 2012).

Conclusions

An experimental and kinetic analysis of the interaction of soot with SO_2 at different reaction temperatures was carried out. The soot samples used in this study were
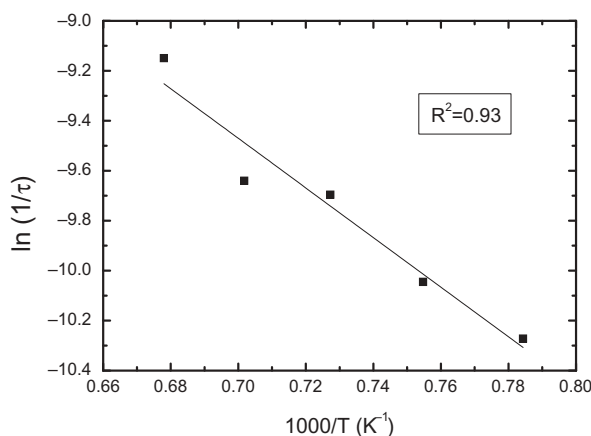
Figure 4. Arrhenius plot, according to Eq. (9), for the soot interaction with 1% SO_2 in the 1275–1475 K temperature range.

generated under well-controlled lab-scale conditions from the pyrolysis of ethylene in a N_2 atmosphere at 1375 K. The reactivity experiments involved the interaction of soot with 1% SO_2 at 1275, 1325, 1375, 1425, and 1475 K.

Experimental results showed that CO is the main product obtained from the soot-SO_2 interaction under all of the operating conditions analyzed. CO_2 was also detected but in almost negligible amounts. The formation of CS_2 was detected under specific operating conditions (i.e., temperatures higher than 1275 K and at the very first stages of the reaction). The analyses of the product distribution indicate that the possible mechanism for the reactivity of soot with SO_2 is complex, involving a number of reaction paths that can occur in parallel, but all of them deriving in the final formation of CO, CO_2, and CS_2.

The Shrinking Core Model equations with decreasing size particle and chemical reaction control were used, first to determine the time for the complete consumption of carbon, τ, and further to calculate the activation energy, E_a, of the process. The τ values indicated that the soot reactivity is increased by a factor of about 3 when increasing the reaction temperature from 1275 K to 1475 K. In this way, results show that the higher the temperature, the higher the carbon conversion. An activation energy of about 82 kJ/mol was obtained for the interaction of soot with SO_2, which is lower (by about half) than the one corresponding to the oxidation of soot with O_2.

Funding

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