

THE ROLE OF CARBONIZATION IN THE EVOLUTION OF COAL CHAR GASIFICATION REACTIVITY

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INTRODUCTION

The relevance of thermal annealing of coals to the physico-chemical properties of the residual coke or char has been often addressed in the literature. The emphasis is most frequently on the structural modifications induced by carbonization in relation to mechanical properties. More limited and sparse information is available on the influence of the severity of pyrolysis and of carbonization conditions on the reactivity of chars in the context of coal gasification.

Thermal annealing affects char gasification along two paths: on one side it induces reordering of the turbostratic structure of coals, on the other side it affects the activity and distribution of mineral inclusions. Both processes lead to char deactivation, their relative importance being dependent on the nature of the parent coal.

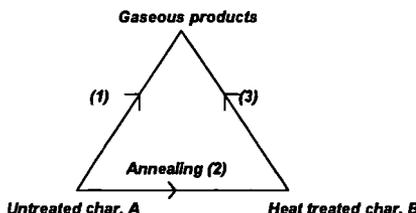
In this paper the effect of thermal annealing on the reactivity of char from bituminous coal in carbon dioxide atmospheres is investigated. Experimental results are interpreted in the light of a simple reaction model.

MODEL DEVELOPMENT

The effect of thermal annealing on the reactivity of chars with carbon dioxide is afforded in a simplified manner. The detail of the individual processes that occur during thermal annealing is not considered: the whole spectrum of phenomena, including catalyst deactivation and carbon structure reordering, is lumped into a single deactivation step.

It is assumed that before thermal annealing only carbon of type A is present. Along heat treatment carbon A transforms into a less reactive carbon, B. This is at the origin of deactivation. The two types of carbon, A and B, may be thought as differing by degree of graphitization, catalytic activity or pore structure.

The kinetic model is based on a triangular network of reactions:



- (1) the heterogeneous reaction of char A;
- (2) thermal annealing transforming A into B;
- (3) the heterogeneous reaction of char B. This reaction is slower than reaction (1).

The following simplifying hypotheses are made:

- i. all reactions are irreversible;
- ii. all reactions are activated by temperature according to an Arrhenius type expression;
- iii. the kinetics of reactions (1) and (3) is first order with respect to the mass of A and B respectively;
- iv. the kinetics of reactions (1) and (3) is first order with respect to the concentration of the gaseous reactant (CO_2);
- v. the annealing process (2) is influenced neither by the gaseous atmosphere, nor by pressure;
- vi. the annealing process (2) is irreversible;
- vii. the kinetics of the annealing process (2) is first order with respect to the mass of A.

At a given temperature mass balances for chars of type A and B are as follows:

$$1) -\frac{dm_A}{dt} = m_A \cdot k_A \cdot p_{\text{CO}_2} + k_{A \rightarrow B} \cdot m_A$$

$$2) -\frac{dm_B}{dt} = m_B \cdot k_B \cdot p_{\text{CO}_2} - k_{A \rightarrow B} \cdot m_A$$

Initial conditions:

$$t=0$$

$$m_{A0} + m_{B0} = w_0$$

$$m_{A0} = w_0 \cdot \exp(-k_{A \rightarrow B} \cdot t_{HT})$$

where m_A , m_B are the mass of type A and type B char, w_0 is the initial total mass of char, k_A , k_B are the rate constants for the heterogeneous reaction of type A and B char respectively, p_{CO_2} is carbon dioxide partial pressure, and $k_{A \rightarrow B}$ is the rate constant for the annealing reaction.

Initial conditions take into account the possibility that heat treatment under inert atmosphere occurred for a time t_{HT} , prior to gasification.

The reaction rate at zero carbon burn-off, expressed as the rate of change of carbon conversion degree, f , is given by:

$$3) \left[-\frac{df}{dt} \right]_0 = k_A \cdot p_{CO_2} \cdot \exp(-k_{A \rightarrow B} \cdot t_{HT}) + k_B \cdot p_{CO_2} \cdot (1 - \exp(-k_{A \rightarrow B} \cdot t_{HT}))$$

At higher burn-off, solution of the system of equations (1)+(2), with the assigned initial conditions, yields the following expression for the instantaneous carbon gasification rate:

$$4) \left[-\frac{df}{dt} \right]_f = k_B \cdot p_{CO_2} \cdot \left(1 - \frac{m_{A0}}{w_0} + \frac{m_{A0}}{w_0} \frac{1}{1 + \frac{k_A \cdot p_{CO_2}}{k_{A \rightarrow B}} - \frac{k_B \cdot p_{CO_2}}{k_{A \rightarrow B}}} \right) \cdot \exp(-k_B \cdot p_{CO_2} \cdot t) + \frac{m_{A0}}{w_0} \cdot (k_A \cdot p_{CO_2} + k_{A \rightarrow B}) \cdot \left(1 - \frac{1}{1 + \frac{k_A \cdot p_{CO_2}}{k_{A \rightarrow B}} - \frac{k_B \cdot p_{CO_2}}{k_{A \rightarrow B}}} \right) \cdot \exp((k_A \cdot p_{CO_2} + k_{A \rightarrow B}) \cdot t)$$

It can be noted that the reaction rate at any burn-off is a function of the duration of heat treatment (t_{HT}) and is parametric in the value of the three kinetic constants, k_A , k_B and $k_{A \rightarrow B}$.

The basic approach of the proposed model resembles that of a former one by Nagle and Strickland-Constable (NSC) (8). Formulated in 1961 to describe the oxidation of pyro-graphite at high flow rates, pressures of 0.2 atm, temperatures comprised between 1050 and 1700°C, the NSC model took after the theory of Blyholder, Bindford and Eyring (9) and assumed that two sites are present on the carbon surface, namely A, a more reactive one, and B, a less reactive one. Two heterogeneous reactions and one reaction of annealing were also considered, but their network differed from the one proposed in the present work. In particular the mass fraction of A was treated under a pseudo-steady state approximation.

EXPERIMENTAL

Experimental work has been focused on the gasification of chars with carbon dioxide. It has been directed to the evaluation of model parameters (kinetic constants for reactions (1), (2), and (3)), and to comparison with model predictions.

Samples of South African (SA) coal, ground and sieved to the size range of 75-125 μ m, have been carbonized in inert atmosphere at 900°C for different times, comprised between 1 and 300 min. Heat treated chars have, then, been checked for reactivity with CO_2 under standard conditions.

Heat treatment was performed isothermally in a PL-TG1000M thermobalance after heating up the sample at a rate of 999°C/min. The thermobalance operated at atmospheric pressure with a 50 ml/min flow of nitrogen.

Standard reactivity tests were carried out isothermally in the thermogravimetric apparatus at 900°C and atmospheric pressure, with a 50 ml/min flow of carbon dioxide. Reaction rates have been expressed as rate of change of carbon conversion degree throughout the paper.

RESULTS

Experimental results

The dependence of the instantaneous reaction rate df/dt on carbon burn-off, f is shown in figure 1. Data are relative to SA coal heat treated at 900°C for different t_{HT} . Notably, reaction rate corresponding to different t_{HT} converge at $f > 0.55$. The interpretation of these curves is deferred until *Model results and validation*.

The effect of t_{HT} on char reactivity at 0% burn-off is reported in figure 2 for char heat treated at 900°C for t_{HT} comprised between 1 and 300 min. Reaction rates at 0% burn-off have been evaluated from df/dt versus f curves of figure 1 by linear extrapolation of data up to 10% burn-off. A non linear decrease of initial char reactivity with duration of heat treatment is observed.

Evaluation of model parameters

Model parameters have been evaluated from reactivities of samples heat treated at 900°C for different tHT.

The reaction rate constants of the heterogeneous reactions of type A and B char have been evaluated from df/dt versus f curves of samples heat treated for 1 and 300 min respectively (fig.1). The rate constant k_A has been assumed equal to the extrapolation to 0% burn-off of the first curve, using data points corresponding to $0 < f < 0.1$; the rate constant k_B , instead, has been based on the extrapolation to 0% burn-off of the second curve, using data points corresponding to $f > 0.65$. The annealing constant has been evaluated from instantaneous reaction rates at 0% burn-off of samples heat-treated for different tHT (fig.2). On the basis of equation (3) of the model, once the rate constants k_A and k_B are known, regression analysis of data in figure 2 yields the annealing constant $k_{A \rightarrow B}$. Accordingly, $k_{A \rightarrow B}$ turns out to be about 0.02 min^{-1} . The best fit curve through the data is reported in fig. 2.

Model results and validation

Figure 1 compares computed profiles of gasification rate versus burn-off with those obtained in experiments using different tHT. Fair agreement of model prediction with experimental data is observed. It can be noted that at $f < 0.55$ reaction rates are higher and fall off quicker, the shorter the heat-treatment, while at $f > 0.55$ curves corresponding to different tHT converge, and reactivity appears no longer influenced by the duration of heat-treatment.

The convergence of curves relative to different tHT can be explained considering that in the first stage both annealing of carbon A, and char oxidation are active at the same time, whereas, once carbon A is depleted, oxidation of carbon B remains the main process active.

Notably, the occurrence of gradual transition from the reactivity of char A to that of char B, rather than a stepwise drop of reaction rate, is a consequence of the fact that the time scale over which annealing takes place at 900°C is comparable with those of the heterogeneous reactions 1) and 3). On the contrary, the pseudo-steady state approximation invoked by the NSC model implied that a stationary value of mass fraction of A was reached over a time scale much shorter than that of the gasification reaction.

On account of the closeness of annealing and gasification time scales at temperatures around 900°C, it can be argued whether annealing is the key factor for the evolution of char reactivity throughout conversion.

DISCUSSION

A rough order of magnitude evaluation of the time scale of the annealing process as compared with those of reactions with oxygen and carbon dioxide over a wide range of temperatures will be attempted in the following.

A kinetic constant of annealing of 0.02 min^{-1} has been evaluated at 900°C in this work. Accordingly the time required to transform the 95% of mass A into B would be approximately 140 min. Estimates of time scales of annealing at different temperatures are directly or indirectly provided in a number of papers (1,3,7). All these points have been located in the diagram of figure 3, reporting the process time scale versus reciprocal absolute temperature.

The solid line in figure 3 has been simply obtained by extrapolation to different temperatures of the annealing time evaluated in the present work at 900°C. The activation energy value of 97000 cal/mol has been used in the extrapolation. This value is that suggested by NSC and lies within the broad range of activation energies for annealing proposed in the literature (between 20000 (2) and 200000 (9) cal/mol).

The analysis is pursued further by comparing the time scale of annealing with those of the C-O₂ and C-CO₂ reactions.

In figure 3 a characteristic time of reaction, defined as the inverse of the reaction rate $(df/dt)_{f=0}$, is also plotted as a function of $1/T$. Plots are relative to heterogeneous gasification of SA char with carbon dioxide and with oxygen in air, and have been obtained from extrapolation of experimental data at 1173K (10) and 693K (11) respectively. Activation energies suggested by Salatino et al. (10) and D'Amore et. al (11) (4500 cal/mol for reaction with carbon dioxide and 29000 cal/mol for reaction with oxygen) have been assumed.

The limitations of the comparison afforded in figure 3 lie, on one side, in the considerable uncertainty as regards the activation energy of annealing, and, on the other side, in the inadequacy of extrapolations of intrinsic kinetic data to temperatures where diffusion resistances may be relevant. Being aware of all the above approximations, it can be speculated that: at temperatures lower than 1173 K the rate of annealing is lower than the rate of reaction with both CO₂ and O₂. At about 1800K the time of annealing and the time of reaction with oxygen are comparable, as Davis et al. (7) found experimentally, and both are shorter than the time of reaction with carbon dioxide. At temperatures typical of entrained coal gasification processes (>1800K) the time scale of thermal annealing should be shorter than the time-scale of both gasification reactions considered: under these conditions, neglecting annealing when estimating reaction rates for entrained coal gasification processes may lead to serious overestimation.

CONCLUSIONS

A very simple approach has been undertaken to clarify the interactions between annealing and gasification reactions. A model based on a triangular network of reactions shows some ability to match experimental reactivity profiles over the entire range of carbon burn-offs.

A pronounced effect of the heat treatment of coal on the reactivity of its char towards CO_2 has been observed at the temperature of 900°C . Under the experimental conditions investigated thermal annealing occurs over time scales comparable with those of gasification reactions.

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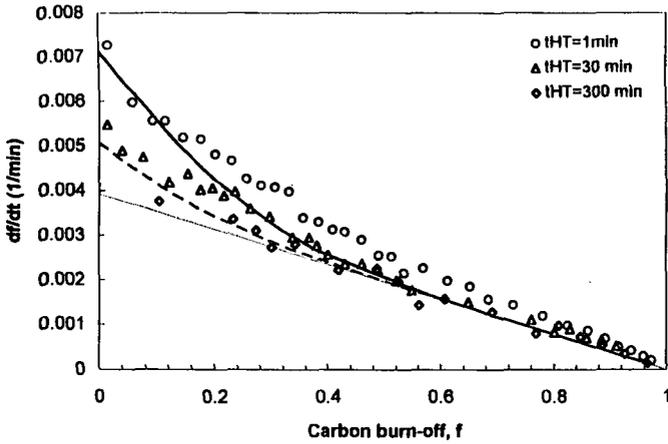


Fig. 1 Reaction rate of SA char versus burn-off for HTT=900C and different tHTs. Lines represent model results

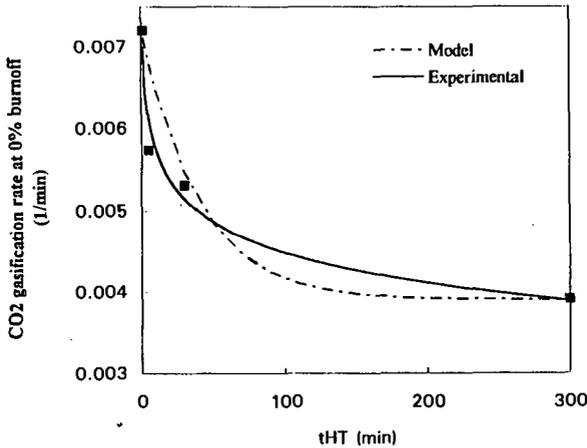


Fig. 2 Effect of tHT on reactivity at 0 % burn-off of SA char treated at 900C

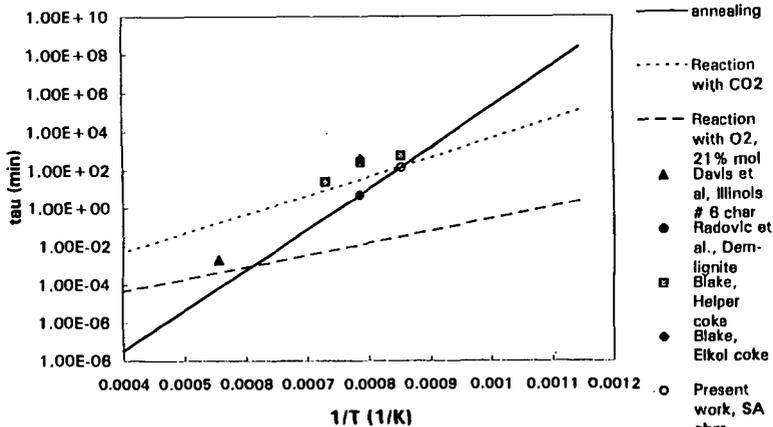


Fig. 3 Characteristic times and comparison of experimental data from different authors.