

ASSESSMENT OF THE KINETICS OF COAL COMBUSTION UNDER OXY-FUEL CONDITIONS BY MEANS OF DIFFERENT EXPERIMENTAL TECHNIQUES

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Abstract

A very large number of papers have been carried out to measure the rate of char conversion under combustion and gasification conditions, involving a variety of coal and char types, as well as different experimental techniques, ranging from TGA to wire mesh reactor and drop tube furnaces. For oxy-combustion with flue gas recirculation the impact of CO₂ on the rate of combustion of char combustion is controversial.

In the present paper the rate of carbon conversion in O₂/CO₂ mixtures typical of oxyfuel conditions has been investigated by conventional as well as innovative experimental techniques, namely isothermal and non isothermal thermogravimetric analysis and reaction in an aerodynamic levitator particle reactor. Experiments have been carried out up to 1000°C and with 1-30% oxygen in carbon dioxide.

Results show that in a limited range of temperature and O₂ non isothermal thermogravimetric analysis and isothermal reaction in the aerodynamic levitator particle reactor produce similar results. At high temperature and oxygen concentration thermogravimetric analysis fails while the aerodynamic levitator particle reactor still provides reliable results.

Experimental results are worked out to obtain reliable kinetic rate expressions for oxy-fuel combustion. The simple approach of describing the conversion of carbon with O₂ and CO₂ by means of two parallel independent reactions each characterized by a power law kinetics expression proved unable to fit experimental data, however also the series-parallel reaction network of Liu and Niksa [1] is unable to fit experimental data throughout the temperature range investigated.

Introduction

The rate of coal combustion in oxyfuel conditions is a key point in design and modelling of coal oxy-combustors, since it determines burnout and carbon levels in ash. This issue is particularly relevant to the retrofit of boilers, which had been designed on the basis of coal reactivity in air. Because of the evident uncertainties as regards coal reactivity under oxy-fuel conditions remains, accurate experiments and reliable kinetic models of char conversion under the concurrent action of oxygen and carbon dioxide are necessary.

A very large number of papers have been carried out to measure the rate of char conversion under combustion and gasification conditions, involving a variety of coal and char types, as well as different experimental techniques, ranging from thermogravimetric analysis to drop tube furnaces and wire mesh reactors, however these techniques do not allow a reliable and straightforward control and monitoring of the temperature, of the mass and of the release of gaseous products at the same time.

Experimental

The rate of char gasification in O₂/CO₂ mixtures has been measured by thermogravimetric analysis as well as in an innovative aerodynamic levitator particle reactor that will be described shortly. A South African bituminous coal has been used for the experiments. Coal was pyrolysed at 850°C in a fluidized bed reactor under inert conditions, the char was then ground and sieved to obtain particles 50-100µm.

Experiments in the TGA have been carried out with a Netzsch TG409 using mixtures of oxygen in carbon dioxide or nitrogen, oxygen ranging from 0 to 30%. Both isothermal and non isothermal experiments have been performed. In non-isothermal the temperature was raised at the rate of 5°C/min up to 900°C in a flow of reactive gas of desired composition. In isothermal TG tests the set temperature of 500-700°C was reached in a flow of nitrogen before the gas was switched to the desired composition. Notably in each test approximately 20mg of char was spread evenly on a pan of 16 mm diameter, in order to form a relatively thin layer. The gas flow rate was 150ml/min.

The aerodynamic levitator particle reactor was designed in order to carry out experiments of char combustion under suspension conditions at strictly controlled temperature. The device, described in the scheme of fig. 1, consists of a gas preheater and a small reaction chamber, indicated by a red circle in the figure.

During operation the gas is fed from the bottom and flows upwards through the preheater. It then enters section C where it experiences a sensible increase in velocity due to the sudden section reduction and is able to fluidize a bed of silica sand. In section B the velocity decreases gradually due to enlargement of the reactor diameter. Particles are fed from the top in counterflow. In section A they encounter relatively small gas velocity, this avoids entrainment of the particles and allows particles to fall down to section B. Falling through section B particles encounter a progressively larger gas velocity and eventually find a quote where the gas velocity is large enough to hold them back. Particles too large or heavy to be levitated fall down to section C where they are retained in the quartz fluidized bed. The reaction progress is monitored by on-line analysis of the effluent gas, by means of IR CO/CO₂ analysers.

Experiments in the ALPR were carried out at temperatures in the range 500-1000°C and mixtures of 0-30% oxygen in carbon dioxide. In each experiment 2-10 mg of sample were loaded with particle size 50-100µm. The bed was constituted

of silica sand of 300-400 μ m and the gas flow rate was tuned in the range 1-2 Nl/min. The progress of the reaction was followed through the evolution of CO.

Results and discussion

An example of CO profiles measured during experiments in the ALPR is reported in fig.2. Notably an initial sharp peak is observed associated to release of CO from oxygen complexes formed at the char surface at ambient conditions.

Figure 3 reports the Arrhenius plots obtained with different experimental techniques at different oxygen concentrations.

The comparison of results obtained by isothermal and non isothermal thermogravimetric with 3% O₂ suggests that up to 550°C the two techniques produce similar results. However above 550°C the Arrhenius plot obtained by isothermal analysis exhibits a marked slope reduction suggesting that transfer of oxygen from the gas phase to the particle surface may be insufficient.

The Arrhenius plot obtained from non isothermal thermogravimetric isothermal tests with 3% oxygen overlap instead with the one obtained from isothermal tests carried out in the ALPR in the entire temperature range investigated thanks to the efficient mass transfer that takes place in this type of reactor.

With 30% oxygen the results obtained by non isothermal thermogravimetric analysis and by isothermal tests in the ALPR are in very good agreement up to 600°C. Non isothermal thermogravimetric techniques does not allow to estimate Arrhenius plots above this temperature, because with such large oxygen concentration complete char conversion is attained by the time the thermobalance reaches 600°C. The Arrhenius plots obtained from isothermal tests in the ALPR, instead, produce reliable results well above this temperature. Altogether fig.3 confirm the validity of the ALPR tool for the assessment of reaction rate at high temperature. However at low oxygen concentration also NI-TGA provides reliable and probably more detailed information.

Kinetics of reaction with O₂/CO₂

As a first tentative approach the experimental results obtained in the present work have been with fitted assuming that the overall char conversion is due to additive contribution of the C-O₂ and C-CO₂ reaction:

$$r = x_{O_2} R_{O_2} + (1 - x_{O_2}) R_{CO_2} = x_{O_2} k_{O_2} \exp\left(\frac{-E_{O_2}}{RT}\right) p_{O_2}^{n_{O_2}} + (1 - x_{O_2}) k_{CO_2} \exp\left(\frac{-E_{CO_2}}{RT}\right) p_{CO_2}^{n_{CO_2}}$$

using kinetic parameters reported in previous papers. [2]

The rate of carbon conversion calculated accordingly for different O₂/CO₂ values from are reported as straight lines in Fig. 3. Notably experimental data points are reasonably fitted only in a limited temperature range. This simple approach cannot in fact reproduce the complex pattern of the experimental Arrhenius plots in the high temperature range.

The multiplicity of linearity region observed in the Arrhenius plots can be described only considering a multi-step reaction scheme, as the one proposed by

Liu and Niksa [1] Results of this kinetic model are compared with experimental data in fig. 8B. It can be observed that the latter kinetic model is able to predict the complex Arrhenius plot obtained with 21% oxygen. However in the higher temperature range the model overestimates the rate of reaction at low oxygen concentration and underestimates the rate of reaction at 30% oxygen.

Conclusions

Experiments of gasification of a coal char from a South African Bituminous coal with mixtures of oxygen and carbon dioxide have been carried out by means of three experimental techniques: isothermal thermogravimetric analysis, non isothermal thermogravimetric analysis and isothermal reaction in an aerodynamic levitated particle reactor.

Results can be summarised in the following points.

- isothermal thermogravimetric analysis is confirmed to be inadequate to provide kinetic data at high temperature due to the onset of resistances in oxygen transfer from the gas phase to the particles.
- The ALPR represents a valid alternative for reliable isothermal tests at high temperature
- Arrhenius plots reveals the existence of multiple linearity regions.
- The simple approach to consider combustion and gasification as independent parallel reactions each characterized by power law kinetics provides a rough estimate of the rate of reaction and fails completely to predict the complexity of the Arrhenius plots. A semidetailed reaction network such as that proposed by Liu and Niksa [1] predicts articulate Arrhenius plots but does not fit well experimental results at high temperature.

Acknowledgements

The present work was supported by MSE-CNR Accordo di Programma per l'Attività di Ricerca di Sistema.

References

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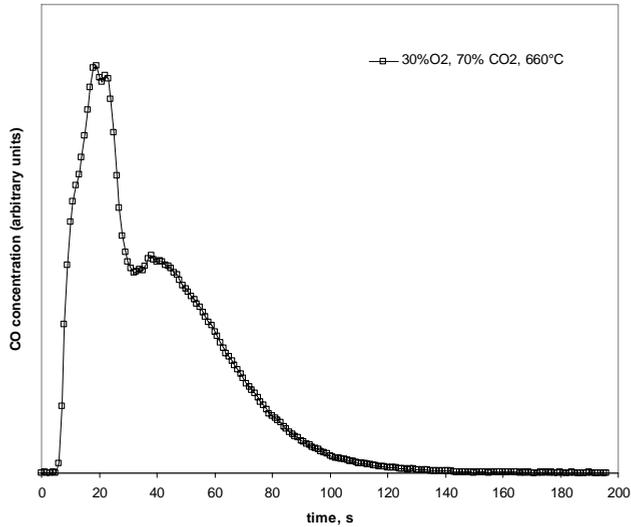


Figure 2. Example of CO profile during an experiment in the ALPR.

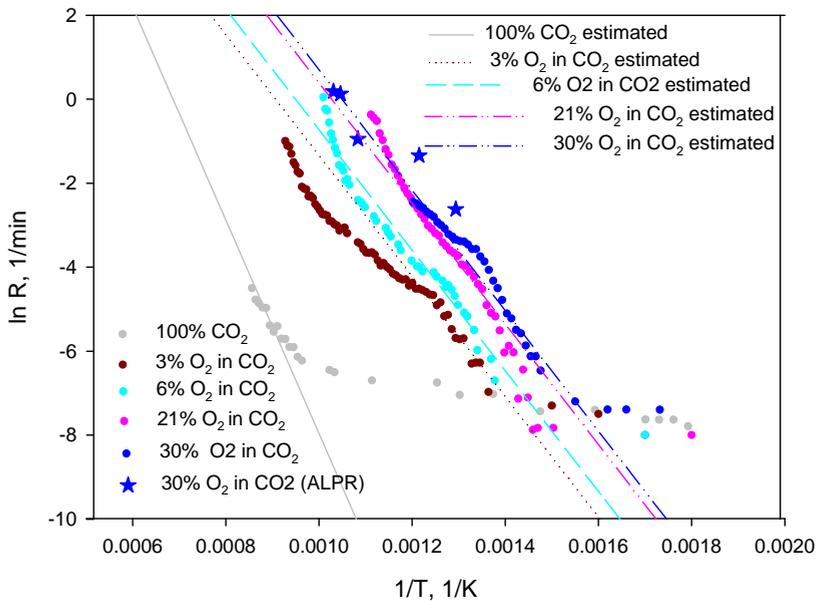


Figure 3. Arrhenius plots obtained at different O₂/CO₂ compared with power law kinetic expressions.

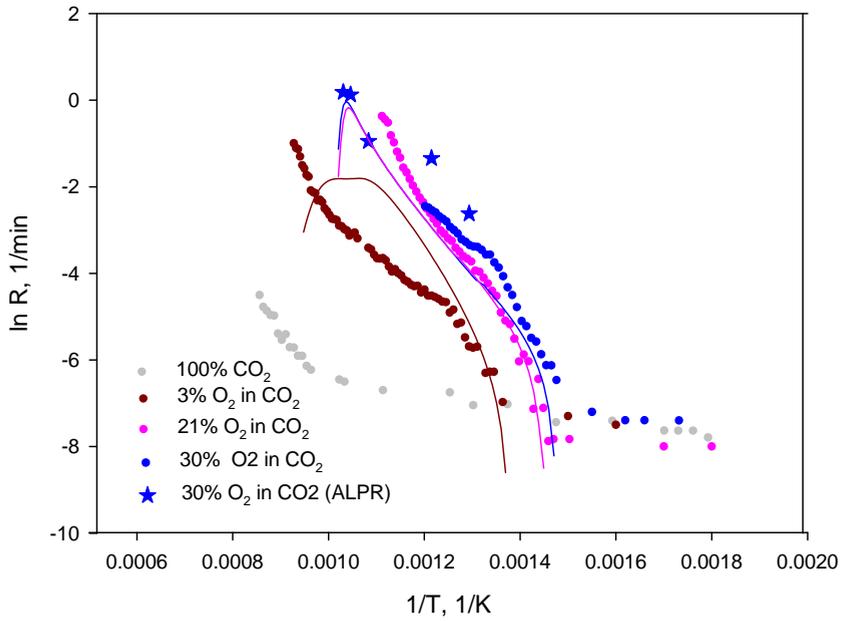


Figure 4. Arrhenius plots obtained at different O₂/CO₂ compared with semi-detailed kinetics.