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Fundamental Issues in Control of Carbon Gasification Reactivity

Fundamental Issues in Control of Carbon Gasification Reactivity

edited by

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and

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PREFACE

During the last decade there has been a renewed interest in understanding from a fundamental point of view the gasification of carbon. Basically there are two major issues in controlling the reactivity of carbon :

i) reduction of the gasification rate of carbon materials in hostile environment

ii) increase of the gasification rate in order to utilize carbonaceous compounds more effectively.

Although these two objectives look somewhat contradictory, they are part of the general topics of understanding gasification reactivity of carbon.

Refractory applications of carbon in furnace linings, seals and vanes, as well as the use of carbon-carbon or carbon-ceramic composites in structures able to withstand corrosion at high temperature require a better understanding of the fundamentals involved in carbon-oxidizing gas (O_2, CO_2, H_2O) reactions. Furthermore a great interest of aluminium producers is in extending the lifetime of carbon electrodes in alumina electrolysis which primarily depends on reducing their consumption rates by air or carbon dioxide.

Proper control of gasification reactions is also of prime importance in manufacturing carbonaceous adsorbents like granular activated carbon clothes of high adsorption characteristics. The balance between increase of porosity and decrease in mechanical strength during activation is critical for developing new porous types of carbon materials in particular for carbon blacks and this can only be achieved by a careful control of the gasification reaction.

Carbon materials are invariably associated with mineral or metallic impurities originating either from their precursors (coals, petroleum feedstocks) or their processing conditions. Catalytic effects therefore cannot be overlooked. Furthermore catalytic activity is a way to increase gasification rates of coals and chars. In assessing the reactivity of carbon, the relative importance of diffusion and chemical control on the gasification rate has to be established. This point is of prime importance when dealing with large scale applications of carbon reactivity control like inhibition of oxidation or catalytic gasification. For gasification with oxygen, an important consideration is whether the product is CO or CO_2 and whether the CO_2 is produced as a primary product at the carbon surface or as a consequence of oxidation of CO in the pores or external boundary layer.

From the above mentioned considerations, it is clear that a better and up-dated understanding of the basic phenomena involved in carbon gasification is a major challenge in developing new applications of carbon materials or improving current processes. Several laboratories are active in this

field and a synthesis of the present state of art is timely and relevant.

Although carbon reactivity is one of the major topics discussed in international carbon conferences, no workshop dealing specifically with this topics has been recently organized, to our knowledge. It was the objective of this workshop to fill this gap.

More precisely, the purpose of the workshop was to give to specialists concerned with carbon reactivity an opportunity :

- to establish the state of the art on control of carbon reactivity by putting into contact people involved in similar or complementary activities.

- to outline the new trends in lowering or increasing the reactivity of carbon materials.

- to present recommendations for future research programmes.

A large part of the available time was used fort discussions. Indeed, for each lecture or communication, the time for the discussion was equal to the time of the presentation. The last part of the meeting (half a day) was devoted to a synthesis of the workshop by three sub-committees. The comments, questions and answers submitted in a written form (more than 80 % of them) have been edited in the present volume.

Special thanks are addressed to the Scientific Committee, Profs and Drs K. van Heek, H. Marsh, B. McEnaney, D.W. McKee, A.F. Sarofim, I.W. Smith and E.M. Suuberg.

We are grateful to S. and P. Wagner, F. Rabillaud, N. Pusset and J. Dentzer for their assistance before and during the meeting.

We acknowledge the "Centre d'Etudes Nucléaires" of Cadarache for giving us the possibility to organize the meeting in the guest house of the Research Center of Cadarache.

The support of the Scientific Affair Division of NATO is gratefully acknowledged.

Jacques LAHAYE

Pierre EHRBURGER

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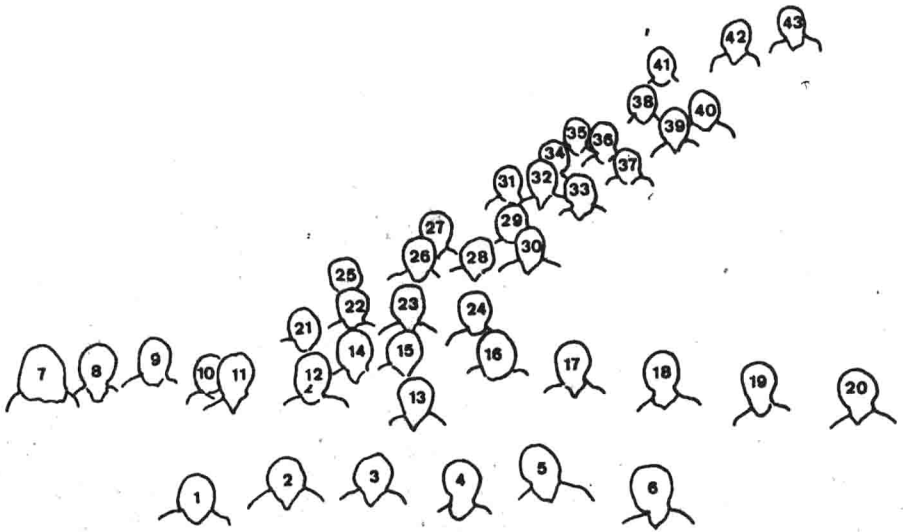

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CHEMICAL KINETICS OF CARBON AND CHAR GASIFICATION

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ABSTRACT. After introducing the basic processes the lecture focusses on the phenomena of coal gasification as there are the impacts of rank, mineral matter composition, particle size and pyrolysis conditions applied before gasification takes place. Then it concentrates on the elemental reaction steps and the therefrom derived kinetic expressions as function of the partial pressures of all product gases, total pressure, temperature and burn-off. Special attention is paid to the influence of hydrogen on the burn-off behaviour and on the question whether pore diffusion or product gas inhibition causes the retardation of the conversion rates of larger particles.

1. Basic Processes and Reactions

The Italian priest and scientist, Felice Fontana (1730-1805), professor of physics in Pisa, mainly concerned with research of muscels, nerves and poison from snakes wrote 1780 in his laboratory book:"If one quenches glowing coal with destilled water one obtains ignitable air." Also his famous colleague, Antoine Lavoisier (1743-1794), member of the Academy of Science of France, found the same results in 1783:"We have also found that coal immersed into water develops ignitable air." The scientists, especially Lavoisier, made this experiments not just as academic studies. At the same time the Montgolfiers started their first flights and obviously it had been noticed that if the straw fire, which gave the hot air to lift the ballon, was quenched with water, the lifting effect was improved. Thus Lavoisier and his laboratory were supported by the French king, whose military advisers had recognized the importance of a good flying machine.

The invention of Fontana and Lavoisier and the results of research and developement done by a long chain of scientists and engineers are since a long time used in processes of industrial importance like:

- Gas production from coal and other solid fuel for the use in synthesis and reduction processes, for heating purposes and fuel gas, the latter becoming more and more important for the clean power production in combined cycle power plants.
- Activation of carbonaceous materials to produce adsorbents.
- Regeneration of adsorbents and catalysts by the removal of carbon deposits.

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Corrosion of graphitic materials.

For the production of gas from coal as well as from other solid feedstocks two different approaches are possible: Devolatilization and gasification. In the case of devolatilization, the gas which envolves from he coal upon heating to temperatures beyond 400 °C is employed. Coke and tar occur as byproducts and are used separately. By gasification of coal its organic component is completely converted into gas, and so only ash remains. This is achieved by subjecting the coal to a reaction with a gasifying agent, such as steam, at a temperature exceeding 700 °C. Concerning the basic process, this lecture is concerned exclusively with gasification. However, devolatilization or pyrolysis always occurs, when coal is heated up. In this step coal is converted into char or coke as an intermediate product which is subsequently or simultaneously gasified. Its reactivity is affected by the conditions under which pyrolysis is carried out. Also phenomenae like coking and swelling, which occur during pyrolysis of some coals can affect the operation of gasifiers. On the whole, pyrolysis is an important step as will be explained in this lecture.

Considering the fact, that the main constituent of the char is carbon, fundamental gasification reactions are as given in table 1:

Table 1. Gasification reactions

	Steam Gasification:			**heat consumption kJ/mol**
[1]	$C + H_2O$	<——>	$H_2 + CO$	+ 118.5
[2]	$CO + H_2O$	<——>	$H_2 + CO_2$	- 42.3
[3]	$CO + 3H_2$	<——>	$CH_4 + H_2O$	- 206.0
	Hydrogasification:			
[4]	$C + 2H_2$	<——>	CH_4	- 87.5

The main reaction is the heterogeneous water gas reaction [1], in which the carbon reacts with steam to form hydrogen and carbon monoxide. The products of the reaction, in turn, can participate in two further reactions: the homogeneous water gas reaction, also called shift-reaction [2], and that of methanation [3]. They thereby react either with the gasifying agent or with one another, generating carbondioxide and methane. The subsequent reactions [2] and [3] are exothermic; however, the endothermic main reaction [1] is dominant. Hence the overall reaction, which is the sum of the three reactions included under steam gasification, is endothermic. To produce methane from coal as a natural gas substitute, hydrogasification [4], i.e. direct reaction of hydrogen with carbon, can be used. At a first glance the reader may note that the set of reactions given in table 1 seems to be not complete. For instance it does not show the Boudouard reaction $C + CO_2 \longrightarrow 2CO$, which can be derived by substracting eq. [2] from eq. [1], however.

In view of industrial importance of coal gasification, fundamental studies of the nature and course of the reactions involved have been carried out in the past by numerous workers. Among the different aspects investigated, kinetics play a very important role since it provides useful data for the correct dimensioning of gasifiers. The state of knowledge has been presented in a number of review papers, contributions to handbooks etc., some of which are quoted as references /1-5/.

An assessment of the state of knowledge 30 years ago /1/ shows that most of the previous work was aimed at investigating the kinetics of carbon-steam and carbon-CO_2 reactions. The results had already led to a well established theory, and the coaction of chemical reaction on transport phenomenae is especially well understood. With increasing temperature, first the chemical reaction, then pore diffusion and subsequently film diffusion become rate determining. Furthermore, a discussion was presented on the influence of carbon particle properties such as diameter and internal surface, and on gasification conditions such as pressure and partial pressure of the gasifying agent, on the coaction of transport and chemical reaction. In addition, the main steps of the mechanisms of the chemical reactions occurring during gasification have also been evaluated and reported.

The renewed interest in coal gasification during the 70's has stimulated further research. Especially natural coal and different chars relevant to industrial processes have been preferred over pure carbonaceous material. A better understanding of the influence of gasification conditions such as temperature, pressure and gas composition /6-9/, factors relevant to char reactivity and the effect of mineral matter and catalytically active species were the most important topics.

2. Definition and Measurement of Reaction Rates

It seems to be appropriate to start with a definition of reaction rates and reactivity:

$$r' = \frac{dX}{dt} \qquad (1)$$

$$r'' = \frac{dX}{dt}\,(1-X)^{-1} \qquad (2)$$

$$r_s = \frac{dX}{dt}\,(1-X)^{-2/3} \qquad (3)$$

$$X = 1 - \frac{m_c(t)}{m_c(t=0)} \qquad (4)$$

The rate of the reactions are defined as the change of the mass of carbon as function of time expressed by the degree of gasification "X" - also called "burn-off". "r'" is the rate related to the initial mass "$m_c(t=0)$". If it is constant with burn-off the reaction is of zero order, which often is found for catalytically influenced reations. "r'" and "r_s" relate the rate to the mass of carbon present in the reactor at time t. A constant value over burn-off indicates a first order reaction in the first case or an order of 2/3 in the second one. The latter can be explained by the progress of the reaction at spherical surfaces. It has been found that in many cases that "r_s" leads to a constant value over the whole range of burn-off.

The term "reactivity" describes a property of the solid fuel. It is expressed by the value of a reaction rate under well defined conditions concerning gasifying agent, temperature and pressure.

An useful instrument for the investigation of the kinetics of gasification is a thermobalance as shown in fig. 1 /10,11/. It can operate at temperatures up to 1,100 °C and pressures up to 100 bar whereby the sample is treated isothermally or with controlled temperature increase normally at a few K/min. The sample of 0.05

to 1 g can be introduced by a lock into the reactor and can be treated either with steam, different reactive or inert gases or steam/gas mixtures. The progress of the reaction is measured by the loss in weight, continously monitored as a function of time.

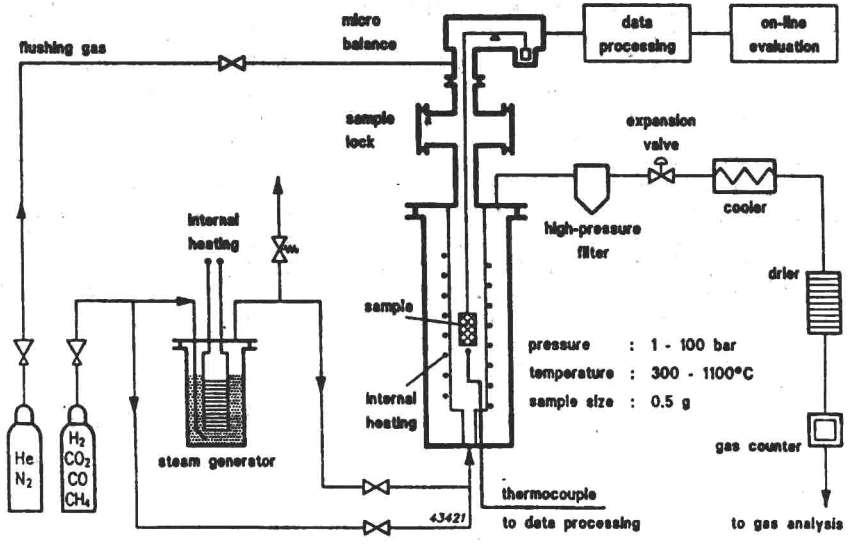

Fig. 1. Laboratory apparatus for determining the reaction rates by thermogravimetric analysis /10,11/

3. Dependence of Reaction Rates on Reactor Conditions, Type of Coal and Mineral Matter

Fig. 2 compares the reactivities of lignites, coals, chars, metallurgical coke and pitch coke against steam at 40 bar depending on temperature. In all cases the rate of reaction increases exponentially with temperature. However, there are considerable differences between the various solid fuels used. The reactivities of the lignites are highest, those of the coals and chars are found in a relatively narrow range, regardless of rank. Finally coke and pitch coke, i.e. carbonaceous material which has been treated at temperatures exceeding 1,200 °C, show the lowest reactivity. The main factors for these differences are the catalytic influence of the ash constituents which will be discussed in the following and the physical structure of the material especially of its internal surface as it will be explained lateron.

In the case of lignite minerals play an important role in the steam reactivity as can be seen in fig. 3, in which the reaction rates depending on temperature are given for different samples taken from European mines. Some correlation exists between the reactivity of the lignites and their content of alkaline-earth compounds /12/. These are found finely dispersed in the raw samples as salts of the humic acids. If they are removed by demineralisation the samples are much less reactive, even coming close to the reactivity of chars from hard coal. There is still some scatter for the different demineralised samples which may be due to the fact that demi-

neralisation has not been completed in all cases. It also could be ascribed to the differences in chemical and physical structure.

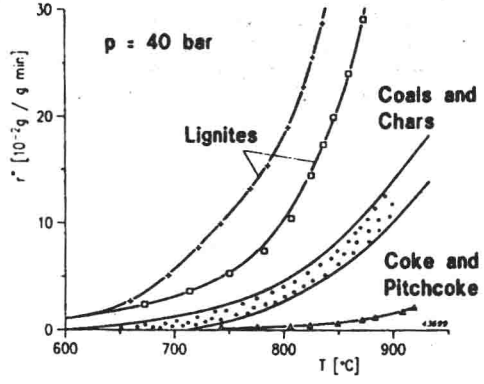

Fig. 2. Reaction rates of different solid fuels against steam (40 bar) depending on temperature

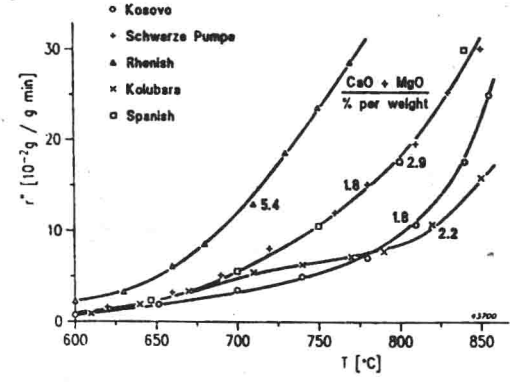

Fig. 3. Reaction rates of different lignites in 40 bar H_2O

Another example how dramatically mineral matter can influence reactivity and course of gasification of coals shall be given: For a better understanding fig. 4 shows first for the demineralised subbituminous coal "San Pedro" the CO_2 and H_2O reactivities as a function of burn-off for 1 and 40 bar /13/. The course of reactivity is as expected whereby the relatively high values at low burn-off can be ascribed to some devolatilisation effect even with the char. In particular the reactivity at 40 bar is much higher than at 1 bar as it is predicted from theory and confirmed for many carbons and chars.

The char from the natural coal containing the ashes with a high amount of calcium shows an unexpected behaviour (fig. 5). In the case of CO_2 reactivity the values

both for 1 and 40 bar are increased compared to the demineralised samples, however, no difference is found for the two pressures. For "Peckett" coal even a much higher value for 1 bar than for 40 bar has been measured. The same is valid in general for H_2O reactivities. These curves show even a more complicated course with burn-off. The explanation in these cases is that especially at high pressures back reactions of the calcium oxide with CO_2 and steam have to be taken into account, which diminish the catalytic activity and can even block the pores for further gasification /14/.

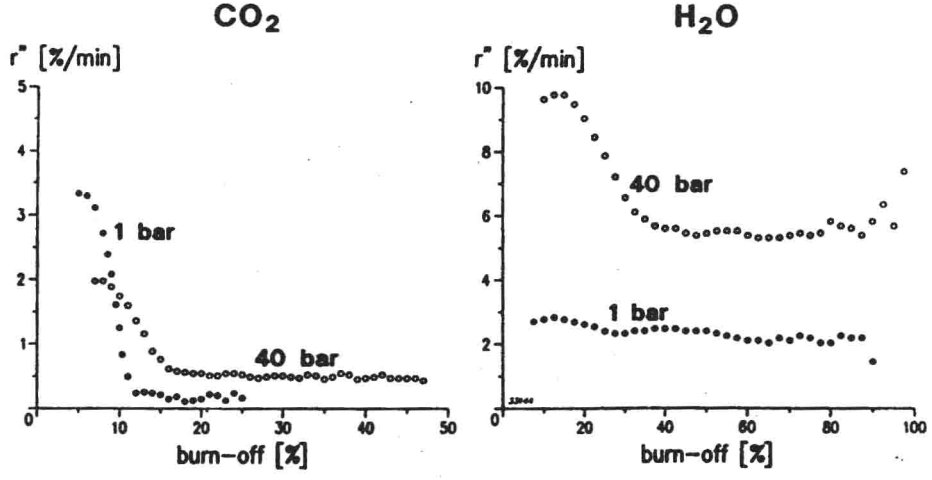

Fig. 4. CO_2 and H_2O reactivities of char from demineralised Chilenean coal ("San Pedro", 51.3 % V.M. daf, 800 °C) dependent on burn-off /13/

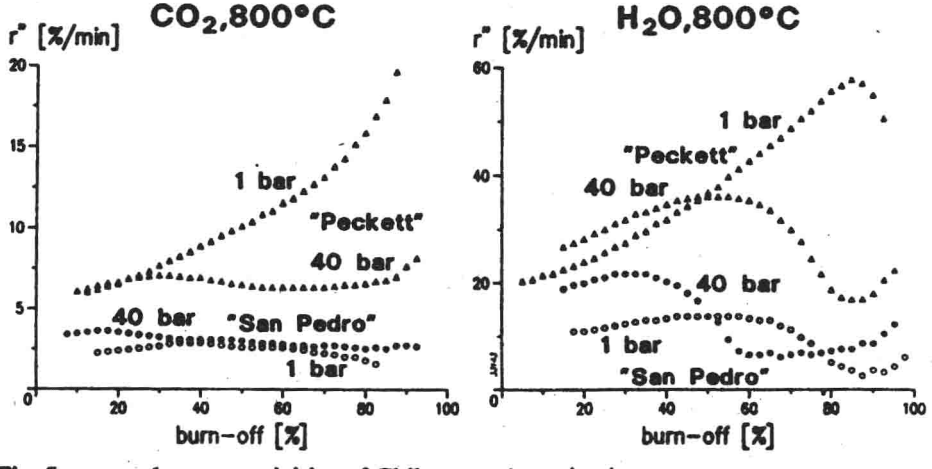

Fig. 5. CO_2 and H_2O reactivities of Chilenean chars /13/

Findings for a large number of hard coals indicate that the minerals seem to be less important for reactivity than those in lignites. In some cases especially for the high-ash coals they may inhibit the gasifying agent from reaching the carbon surface.

The kind of minerals in the native coals are also important for steam gasification, catalysed by potassium compounds. Fig. 6 shows in the left diagram the reactivity versus burn-off for a low ash char doped with 1, 3, 5, 10 wt-% K_2CO_3. The strong impact of the potassium on the reactivity can be seen. In fact reactivity increases linearly with the amount of K_2CO_3 /15/.

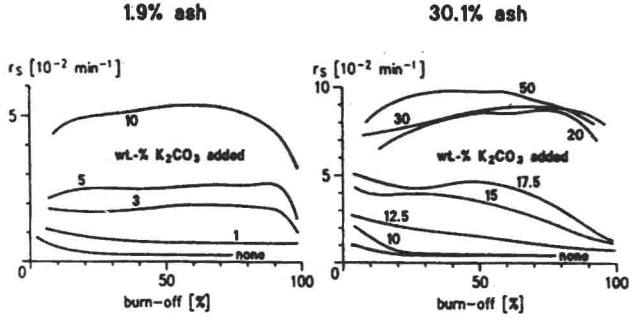

Fig. 6. Role of coal minerals in the potassium catalysed steam gasification of a char made from coal "Westerholt" /15/

In the right diagram results with a high-ash char are given. Reactivity is only influenced if the amount of K_2CO_3 exceeds 10 wt-%. Beyond this value reactivity increases if more K_2CO_3 is added and reaches saturation between 20 and 50 wt-%. This behaviour is due to the ash constituents reacting with the active potassium and consuming a considerable amount which is then not available for catalysis. The curves for 10, 12.5, 15 and 17.5 wt-% fall from low to high burn-off at first relatively fast afterwards slower, indicating that the side reactions of the catalyst with the ash compete with gasification. Further investigations have shown that the clay minerals kaolinite and illite are the main consumers of alkaline catalysts. Measurements of reaction rates between isolated minerals and K_2CO_3 /16/ show that kaolinite consumes the potassium carbonate in a quick reaction, and that the illite reacts much slower (fig. 7).

For the reactor design of catalytic gasification the following kinetic expressions have been developed which combine the gasification reaction on the one hand and the deactivation processes on the other /17/:

$$r' = 0{,}319\, C_{K2CO3} + r'_o \qquad (5)$$

$$C_{K2CO3} = C_{K2CO3,o} - C' \left[1 - (1 - (kt)^{1/2})^3\right] \qquad (6)$$

with "$C_{K2CO3,o}$" initial and "C_{K2CO3}" actual catalyst loading, "r'_o" uncatalysed rate, "C" stoichiometric amount of catalyst to be deactivated and "k" rate constant of catalyst mineral reaction.

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