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HIGH TEMPERATURE, HIGH PRESSURE THERMOGRAVIMETRY OF COAL GASIFICATION - APPARATUS, DATA ACQUISITION AND NUMERICAL EVALUATION

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ABSTRACT

A thermogravimetric apparatus is described which allows weight recordings for samples in a flow of steam or steam/gas mixtures or other gases under non-isothermal and isothermal conditions (300 - 1,100 °C) and pressures up to 100 bar. Further , the data acquisition and the statistical treatment of the signals, including the problems encountered with temperature measurement, are presented.

INTRODUCTION

The experimental determination of reaction rates of coal char samples during gasification under different gas atmospheres (H_2O, H_2, CO_2, CO) and pressures can be done advantageously by a thermogravimetric apparatus allowing heating under non-isothermal (using definite heating rates) as well as isothermal conditions up to 1,100 °C. Because of the required differential behaviour of the system, that means negligible product gas formation, the initial weight of the sample should be minimized and the flow rates of the gasifying agents maximized. For evaluation of gasification rates the weight needs to be corrected for systematical errors induced by buoyancy and by uplift due to gas flow.

APPARATUS

Fig. 1 shows a schematic diagram of the apparatus. A SARTORIUS-microbalance (typ: 4406) with a maximum load of 25 g per side and a resolution of 0.1 mg in the 2 g weighing range is situated at the top. The sample holder is connected to the quartz beam of the balance via a silver chain in the upper part of the autoclave - where the temperature is low - and via an NiCr chain in the hot zone. The reaction tube is made of Incoloy 800 and is heated electrically by a bifilar winding of coated heating wire. The instantaneous temperature of the sample is measured directly underneath the sample holder whereas the geometry of this arrangement viz. the practicability was determined during numerous test-runs (see below). The gasifying agents are mixed at the reactor entrance and preheated to the reaction temperature inside the reactor. Because of the earlier mentioned differential behaviour of the reactor, flow rates in the range of 4 to

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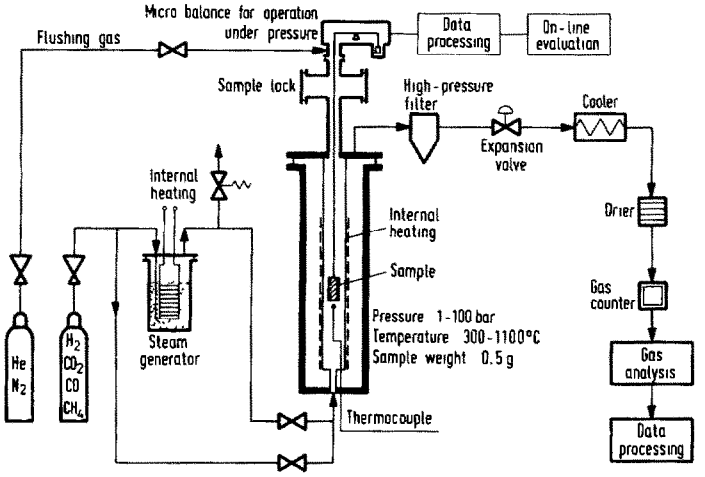

Fig. 1. Laboratory apparatus for gasification tests by pressurized thermogravimetry.

8 l/min (s.t.p.) have to be used and therefore the dimensions of the sample holder and the inner diameter of the reaction tube are chosen in such a way that under all attainable reaction conditions the flow remains laminar. The significance of this effect is described later.

The expansion of the gases is carried out by two motor-driven valves with different k_v-values so that in the whole pressure range and for all gasifying agents used the pressure can be adjusted carefully and maintained constant. Otherwise fluctuations of the pressure could cause variations of the flow rates and these produce uncorrectable errors of the weight signal. A steam condenser is placed just under the valves and the condensate is weighed by means of a balance. The corresponding weight signals together with those of the thermocouples and the SARTORIUS-microbalance are transferred on-line to a computer.

To perform experiments under isothermal conditions in which char samples should be heated up as quickly as possible the system is equipped with a sample lock with an electrically driven winch system. This enables the reaction conditions to be adjusted while the sample is hanging in the cold lock, after which the sample is lowered within two seconds into the reaction zone. Hereby maximum heating rates are obtained in the order of magnitude of 500 K/min.

Moreover this equipment allows quick and smooth changing of the sample without disturbing the sensitive balance. All parts of the winch system are constructed in such a way as to prevent the balance from any thermal radiation from the hot reaction tube.

DATA ACQUISITION

In order to minimize statistical errors encountered during recording, the weight signal is read 12 times in 100 ms at each measuring cycle and averaged. This procedure will be repeated after preset intervals. The maximum number of recordings is set to 600. After finishing the run, the measured weight values (see Fig. 2) are fitted to a 6th degree polynomial as a function of time. This helps in smoothening of the data and simplifies any further evaluation e.g. numerical differentiation for rate determination. The resulting standard deviations of these approximations are always in the range of experimental errors.

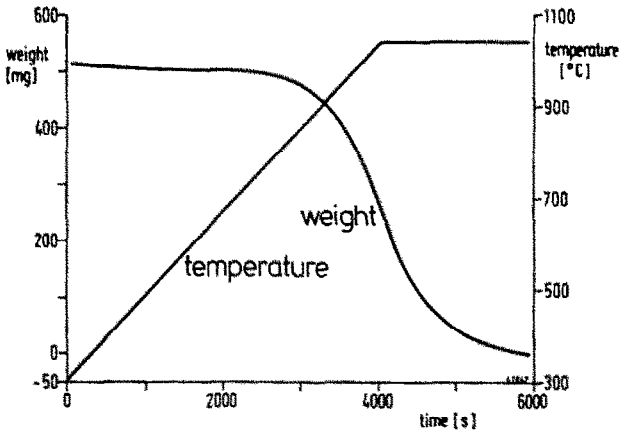

Fig. 2. Weight-loss curve of CO_2-gasification at 40 bar.

BUOYANCY CORRECTION

Because of the high pressure (up to 100 bar) and the increasing temperature during a non-isothermal run the densities of the gases - and therefore the buoyancies of the sample holder and the char sample - vary significantly with the temperature change during the experiment. The densities of the non-ideal gases (H_2O, CO_2) can be approximated at constant temperature for different pressures by using experimentally determined densities (ref.1,2) and fitting them with a polynomial of 6th degree:

$$\rho(p,y,T) = \frac{1}{T} \sum_{i=0}^{5} \frac{a(p,y)_i}{T^i} \qquad (1)$$

$$p = \text{const}$$

After that the temperature dependency of the single coefficients of the polynomial can be desribed in a similar way:

$$a(p,y)_i = \sum_{j=0}^{5} c(y,i)_j \; p^j \qquad (2)$$

The deviations between the measured data and the calculated are for all conditions smaller than 1 %. Using these equations the buoyancy of the sample hold-

er (3,500 mg) filled with 600 mg char can be calculated as a function of the temperature for different pressures of CO_2 and steam. The results are shown in Fig. 3. As can be seen the changes in weight caused by buoyancy changes reach up to 5 % of the initial char weight. If it is assumed that the char is consumed by the reactions with steam or CO_2, an additional weight change occurs mainly in the high temperature range with high reaction rates. To avoid these errors the data acquisition program corrects at first the buoyancy influences on the full sample holder assuming initial conditions. Then it calculates from the instantaneous and initial weights the percentage of char consumed. From the decrease in char volume the buoyancy of the remaining char is then calculated.

Further weight errors are due to the change of the gas velocities during non-isothermal runs. During heating up of the reaction tube, the densities of the gases are decreased and this lead - at constant mole through-put - to a

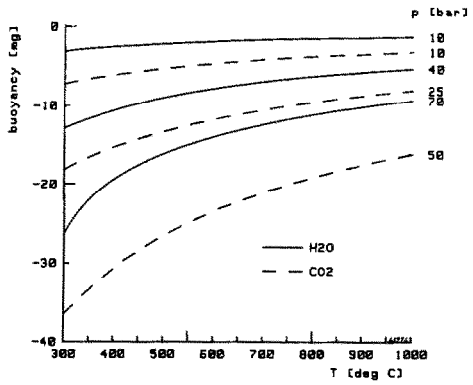

Fig. 3. Buoyancy of the sample holder (3,500 mg) filled with 600 mg char as function of the CO_2 viz. steam pressure and temperature.

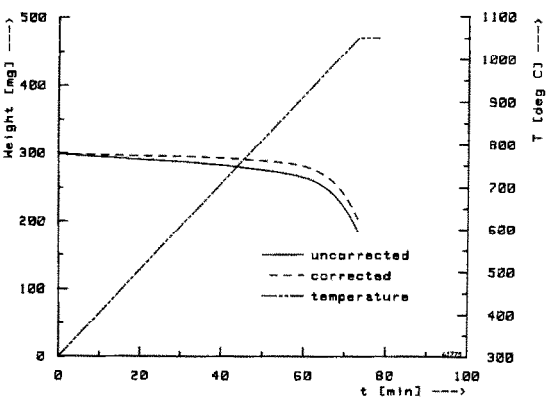

Fig. 4. Influence of gas flow on the weight signal as a function of temperature (P_{CO_2} = 2 bar).

higher gas velocity. Since only laminar flows occur, the forces acting on the sample are directly proportional to the changes in temperature. This effect, however, has to be taken into account when the weight of the residue is on hand. The difference between this weight value and the last measured weight is assumed to be due only to flow effects and is corrected linearly. The significance of this effect is shown in Fig. 4 in which corrected and uncorrected weight-loss curves are compared.

TEMPERATURE MEASUREMENT

In thermobalances it is impossible to measure the sample temperature inside the char layers using thermocouples, because of the disturbance of the balance signal. Therefore we placed a thermocouple directly underneath the sample holder. To ensure that the so measured temperatures are the same as those in the sample, we firstly determined the axial temperature profile inside the empty reaction tube for different pressures, gas compositions and flow rates. The results indicate a region of constant temperature in the middle of the tube. Then we placed the sample in the middle of this plateau which caused some disturbances in the temperature distribution and carried out gasification experiments. Changing the position of the sample holder and maintaining the same position of the thermocouple we measured rates which are a function of the distance of the thermocouple and the sample holder.

This procedure indicates the region inside the reaction tube where the temperature profile is flat (see Fig. 5). The thermocouple was then placed a few millimeters underneath the bottom of the sample holder taking into account the increment in length due to thermal expansion of the connecting chain.

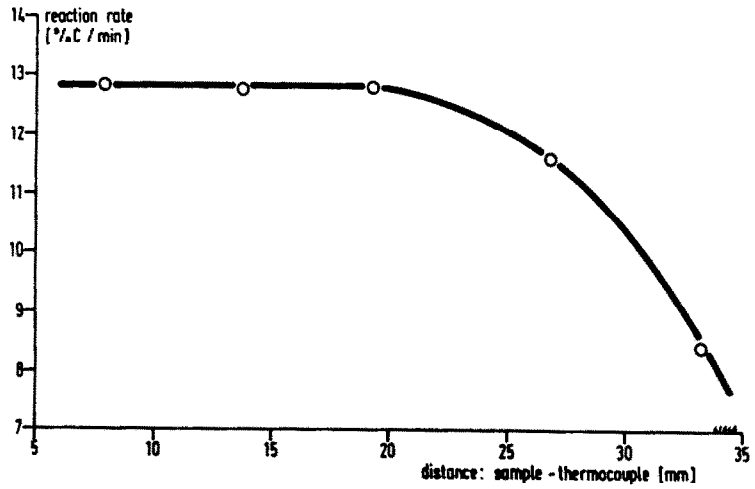

Fig. 5. Measured reaction rates as a function of the distance between sample holder and thermocouple (the place of the thermocouple is fixed).
(T = 950 °C, P_{H_2O} = 40 bar)

CONCLUSION

Four thermogravimetric units similar to the one described above in combination with SARTORIUS-microbalances are being used in our laboratory for the past six years whereby approximately 500 runs per year and unit have been performed. The apparatus were used not only for investigations of coal gasification (ref.3) but also for pyrolysis (ref.4,5) or combustion experiments.

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