A NEW REACTOR FOR THE ANALYSIS OF THERMAL DECOMPOSITION REACTIONS

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(Received 11 November 1981)

ABSTRACT

For the investigation of complex thermal decomposition reactions, i.e. consecutive or reversible reactions, a new reactor has been developed, viz. a gradientless reactor operated like a batch reactor with a programmed linear temperature rise. As the result of the gas circulation in the reactor an accumulation is enforced. Only in this way can consecutive reactions be observed in which gaseous decomposition products participate. In connection with the well-known flush reactor it is possible to investigate the total reaction as well as the single reaction steps.

The results from experiments with the new gradientless reactor and a flush reactor indicate characteristic differences in the case of the decomposition reactions of active coke loaded in flue gas cleaning experiments. A reaction scheme for the decomposition of sulfuric acid and ammonium sulfates is also derived.

INTRODUCTION

The mechanisms and kinetics of the thermal decomposition of solids or the thermal desorption of adsorbed species are usually investigated in differential reactors purged by inert gas (flush reactor) [1] [see Fig. 1(a)].

The inert gas (helium) measured by a flow meter flows with a constant velocity through the sample which is heated at a constant rate. The gases formed during this process are carried away by the helium stream to a mass spectrometer or to a gas chromatograph for analysis. From the measured values of the flow rate $\dot{V}_T$ of the inert gas, the concentration of the gases and the weight of the sample, the rates of the decomposition reactions or of the desorption per unit weight dc/dt can be calculated.

The main advantage of this method is that the kinetic constants of the decomposition reaction or of the desorption can be determined easily. This is true especially in the case of irreversible reactions of the first order with respect to the solid concentration. But a large number of reactions cannot be described as simple irreversible reactions as shown in the scheme
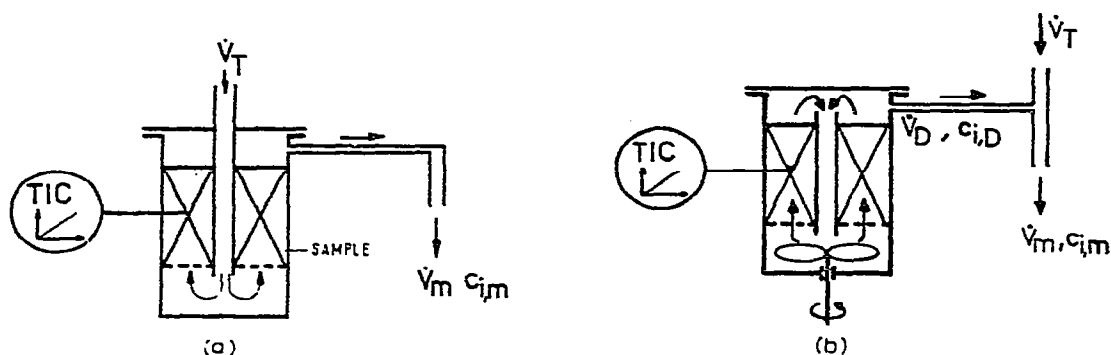
$$solid \xrightarrow{temp.} gaseous\ products$$

Fig. 1. Flow sheets of (a) the flush reactor and (b) the batch reactor.

They are complex reactions, i.e. reversible solid $\rightleftharpoons$ gaseous products or consecutive solid (1) $\rightarrow$ solid (2) + gas (1) $\rightarrow$ gas (2) + gas (3) reactions, of which the total reaction velocity depends on the concentrations of gaseous products, too. A lot of other reaction schemes are well-known.

Because the concentrations of the gaseous products are kept small by purging, the rate of the reverse reaction in the case of the reversible reaction and the rate of the second step in the reaction series are negligible. Therefore no yield of these particular reactions is observed.

It is impossible then to design dimension technical apparatuses, where high concentrations of gaseous products are aimed at [2]. Therefore we have developed a new type of reactor, viz. a gradientless reactor [see Fig. 1(b)] operated like a batch reactor with a linear temperature rise: temperature programmed batch desorption (TPBD). In this reactor, the gaseous decomposition products accumulate during the operation, coming up to concentrations as in technical processes. Table 1 gives a survey of the advantages and disadvantages of both methods.

TABLE 1

Comparison of the flush and batch reactors

	Advantages	Disadvantages
Flush reactor	In the case of simple reactions, activation energy and frequency factor can be determined by the results of one run. Simple construction	Only use for simple reactions. No prediction of the gas composition for technical application
Batch reactor	The investigation of processes, like reversible or consecutive reactions, is possible Simulation and calculation of technical processes.	Probable intermediates are not observed. Test evaluation can be more complex.

The linear temperature rise in the solid is attained by temperature controlled electrical heating outside the wall of the reactor. Even in the case of a negligible rate of the decomposition reaction, gas leaves the reactor because of thermal expansion. The composition $c_{i,D}$ of the gas can be analysed without problem. For a material balance, from which the rate velocities of the decomposition reactions can be derived, the flow rate $\dot{V}_D$ must be known. This flow rate is determined indirectly. The gas flow from the reactor is mixed with a gas flow of an inert carrier gas, of which the flow rate $\dot{V}_T$ is adjusted constantly. Taking this into consideration the gas flow rate $\dot{V}_D$ can be calculated from the concentrations $c_{i,m}$ of all components, which are analysed in the gas mixture [see Fig. 1(b)].

To have uniform conditions in the reactor with regard to the composition as well as the temperature of the gas in the space volume the gas must be ventilated with a fan which is adjusted up to high temperatures. The gas is conducted in a circuit going up through the annulus fixed bed and going down to the fan through a small pipe in the centre.

EXPERIMENTAL DEVICES

Figure 2 shows the experimental set up. The reactor (length = 37 cm, diameter = 5 cm) is made from steel and has separately controlled electrical heatings inside and outside the annulus fixed bed. The solid particles (cylindrical: diameter ≈ length = 4 mm) lie on a sieve plate. To avoid temperature gradients in an axial direction the fixed bed makes up only one third of the whole reactor length. The temperature inside the reactor and at the tube are measured at several points. Below the sieve plate the fan is situated sitting on a long shaft. In the region of the slip ring seal the shaft is hollow and cooled with water. Outside the drive of the shaft is installed.

In the apparatus, a maximum linear temperature rise of 40 K min^{-1} has been realized. It can be operated up to 1100 K.

Before starting an experiment, the reactor is purged with argon from the steel cylinder B102. During the heating period expanding argon and the decomposition gases leave the reactor via a heated tube H202. This product gas, whose pressure is indicated by a U-tube manometer U301, is mixed with helium (injector type mixer I301). The latter comes from a steel cylinder B101 and is metered in a flow meter F101. The gas mixture then goes to analysis or, after passing through a condensation unit K401, directly off. Gas analysis is done in a mass spectrometer M301 because several gases must be analysed quickly especially in the case of a high rate of linear temperature rise. The data from the thermocouples as well as from the mass spectrometer are registered and used for later evaluation in the electronic desk computer consisting of a scanner S301, an ADC unit D301, a real-time clock T301 and the desk computer C301. In comparison with the batch reactor and for the
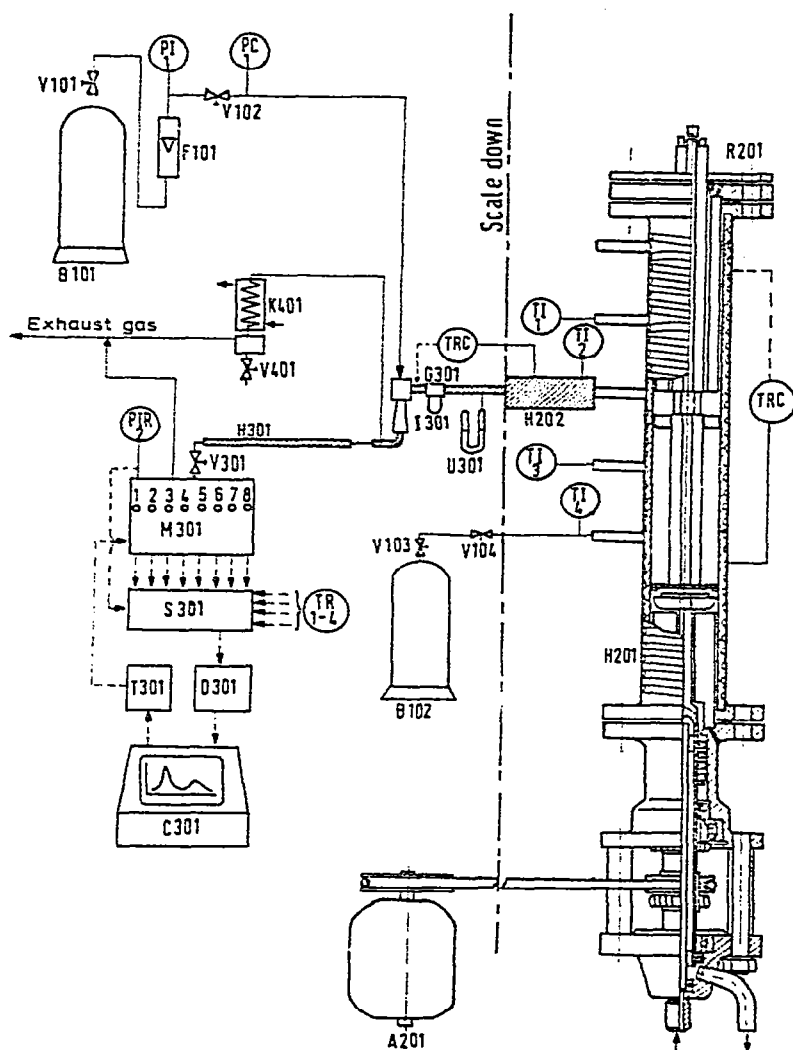
Fig. 2. The experimental set up for the batch reactor. For explanation of symbols, see pp. 171 and 172.

analysis of single steps in consecutive reactions, experiments are conducted in the flush reactor. The experimental set up (see Fig. 3) is similar to the set up in Fig. 2.

The condensation bottle K401 and the cleaning bottle W401 are additional options for testing the degree of acidity of the gases. The pump P401 prevents a pressure increase in the reactor caused by the pressure drop in these units.

THEORY

The main differences between the temperature programmed desorption in a differential flush reactor and in a batch reactor are demonstrated by the
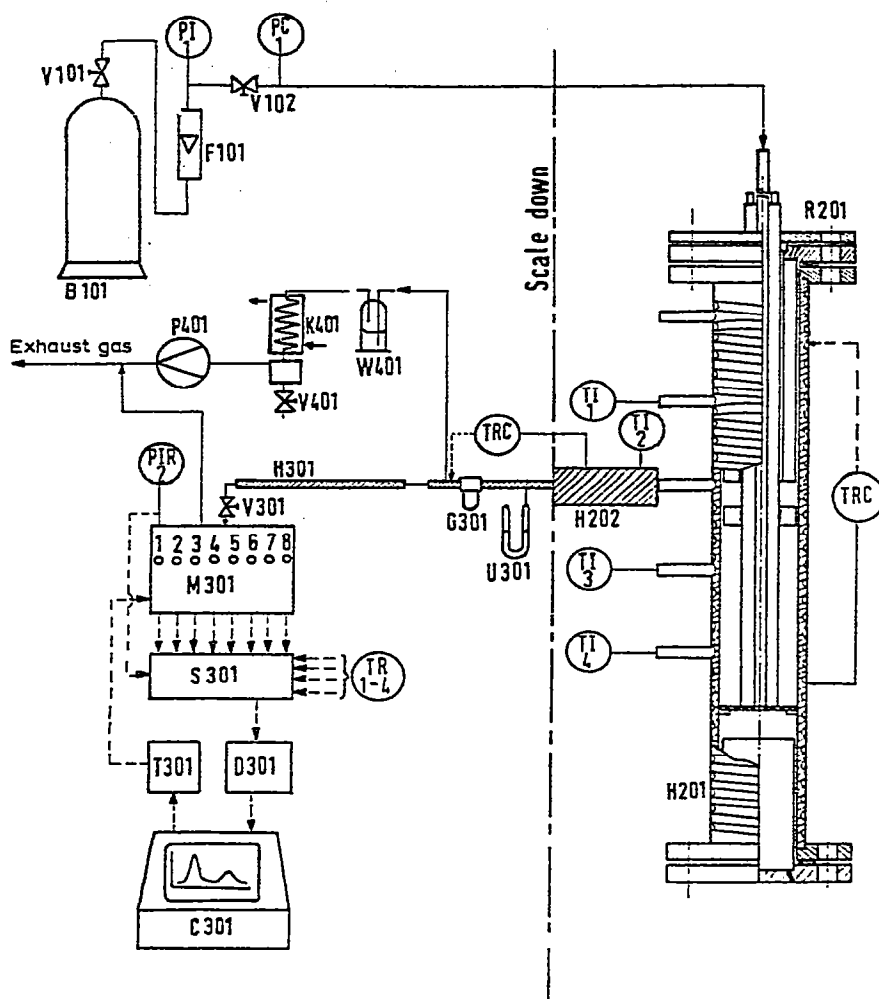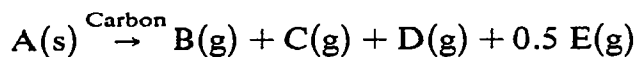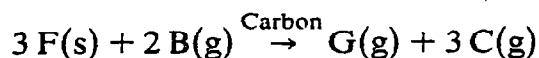
Fig. 3. The experimental set up for the flush reactor. For explanation of symbols, see pp. 171 and 172.

following reaction scheme, which contains a consecutive reaction for the gaseous product B (g).

Reaction 1

$$A(s) \xrightarrow{Carbon} B(g) + C(g) + D(g) + 0.5\ E(g)$$

Reaction 2

$$3\ F(s) + 2\ B(g) \xrightarrow{Carbon} G(g) + 3\ C(g)$$

This scheme is a very rough simplification of the reactions occurring in the thermal decomposition of ammonia bisulfate A(s) on activated carbons containing surface oxides F(s). The ammonia B(g) set free together with steam C(g), sulfur dioxide D(g) and carbon dioxide E(g) reduces surface oxides F(s) at higher temperatures. The products of the latter reaction are

nitrogen G(g) and steam C(g). The thermal decomposition of the surface oxides, which is a very complex problem [3], occurs at higher temperatures and is neglected in this scheme. The following reaction rates, r, are considered

$$r_1 = k_1 \hat{c}_A \exp(-E_1/RT); \quad r_2 = k_2 c_B^2 \hat{c}_F^3 \exp(-E_2/RT)$$

where c are gas phase concentrations, $\hat{c}$ solid phase concentrations, k reaction velocity constants, E activation energies, R the gas constant and T temperature.

In the general case, M reactions can be represented $\Sigma \nu_{ij} A_i = 0$ where ν_{ij} is the stoichiometric coefficient of species A_i in reaction j. The ν_{ij} are negative for the reactants and positive for the products.

The results from balancing these reactions are the rates of decomposition per unit weight dc_i/dt. For the flush reactor the derivation is

$$\frac{dc_{i,m}}{dt} = \frac{m_k}{V_G} \sum_{j=1}^{M} \nu_{ij} r_j - \dot{V}_T c_i \frac{T_0 + k_t t}{T_T} \quad \text{for gases}$$

$$\frac{d\hat{c}_i}{dt} = \sum_{j=1}^{M} \nu_{ij} r_j \quad \text{for solids}$$

For the batch reactor the deviation is

$$\frac{dc_{i,D}}{dt} = \frac{m_k}{V_G} \sum_{j=1}^{M} \nu_{ij} r_j - c_{i,D} \frac{k_t}{T_0 + k_t t} - c_{i,D} \frac{m_k}{V_G} \frac{R(T_0 + k_t t)}{p} \sum_{i=1}^{N_G} \sum_{j=1}^{M} \nu_{ij} r_j$$

for gases or, after mixing with inert gas

$$x_{i,m} = \frac{\dot{V}_D c_{i,D} R}{(\dot{V}_D p/(T_0 + k_t t)) + \dot{V}_T p/T_T}$$

For solids it is the same as for the flush reactor.

Figure 4 shows the numeric solutions of differential equations for a differential flush reactor as well as for the new batch reactor.

In Fig. 4(a) it can be seen that the salt A(s) decomposes with the same velocity in both reactors. In the flush reactor the consecutive reaction is negligible. Rather, no conversion of solid F(s) can be observed. The conversion of F(s) in the batch reactor is limited by the amount of B(g) set free by reaction 1. For the flush reactor the well-known concentration peaks of the gaseous products are plotted in Fig. 4(b). For the batch system the concentrations $c_{i,D}$ of the gas mixture in the reactor are plotted as a function of the desorption temperature in Fig. 4(c), while Fig. 4(d) shows the temperature dependence of the concentrations $c_{i,m}$ in the mixture with the helium carrier gas. During the decomposition period the gaseous products accumulate in the reactor and displace the inert gas. This causes the concentration peak of the inert gas in the mixture with the carrier gas, which is
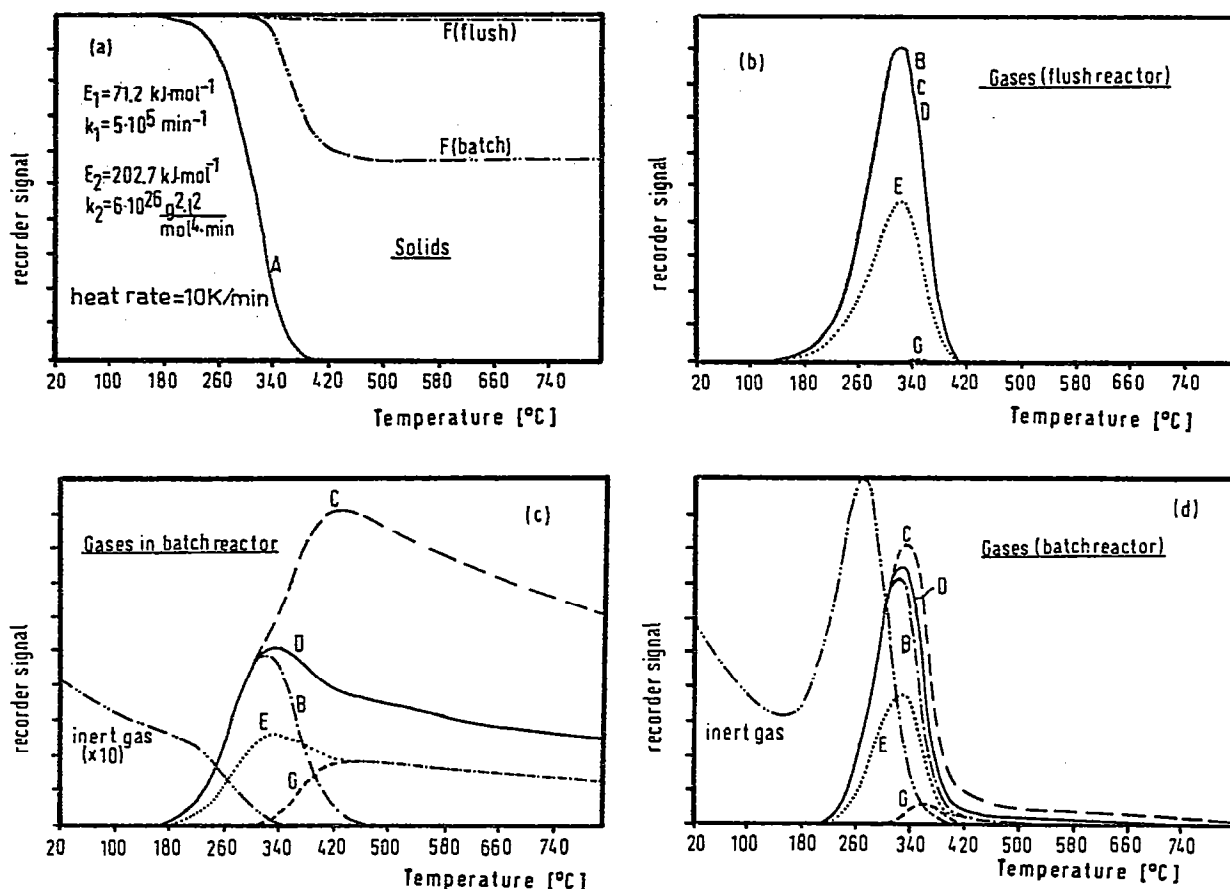
Fig. 4. Temperature-dependent concentration signals for thermal decomposition reactions in the flush reactor (a, b) and the batch reactor (a, c, d).

analysed (see Fig. 1). All the other gaseous decomposition products are registered at higher temperatures than the gases from the flush reactor because of the accumulation in the void volume of the batch reactor. As was expected there is a larger yield of reaction 2 only in the batch reactor .

In a similar way differences between the flush reactor and the batch reactor can be demonstrated for reversible reactions.
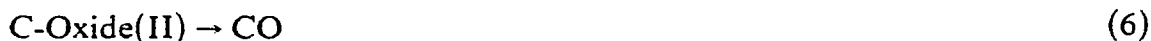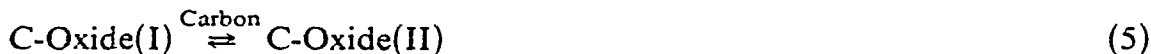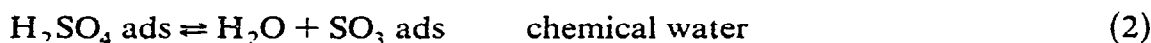
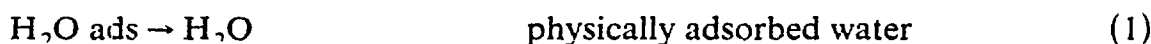## RESULTS AND DISCUSSION

These studies are performed by designing the regeneration unit of the BF-process for the simultaneous removal of SO_2 and NO_x[4]. Activated coke made from bituminous coal is used as the adsorbent/catalyst for flue gas cleaning. Sulfuric acid and, after ammonia injection, ammonia salts deposit on the inner surface of the active coke. Several active coke samples taken

from experiments for flue gas cleaning were investigated in thermal desorption experiments.

For some of the samples, the results from the flush reactor and batch reactor experiments are shown below. If no ammonia is injected, the sample contains only sulfuric acid. Results for such a sample are plotted in Fig. 5.

At lower temperatures, physically adsorbed water vapor desorbs. The decomposition of the sulfuric acid occurs at temperatures about 300°C. Differences between flush and batch reactors can be observed in the concentrations of the gaseous carbon oxides. Furthermore in the batch reactor the gaseous products appear at higher temperatures than in the flush reactor. There the physically adsorbed part of the water shows a greater temperature shift than the chemically adsorbed part. In this batch reactor experiment only one water peak was observed. But if the relation of water adsorbed physically to water bound chemically increases two peaks appear (see Fig. 6).

The following reaction scheme was derived for describing the experimental results (Fig. 5) with the minimum number of reactions possible. It explains as well the appearence of the peaks of all important components as the differences in the yields of the gaseous carbon oxides [5].

$$H_2O \text{ ads} \rightarrow H_2O \qquad \text{physically adsorbed water} \qquad (1)$$

$$H_2SO_4 \text{ ads} \rightleftharpoons H_2O + SO_3 \text{ ads} \qquad \text{chemical water} \qquad (2)$$

$$SO_3 \text{ ads} \overset{Carbon}{\rightarrow} SO_2 + C\text{-Oxide(I)} \qquad (3)$$

$$C\text{-Oxide(I)} \rightarrow CO_2 \qquad (4)$$

$$C\text{-Oxide(I)} \overset{Carbon}{\rightleftharpoons} C\text{-Oxide(II)} \qquad (5)$$

$$C\text{-Oxide(II)} \rightarrow CO \qquad (6)$$

C-Oxide(I) and C-Oxide(II) are different configurations of carbon surface oxides [6].
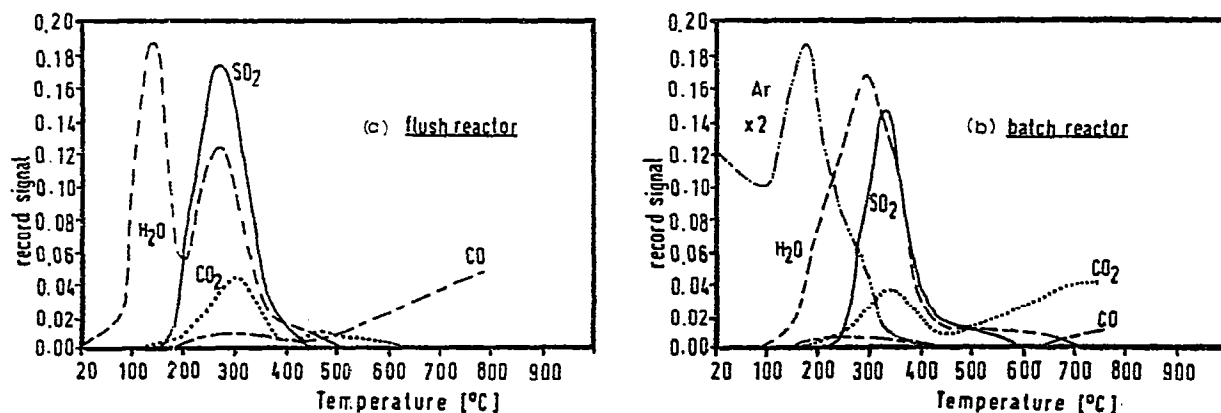

Fig. 5. TPD records for active coke from flue gas desulfurization without ammonia injection.
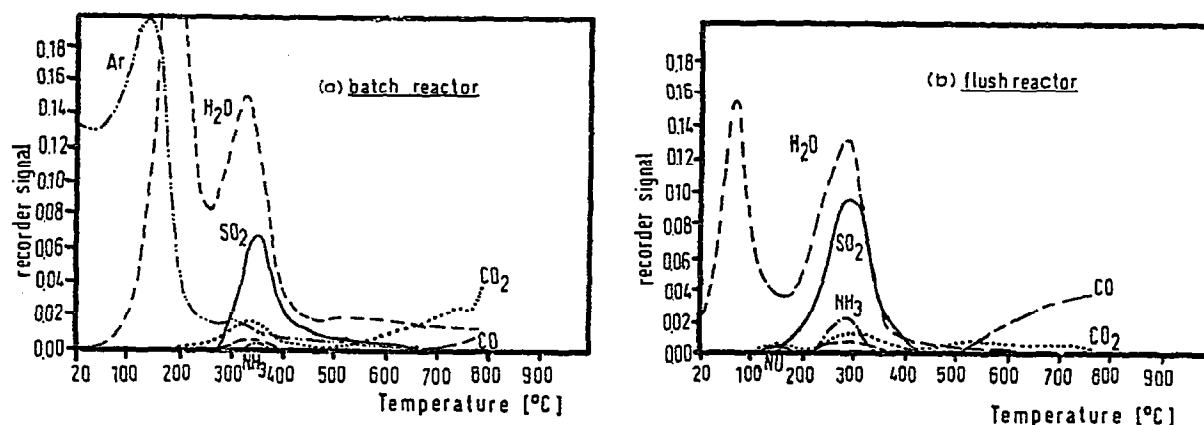
Fig. 6. TPD records for activated carbon from flue gas desulfurization with ammonia injection.

The single peaks of H_2O, SO_2, CO_2^- and CO can be explained by reactions (1)–(4) and (6). As the result of the accumulation of the gaseous products in the batch reactor the reversible reaction (2) becomes more important. Therefore all gaseous products leave this reactor at a higher temperature than for the flush reactor.

The differences in the concentrations of the gaseous carbon oxides can be explained as the result of steam accumulation in the batch reactor. This can be proved by experiments carried out in the flush reactor with a humid helium stream. They have shown similar results for the formation of the carbon oxides as experiments in the batch reactor. Consequently water influences decomposition of carbon surface oxides so that more CO_2 and less CO are formed.

Results for decomposition experiments with another sample which was prepared by desulfurization of synthetic flue gas with ammonia injection are shown in Fig. 6.

By chemical analysis of a sample loaded active coke a mixture of sulfuric acid and ammonium bisulfate were detected. The thermal regeneration of such a sample gives decomposition products at temperatures about 300°C, too. In addition to the known products of sulfuric acid decomposition (Fig. 5) ammonia appears and carbon dioxide disappears in the region about 300°C. The ammonia concentration is much lower in the batch experiment than in the flush desorption. This agrees with the theoretical calculation for the consecutive reaction, at which the second step is the reaction between ammonia and carbon oxide(I). The concentration of both components decreases and with that the CO_2 formation, too.

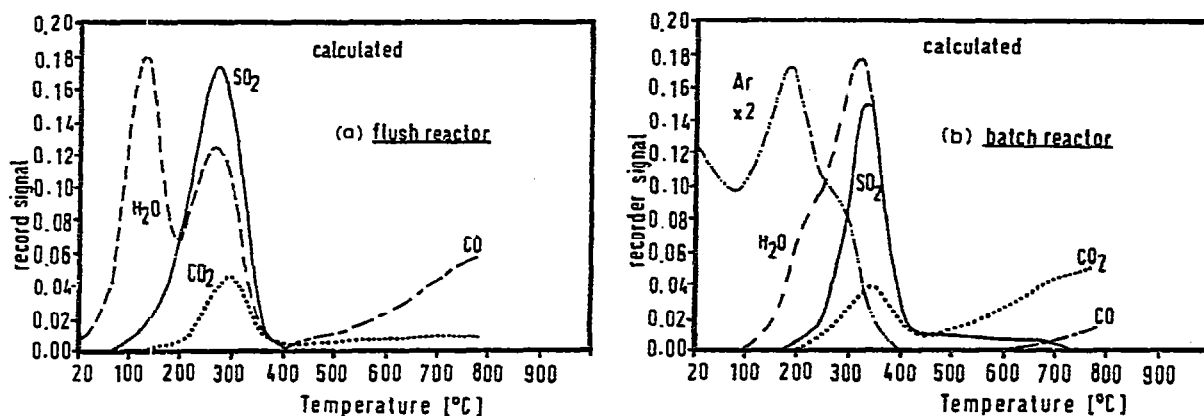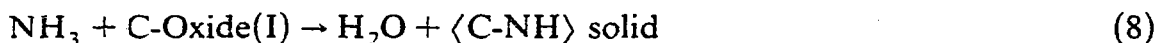In the case of ammonia injection the reaction scheme must be extended by two reactions

$$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3 \text{ ads} \tag{7}$$

Fig. 7. Calculated TPD records for active coke from flue gas desulfurization.

$$NH_3 + C\text{-}Oxide(I) \rightarrow H_2O + \langle C\text{-}NH \rangle \text{ solid} \tag{8}$$

The structure of the secondary product $\langle C\text{-}NH \rangle$ solid is still unknown, but its existence has been proved [7,8].

EVALUATION

From the above specified balances the measurable concentrations cannot be calculated as a function of time directly. Therefore the coupled system of first order ordinary differential equations must be solved numerically, i.e. by the method of Runge–Kutta–Merson [9].

Normally the kinetic constants and the activation energies used in the balances are unknown. They can only be determined by iterative methods for curve fitting. The results of a curve fitting for the experimental results plotted in Fig. 5 are shown in Fig. 7. There are only small differences between experiment and calculation. This means that the above mentioned scheme for the thermal decomposition of sulfuric acid on active coke describes the reactions sufficiently. In this connection it is very important that the reaction scheme has been applied in the same manner for the balances of the flush reactor as well as of the gradientless reactor.

During the evaluation other reaction schemes were also tested, giving less sufficient results. All these tests showed that reverse reactions do not influence the distribution of the gaseous reaction products at the exit of the flush reactor. More details can be found elsewhere [5].

ACKNOWLEDGEMENT

SYMBOLS

A	component
c	gas phase concentration mole l^{-1}
$\hat{c}$	solid phase concentration mole g^{-1}
k	reaction velocity constant
E	activation energy
R	gas constant
t	time
T	temperature
T_T	room temperature
m_k	weight of sample
V_G	free reactor volume
r	reaction rate
$\dot{V}_T$	flow rate of inert gas
k_t	heating rate
p	pressure
x	dimensionless concentration
ν	stoichiometric coefficient

Indices

i	number of component
m	after mixing with inert gas
j	number of reaction
M	last number of reaction
N_G	last number of gas phase component
D	for mixing with inert gas

Apparatus shown in Figs. 2 and 3

B 101	steel cylinder for helium
B 102	steel cylinder for argon
F 101	flow meter for helium
V 101	reducing valve
V 102	flow controller
V 103	reducing valve
V 104	valve
A 201	electric motor (185 W)
H 201	electric heating 2 kW outside, 1 kW inside
H 202	electric heating 100 W
R 201	reactor
C 301	desk computer
D 301	ADC unit
G 301	gas filter
H 301	heating capillary tube

I 301   injector type mixer
M 301   mass spectrometer
S 301   scanner
T 301   real-time clock
U 301   U-tube manometer
V 301   valve
K 401   condensation unit
P 401   pump
V 401   outlet valve
W 401   cleaning bottle

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