

# HYDROGASIFICATION OF BROWN COAL\*

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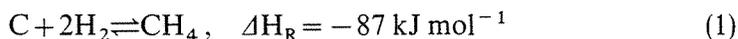
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## Abstract

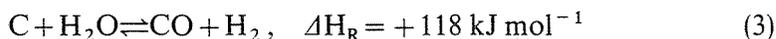
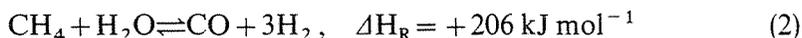
Hydrogasification of Brown Coal as a route for producing substitute natural gas (SNG) is discussed on the basis of experimental results received with two types of Rheinische Braunkohle (3.5 and 17 wt % ash), using slow linear heating, shock heating and hydrogen pressures between 0.2 and 5 MPa. A complete gasification within less than 10 min under conditions of hydrolysis (no coke formation) with maximum methane selectivity is possible by using 5 MPa hydrogen, 950 °C and shock heating. Moisture introduced either with coal or hydrogen strongly inhibits methane formation, probable reasons and possible solutions of the problem are discussed.

## Background

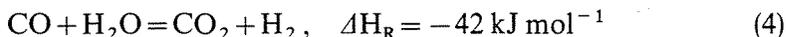
Hydrogasification is one possibility for synthesis of substitute natural gas (SNG).



The advantage of this reaction is its exothermy. But there are two problems. One problem arises from the carbonaceous material to be gasified, which must be a very reactive one. Brown coals or lignites satisfy this precondition. The other problem represents hydrogen, which has to be produced either by steam reforming of methane (eq. (2)) or by water vapour gasification of coke (eq. (3)). These reactions are strongly endothermic.



Including the necessary carbon monoxide shift reaction (eq. (4))



\* Summary of a project on 'Chemism and kinetics of hydrogasification of Rheinische Braunkohle', sponsored by the Federal Ministry of Research and Development of the Federal Republic of Germany<sup>[1]</sup>

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which is necessary for both routes, the same overall reaction results (eq. (5)):



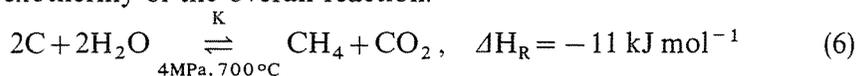
It is remarkable that this reaction is exothermic. Hydrogasification of coal differs from eq. (1). Three steps are generally discussed [2, 3]:

- pyrolysis
- fast hydrogasification (hydropyrolysis)
- slow hydrogasification (coke gasification).

Pyrolysis and hydropyrolysis reactions are initiated by thermally induced bond cleavages, their rate is high. Gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$ ) and volatiles or tar (long-chain aliphatics, one to three ring aromatics) are formed. Hydropyrolysis may be described as the reaction between molecular constituents of coal (radicals) and molecular hydrogen. Coke gasification is necessary, if coke is formed as a residue of pyrolysis and hydropyrolysis reactions by condensation of radicals. Methane is the predominant or single product. The rate of this reaction even at high temperatures is low. Selectivity of hydrogasification may be controlled by the reaction conditions, but it is predetermined by the molecular structure of the coal. The aim of hydrogasification of coal is to avoid tar and especially coke formation. This condition is equivalent to a complete gasification of the coal under conditions of pyrolysis and hydropyrolysis with methane as the only hydrocarbon product. If this condition is not realizable, the residual coke may be gasified with water vapour for producing hydrogen (eq. (2)). The reaction rate of water vapour gasification is approximately 10 times higher than that of hydrogasification.

For this reason, alternatives to hydrogasification must be discussed, namely

- a classical route, starting with non-catalyzed water vapour gasification (eq. (3)), followed by the carbon monoxide shift reaction (eq. (4)) and methanation of a carbon monoxide (back reaction of eq. (2)), and
- a one step catalytic gasification (eq. (6)), which makes use of the exothermy of the overall reaction.



A useful catalyst must accelerate not only the water vapour gasification, but it also must be active in catalyzing the carbon monoxide shift and carbon monoxide methanation reaction. Potassium represents such a powerful catalyst. Optimum reaction conditions are 4 MPa and 700 °C. The feasibility of this process was demonstrated by EXXON. [4, 5] The catalytic activity of potassium in water vapour gasification was shown by many authors [6, 7], the activity of potassium in the carbon monoxide shift and methanation reaction by HÜTTINGER et al. [8, 9].

## Thermodynamics

The gas equilibria of hydrogasification of carbon according to eq. (1)



are known. It is also known, that the activity of various types of carbons including cokes is one [2]. As follows from Fig. 1 increased pressure is a fundamental prerequisite for hydrogasification, because sufficiently high gasification rates are only obtained at temperatures in the range of 1000 °C.

In hydrogasification of coals various radicals are formed, in gasification of brown coals especially methyl and methylene radicals. They may react with hydrogen by formation of methane, ethane or ethylene (eq. s (7)–(11)).



Figure 2 shows the GIBBS free reaction enthalpy changes of these reactions as function of temperature [10, 11]. All reactions are strongly exergonic. This also holds for eq. (7), as a hydrogen radical formed in this reaction will immediately react according to eq. (8), resulting in a strongly exergonic overall reaction. On the contrary, the  $\Delta G_R^0$  values of eq. (1) are positive. This comparison underlines the importance of a reactive carbonaceous material forming high quantities of methyl and methylene radicals by thermal bond cleavages. Formation of such radicals is favoured with aliphatic structures prevailing in brown coals, but it is complicated with coals

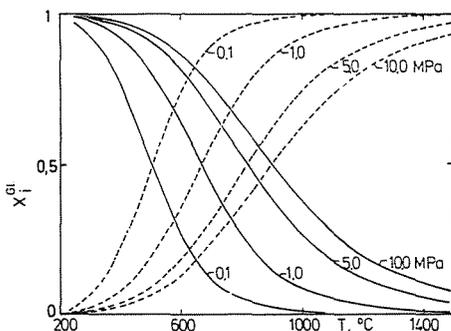


Fig. 1. Equilibrium mole fractions of the reaction  $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$ ; —  $\text{CH}_4$ , ---  $\text{H}_2$

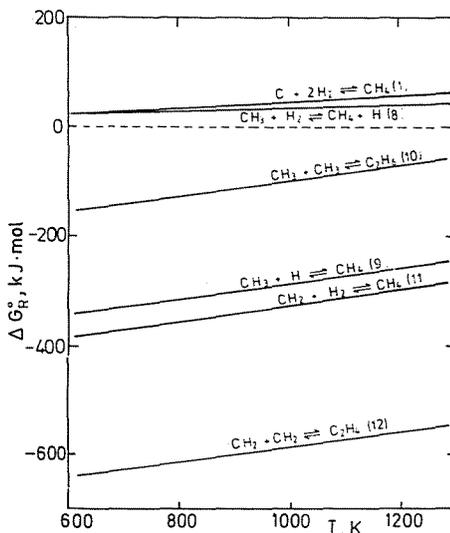


Fig. 2. GIBBS free reaction enthalpy changes of the reactions between methyl, methylene and hydrogen

of higher rank according to their increased aromaticity. Therefore, brown coal represents an ideal raw material for an optimum hydrogasification under conditions of pyrolysis and hydropyrolysis reactions.

### Pyrolysis

Pyrolysis of both coals was studied at low temperature increase ( $4 \text{ K min}^{-1}$ ) up to  $850^\circ\text{C}$ , and also by shock heating ( $100 \text{ K s}^{-1}$ ) to  $850^\circ\text{C}$ , which was held for 1 hour in both cases. Argon pressure was varied between 0.2 and 5 MPa.

Figure 3 shows formation rates of carbon dioxide, carbon monoxide, ethane and methane, related on the initial amount of carbon (coal I), as function of temperature during linear heating at pressures of 0.2, 1 and 5 MPa. Carbon dioxide and carbon monoxide are formed by at least two different reactions, whereas ethane and methane formations extend over the temperature range from 200 to  $800^\circ\text{C}$ . It is remarkable that the influence of pressure on all reactions is very small. The same results were received with coal II (ash content 17 wt% as compared to 3.5 wt% of coal I).

Figure 4 gives a summary of the results, showing the relative mass losses (wf) in the upper part and the carbon conversions to gases and volatiles in the lower part. Carbon conversion to volatiles was determined as follows (eq. (12)):

$$m_{C, vol.} = m_{C, o} - m_{C, gases} - m_{C, res.} \quad (12)$$

$m_{C, o}$  = initial amount of carbon

$m_{C, res.}$  = carbon in pyrolysis residue.

The plots underline that pressure really has a negligible influence on the relative mass loss and the yields of the various products. Similar results were received with coal II except the yield of volatiles which was approximately twice as high. The reason may be a slightly different molecular structure of the coal, but the influence of minerals may also be responsible.

Results found with both coals by shock heating to 850 °C do not decisively differ from those of slow linear temperature increase to 850 °C. The influence of pressure is also negligible, the relative mass losses are nearly the same, only the yields of volatiles, methane and carbon monoxide are slightly increased.

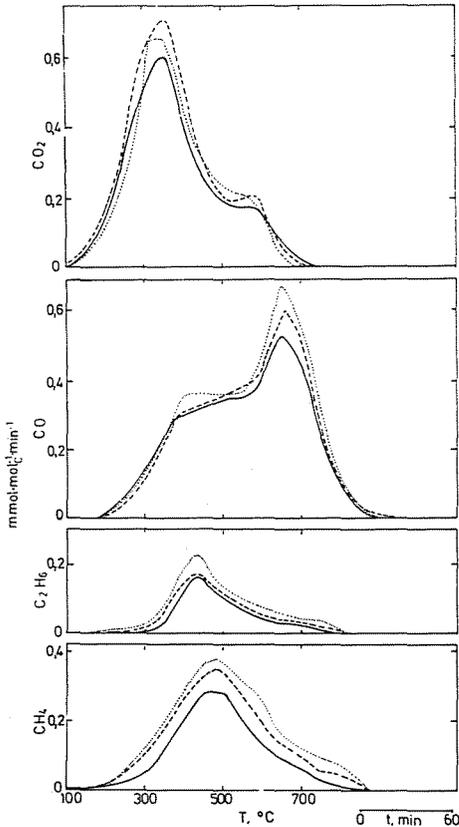


Fig. 3. Formation rates of gases during pyrolysis of coal I (dry) in Ar at linear heating ( $4 \text{ K min}^{-1}$ ); — 0.2 MPa, --- 1 MPa, ... 5 MPa

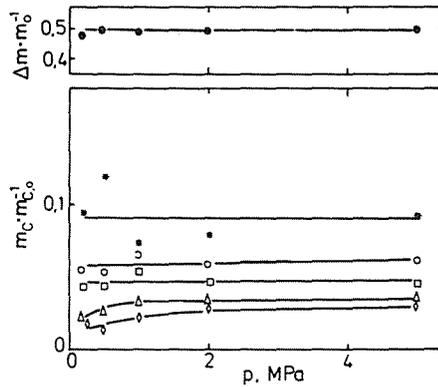


Fig. 4. Relative mass losses  $\Delta m/m_0$  and carbon conversions to gases and volatiles  $m_c/m_{c,0}$  of coal I (dry) after pyrolysis in Ar at  $4 \text{ K min}^{-1}$  to  $850^\circ\text{C}$  (residence time 1 h);  $\Delta$   $\text{CH}_4$ ,  $\diamond$   $\text{C}_2\text{H}_6$ ,  $\circ$   $\text{CO}$ ,  $\square$   $\text{CO}_2$ ,  $\star$  volatiles

As a consequence it may be followed that reaction conditions with the exception of pyrolysis temperature are no tool to influence selectivity of brown coal pyrolysis. This means that the pyrolysis behaviour is predetermined by the molecular structure of the coal. This property is not surprising, because brown coal pyrolysis is a solid phase pyrolysis, comparable to the pyrolysis of thermosetting resins like phenolic or furfuryl alcohol resins, which show the same behaviour.

## Hydrogasification

### *Dry conditions*

Brown coals are hauled with a moisture content of approx. 50 wt%. By predrying in air moisture may be diminished to approximately 15 wt%. Final drying has to be performed in inert atmosphere or in vacuum. In our studies, the coals were dried at room temperature in vacuum to 1.5 wt% (coal I) or 1.0 wt% (coal II) moisture.

Results of hydrogasification of dried coal I at linear temperature increase are shown in Fig. 5 for various pressures. In comparison to pyrolysis the following differences can be observed. (1) The first peak of carbon dioxide and carbon monoxide formation is unchanged by hydrogen pressure; (2) the second peak of carbon dioxide and carbon monoxide formation is decreased with increasing hydrogen pressure; (3) ethane formation is enhanced and shifted from  $450$  to  $550^\circ\text{C}$  ( $T_{\text{peak}}$ ); (4) methane formation is strongly enhanced and resulting from several reactions ( $T_{\text{peak}} = 550, 650, 800^\circ\text{C}$ ).

Carbon dioxide formation may be attributed to labile functional groups (mainly carboxyl and additionally ester, anhydride, lactone), which are decomposed in a similar way under all conditions. Carbon monoxide may be formed from decomposition of aldehydes, anhydrides and aliphatic ethers (lower range), lactones, chinones and hydroxyl groups (upper range). Decrease of carbon monoxide and carbon dioxide formation in the upper range may be caused by increased volatilization of tary, oxygen containing products. Volatilization of such products is favoured with increasing hydrogen pressure by saturation of radical fragments, whereby condensation reactions are hindered and vapour pressure is additionally increased. In the case of carbon monoxide it may also be that the oxygen containing groups are hydrogenated by formation of water. Dehydroxylation instead of decarbonylation in the presence of hydrogen at elevated pressure was found in studies with model compounds [12–14]. In summary, it may be assumed that the formation of

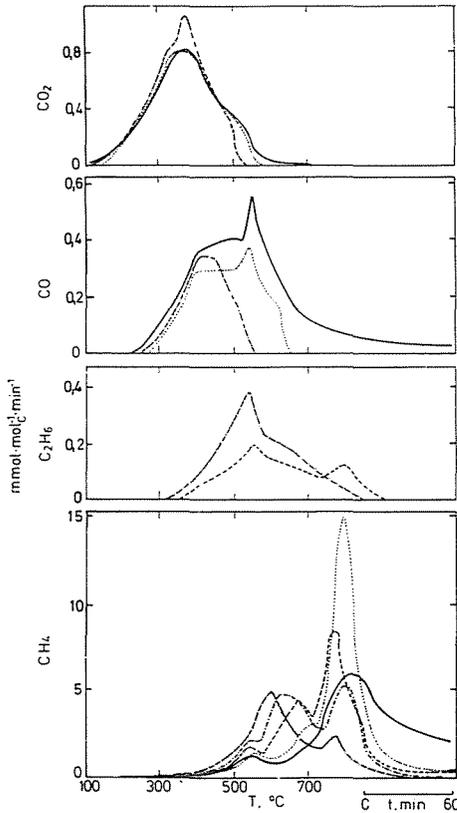


Fig. 5. Formation rates of gases during hydrogasification of coal I (dry) at linear heating ( $4 \text{ K min}^{-1}$ ); — 0.2 MPa,  $\cdots$  0.5 MPa, --- 1 MPa, -·- 2 MPa, -/- 5 MPa

carbon dioxide and carbon monoxide from functional groups has no decisive influence on the formation of hydrocarbons (methane, ethane, volatiles).

Formation of ethane and methane by pure pyrolysis reactions should result from decomposition of alkyl groups, which are less stable than ethyl, methyl and methylene groups as follows from bond energy considerations [1]. Increased ethane formation at higher hydrogen pressure may be caused by cracking and simultaneous hydrogenation of carbon bridges and especially aliphatic rings, which are connected to aromatic ring systems. At temperatures around 550 °C ethane formation is thus competing with methane formation. Cracking of aromatic structural units may be responsible for methane formation at about 650 °C, but the shift of this reaction to lower temperatures with increasing hydrogen pressure lets also suggest a hydrocracking of ring systems.

The third methane formation ( $T_{\text{peak}} = 800 \text{ °C}$ ) may be ascribed to the reaction between a very reactive semi coke and molecular hydrogen. From Fig. 5 could be followed a rate decrease (above 0.5 MPa) with increasing hydrogen pressure, because the rates are related on the initial amount of carbon. If the rates are related on the actual amount of residual carbon, they are independent of the hydrogen pressure (above 0.5 MPa). This result underlines,

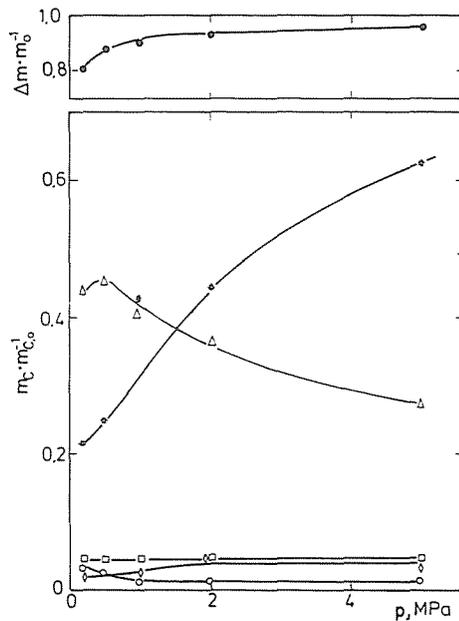


Fig. 6. Relative mass losses  $\Delta m/m_0$  and carbon conversions to gases and volatiles  $m_g/m_{c,0}$  of coal I (dry) after hydrogasification at  $4 \text{ K min}^{-1}$  to  $850 \text{ °C}$  (residence time 1 h);  $\Delta$   $\text{CH}_4$ ,  $\diamond$   $\text{C}_2\text{H}_6$ ,  $\circ$   $\text{CO}$ ,  $\square$   $\text{CO}_2$ ,  $\star$  volatiles

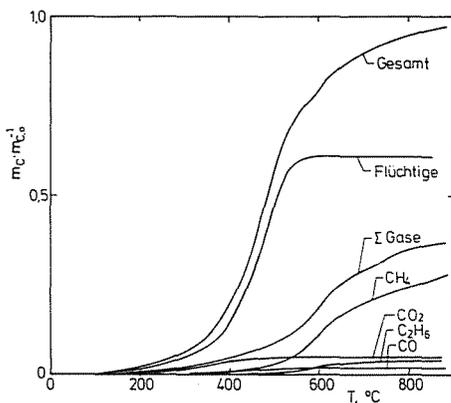


Fig. 7. Total carbon conversion and carbon conversions to gases and volatiles during hydrogasification of coal I (dry) at  $4 \text{ K min}^{-1}$  and  $5 \text{ MPa H}_2$

that a maximum gasification rate for this type of reaction is already achieved with 1 MPa hydrogen.

Volatiles are formed in hydrogasification by saturation of larger radical fragments with hydrogen. Therefore, especially at a slow temperature increase, formation of volatile products is competing with methane formation. The influence of hydrogen pressure on both reactions follows from Fig. 6, which shows the relative mass losses (upper part) and the carbon conversion to the various gases and volatiles (lower part). Increasing hydrogen pressure slightly increases the ethane yield and decreases the carbon monoxide yield, as already revealed by Fig. 5. The yield of volatiles rises from 20% (0.2 MPa) to more than 60% (5 MPa), whereas the methane yields are simultaneously lowered. The reason has already been mentioned. At low temperatures the thermal energy is not sufficiently high in order to produce small radical fragments. This situation may only be changed by a very rapid temperature increase to high temperatures, as will be shown later.

For further illustrating the favoured formation of volatiles the temperature increase was interrupted at various temperatures in order to analyse the residues by elementary analysis. This procedure allowed to make a carbon balance. The result is shown in Fig. 7 for a hydrogen pressure of 5 MPa. It reveals that carbon conversion up to  $500^\circ \text{C}$  mainly occurs by formation of volatiles ( $\sim 0.6$ ). Therefore, methane formation mainly occurring at higher temperatures is limited by the residual carbon.

The hydrogenating effect of increased hydrogen pressure follows from the same experiments, if the carbon/hydrogen ratio of the residues is plotted versus temperature (Fig. 8). A steep increase is found during pyrolysis in argon above  $450^\circ \text{C}$ , whereas the slow increase with 5 MPa hydrogen underlines, that the

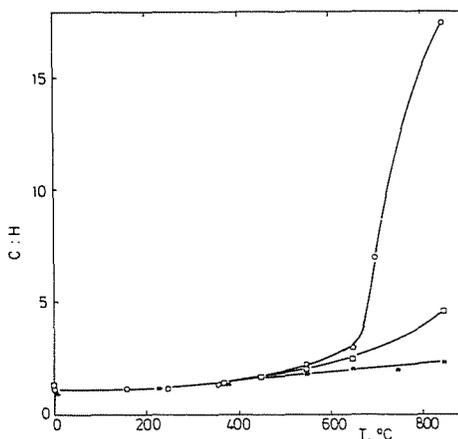


Fig. 8. Carbon/hydrogen ratios of coal I (dry) during pyrolysis (1 MPa Ar, o) and hydrogasification (1 MPa, □ and 5 MPa H<sub>2</sub>, ★) at 4 K min<sup>-1</sup>

residue is kept in a highly hydrogenated state up to the final temperature of 850 °C. This result indicates the possibility, to perform hydrogasification really under conditions of hydrolysis, whereby the rate of temperature increase and the final temperature determine the selectivity towards volatiles or methane. The same conclusions are possible in the case of coal II. Results of isothermal gasification at 850 °C after shock heating are shown in Fig. 9 for hydrogen pressures of 1 and 5 MPa (lower and upper part). Formations of carbon dioxide and carbon monoxide are finished already after 5 min. This also holds for ethane formation at 1 MPa. At 5 MPa hydrogen pressure ethane and methane formations exhibit a double peak, but the hydrolysis reactions are also finished within 7 to 8 min. They are followed by a very slow gasification of the residual coke. The double peaks, which preferentially appear at temperatures starting at 850 °C and at hydrogen pressures of 5 MPa (850 °C and 1 MPa is an exception) may be attributed to a two step hydrolysis, occurring with aliphatic and aromatic constituents of the coal.

A summary of the investigations at 850 °C and various hydrogen pressures is shown in Fig. 10. Methane represents the main product, which is caused by the fast heating, whereby formation of volatiles is depressed due to formation of small radical fragments. Increasing pressure between 0.2 and 1 MPa has the most tremendous effect. Nevertheless, with increasing hydrogen pressure formation of volatiles is favoured again as observed in experiments at slow linear heating. Simultaneously to the increase of volatiles the yield of ethane also rises. With coal I the same pressure dependence was observed.

The influence of gasification temperature at 1 and 5 MPa is represented in Figs 11 and 12. They show, that 850 °C is a minimum temperature for achieving

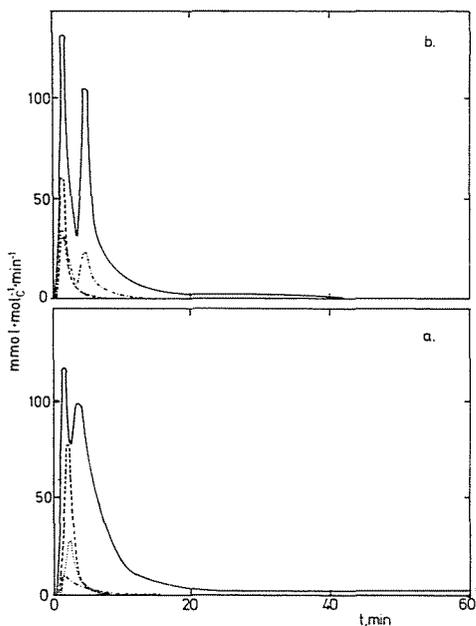


Fig. 9. Gas formation rates during isothermal hydrogasification of coal I (dry) (after shock heating at  $100 \text{ K s}^{-1}$  to  $850 \text{ }^\circ\text{C}$ ) at 1 MPa  $\text{H}_2$  (a) and 5 MPa  $\text{H}_2$  (b); —  $\text{CH}_4$ , ---  $\text{CO}$ ,  $\cdots$   $\text{CO}_2$ , - · -  $\text{C}_2\text{H}_6$

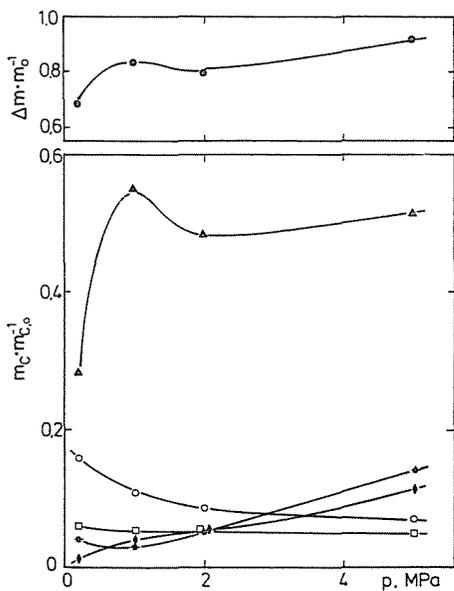


Fig. 10. Relative mass losses  $\Delta m/m_0$  and carbon conversions  $m_C/m_{C_0}$  of coal I (dry) after isothermal hydrogasification at  $850 \text{ }^\circ\text{C}$  (residence time 1 h); ▲  $\text{CH}_4$ , ○  $\text{CO}$ , □  $\text{CO}_2$ , ◆  $\text{C}_2\text{H}_6$ , ☆ volatiles

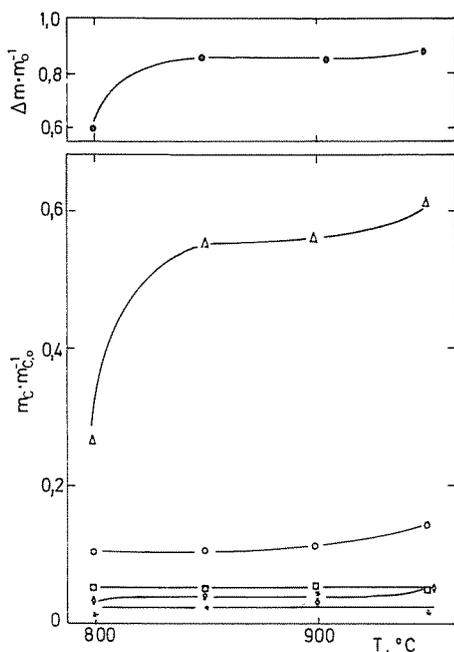


Fig. 11. Relative mass losses  $\Delta m/m_0$  and carbon conversions to gases and volatiles  $m_c/m_{c,0}$  of coal I (dry) after isothermal hydrogasification at 1 MPa (residence time 1 h);  $\Delta$   $\text{CH}_4$ ,  $\circ$   $\text{CO}$ ,  $\text{CO}_2$ ,  $\square$   $\text{C}_2\text{H}_6$ ,  $\star$  volatiles

a high methane yield. An additional increase of the methane yield is found by raising the temperature from 900 to 950 °C. The results at 5 MPa hydrogen (Fig. 12) clearly reveal a simultaneous drastic drop of the volatiles yield. But it is remarkable that the yield of volatiles at 5 MPa is higher than at 1 MPa hydrogen pressure even after shock heating. These results confirm the conclusion drawn from the experiments at slow linear heating, namely that hydrogasification may completely be performed under conditions of hydrolysis, provided that shock heating is applied and the pressure and temperature are sufficiently high, i.e.  $\geq 5$  MPa and  $\geq 950$  °C.

From the results received at slow linear and shock heating at various hydrogen pressures, a general reaction scheme may be developed, which is shown in Fig. 13. The conversion of the coal to all possible products generally occurs by intermediate formation of polyaromatics. With low hydrogen pressure the polyaromatics are transformed to semi-coke and finally to coke. With increasing hydrogen pressure, formation and existence of polyaromatics is shifted to higher temperatures to such an extent, that formation of semi-coke and coke is excluded. This is the situation at which hydrogasification is

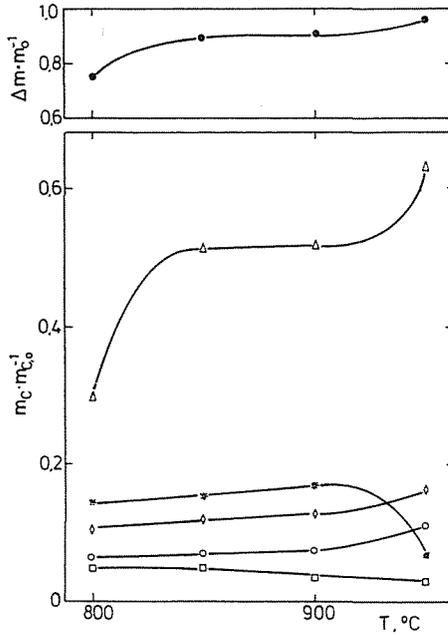


Fig. 12. Relative mass losses  $m/m_0$  and carbon conversions to gases and volatiles  $m_c/m_{c,0}$  of coal I (dry) after isothermal hydrogasification at 5 MPa (residence time 1 h);  $\Delta$   $\text{CH}_4$ ,  $\circ$   $\text{CO}$ ,  $\square$   $\text{CO}_2$ ,  $\diamond$   $\text{C}_2\text{H}_6$ ,  $\star$  volatiles

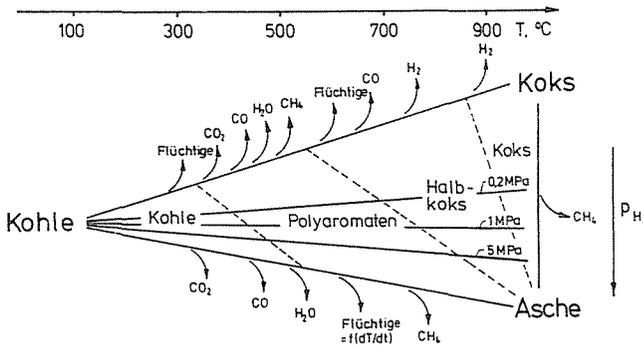


Fig. 13. Reaction scheme of hydrogasification of brown coal at various hydrogen pressures

occurring under pure conditions of hydrolysis. The heating rate determines the selectivity of hydrolysis, i.e. whether volatiles or methane are formed as a main product. High methane selectivity requires fast heating, as given in a fluidized bed, and a temperature of about 950  $^{\circ}\text{C}$ .

### Wet conditions

Using wet coals (15 or 12 wt% moisture), hydrogasification and especially methane formation are strongly altered. As follows from Fig. 14, showing methane formation rates at slow linear heating at hydrogen pressures of 1, 2 and 5 MPa, methane formation is diminished the more the higher the hydrogen pressure is. This result lets suggest, that increased pressure reduces desorption of water with the consequence, that water is blocking active sites at elevated temperature. For clarifying this problem, gasification studies at 1 MPa were performed using wet hydrogen or hydrogen/water vapour mixtures.

Results are shown in Fig. 15. It reveals that even at this low pressure traces of water vapour in hydrogen ( $x_{\text{H}_2\text{O}}=0.02$ ) are sufficient to hinder methane formation to a maximum extent. But it is also remarkable, that no water vapour gasification by formation of carbon monoxide occurs even with very high water vapour contents ( $x_{\text{H}_2\text{O}}=0.75$ ). These results have been confirmed with coal II and also with a coke of coal I (heat treatment temperature 600 °C). With the coke the methane yield decreases from 0.65 in

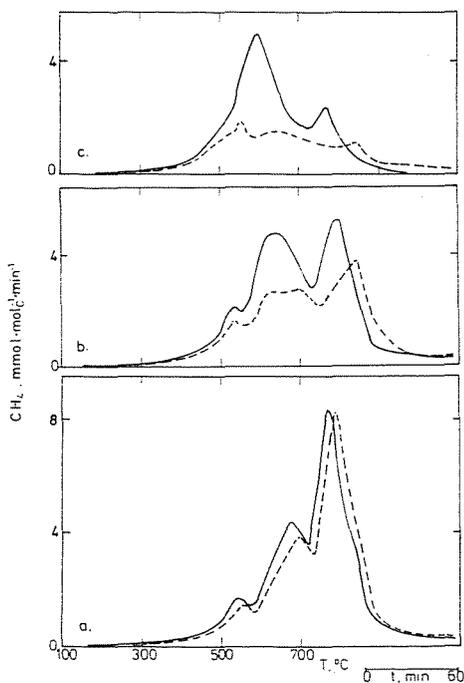


Fig. 14. Methane formation rates during hydrogasification of coal I (wet, 15 wt% moisture) during linear heating ( $4 \text{ K min}^{-1}$ ) at three hydrogen pressures; (a) 1 MPa, (b) 2 MPa, (c) 5 MPa; — dry, --- wet

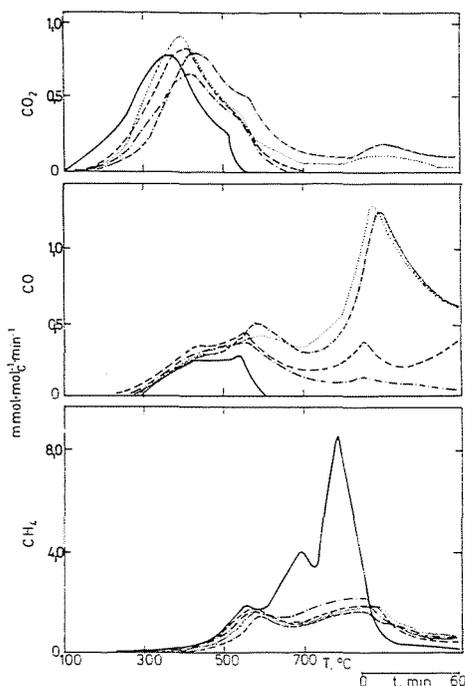


Fig. 15. Formation rates of gases during hydrogasification of coal I (wet, 15 wt% moisture) during linear heating ( $4 \text{ K min}^{-1}$ ) at a total pressure of 1 MPa using pure  $\text{H}_2$  and  $\text{H}_2/\text{H}_2\text{O}$  mixtures; —  $x_{\text{H}_2\text{O}}=0$ , - - - 0.02, - - - 0.1, ··· 0.5, - / - 0.75

dry hydrogen to 0.2 in wet hydrogen ( $x_{\text{H}_2\text{O}} = 0.02$ ). Identical results were received by shock heating.

An explanation of this phenomenon is complicated, but not impossible. First of all it has to be clarified, why traces of water vapour inhibit methane formation. The solution of this problem is closely related to the mechanism of water vapour gasification. It has been found, that water dissociates at the carbon surface (active sites) already at  $500^\circ\text{C}$  forming extremely stable carbon oxygen surface complexes, probably ethers [15–18]. Thermal decomposition of these structures requires temperatures above 800 to  $900^\circ\text{C}$ . They are also stable in a hydrogen atmosphere as follows from Fig. 16, showing desorption experiments in inert atmosphere of frozen in carbon oxygen surface complexes. At  $735^\circ\text{C}$  pure hydrogen does only partially reduce these complexes within 15 min, but they are nearly completely stabilized by a small quantity of water vapour ( $x_{\text{H}_2\text{O}}=0.02$ ). Therefore, it has to be concluded that traces of water vapour are blocking active sites by formation of extremely stable carbon oxygen surface complexes.

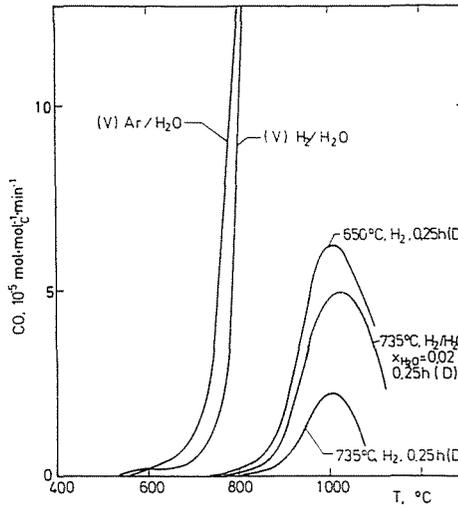


Fig. 16. CO formation rates from a PVC coke (HTT 900 °C) during gasification with equimolar Ar/H<sub>2</sub>O and H<sub>2</sub>/H<sub>2</sub>O mixtures at 10 K min<sup>-1</sup> (V) and during desorption in N<sub>2</sub> at 20 K min<sup>-1</sup> after pregasification at 850 °C (0.5 h), subsequent treatments in H<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O and quenching to room temperature at 300 K s<sup>-1</sup> (D)

It is another question why high contents of water vapour in hydrogen do not result in a water vapour gasification. This effect may be explained by an inhibition of water vapour gasification by hydrogen, however not only by blocking of active sites as generally discussed in the literature [19]. The reason is a molecular or diffusion effect, by which the concentration of the water vapour in micropores is strongly diminished as compared to the concentration in the free gas phase. The explanation is given in Fig. 17, showing water vapour

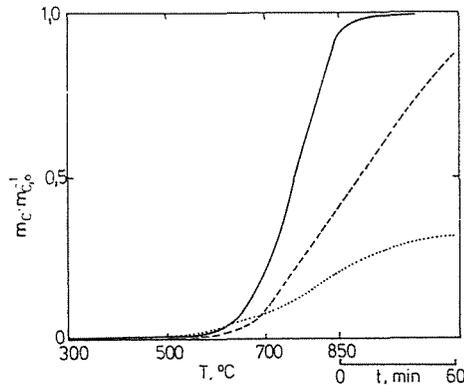


Fig. 17. Carbon conversions to gases of coke of coal I (HTT 600 °C) during gasification at 4 K min<sup>-1</sup> and 1 MPa in equimolar gas mixtures; — Ar/H<sub>2</sub>O, --- He/H<sub>2</sub>O, ··· H<sub>2</sub>/H<sub>2</sub>O

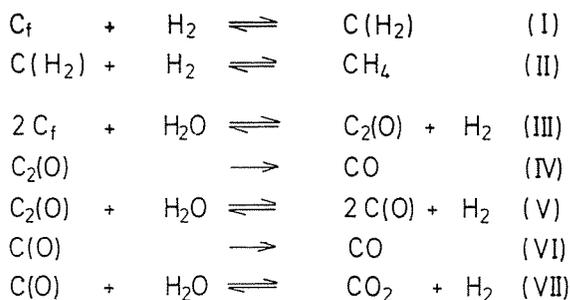


Fig. 18. Reaction scheme of carbon gasification with  $H_2$  and  $H_2O$

gasification with equimolar mixtures of water vapour with argon, helium and hydrogen. Helium, which does not adsorb at active sites, diminishes the rate of water vapour gasification as compared to argon in a similar way like hydrogen. This means, that the partial pressure of water vapour at the micropore surface is extremely small and nearly independent of the partial pressure in the gas phase. However, this small quantity of water vapour is sufficient for blocking active sites.

These considerations are summarized in a reaction scheme involving hydro- and water vapour gasification or gasification with hydrogen/water vapour mixtures (Fig. 18). Hydrogasification may be described by a two-step process (eqs (I) and (II)). Step one is identical to the inhibition of water vapour gasification by adsorption of hydrogen from the gas phase. Eq. (III) shows the formation of the extremely stable carbon oxygen surface complexes, which is possible already at  $500^\circ C$ . Their decomposition (eq. (IV)) in the absence of water vapour requires temperatures above  $800$  to  $900^\circ C$  depending on the heat treatment temperature of the coke. They are also stable in hydrogen containing small amounts of water vapour. Therefore, they are able blocking active sites, as far as the water vapour partial pressure at the reaction surface is small. Hydrogen as a small molecule like helium obviously hinders diffusion of water vapour into the micropores ( $\leq 1$  to  $2$  nm).

Only with high water vapour partial pressures at the reaction surface water vapour gasification is possible according to eqs (V) and (VI), whereby reaction (VI) must be a very fast one, because labile carbon oxygen surface complexes were never found in desorption studies. Very high water vapour partial pressures at the reaction surface are necessary in order to form carbon dioxide according to eq. (VII). This is the case in water vapour gasification with argon or nitrogen as carrier gases, but not with helium [1].

Inhibition of hydrogasification by water vapour may be overcome by raising the temperature in order to decompose the stable carbon oxygen surface complexes. It was experimentally found, that this is a necessary but not

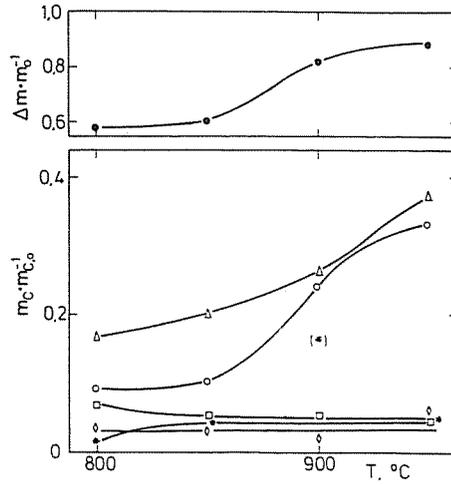


Fig. 19. Relative mass losses  $\Delta m/m_0$  and carbon conversions to gases and volatiles  $m_c/m_{c,0}$  of coal I (dry) after isothermal gasification with wet hydrogen ( $x_{H_2O}=0.1$ ) at 1 MPa;  $\Delta$   $CH_4$ ,  $\diamond$   $C_2H_6$ ,  $\circ$   $CO$ ,  $\square$   $CO_2$ ,  $\star$  volatiles

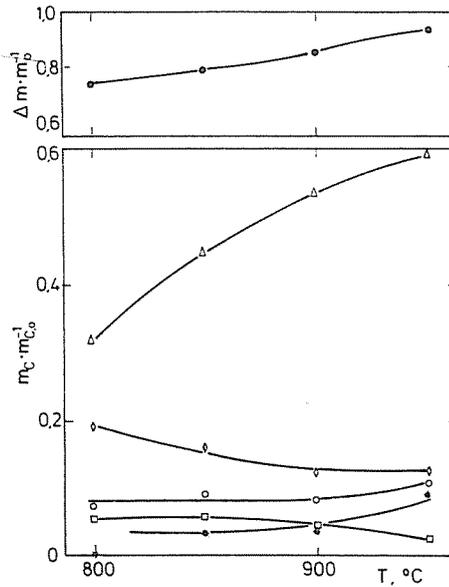


Fig. 20. Relative mass losses  $\Delta m/m_0$  and carbon conversions to gases and volatiles  $m_c/m_{c,0}$  of coal I (dry) after isothermal gasification with wet hydrogen ( $x_{H_2O}=0.1$ ) at 5 MPa;  $\Delta$   $CH_4$ ,  $\diamond$   $C_2H_6$ ,  $\circ$   $CO$ ,  $\square$   $CO_2$ ,  $\star$  volatiles

a sufficient condition, because hydrogen pressure additionally has to be increased to 5 MPa (Figs 19, 20), probably for methanation of primary formed carbon monoxide (eq. (7)). Under these conditions (5 MPa, 950 °C), the methane yield amounts to 60% (Fig. 20). It is remarkable, that the same methane yield was achieved at 1 MPa and 850 °C, if gasification was performed under dry conditions, i.e. with dry coal and dry hydrogen.

### Conclusion

Hydrogasification of brown coal was discussed under the viewpoints of kinetics and selectivity. The scheme of differentiation between (1) pyrolysis, (2) fast hydrogasification (hydropyrolysis) and (3) slow hydrogasification (coke gasification) is applicable. Under high hydrogen pressure (approx. 5 MPa) hydrogasification may completely be performed under conditions of hydropyrolysis, i.e. no residual coke is formed, which can be gasified only at a very low rate. Temperature control decides, whether volatile products (tar) or methane are formed as the main product. Maximum selectivity towards methane requires fast heating, as given in a fluidized bed, to 950 °C.

Small amount of water vapour, introduced into the reactor either with coal or hydrogen can strongly diminish the formation rate and yield of methane. The reason is formation of extremely stable carbon oxygen surface complexes, which block active sites. The problem may partially be overcome by applying a high hydrogen pressure ( $\geq 5$  MPa) and a high gasification temperature ( $\geq 950$  °C).

### Appendix (experimental conditions)

#### *Coals*

The elementary composition of the coals, their ash contents and the composition of the ashes are shown in Tables 1 and 2. The coals were delivered from Rheinische Braunkohlewerke with moisture contents of 15 wt% (coal I) and 12 wt% (coal II) and dried before gasification at room temperature in vacuum (16 h) giving moisture contents of 1.5 and 1.0 wt%. The used particle size was 0.4 to 1 mm in all experiments.

**Table 1**Elementary analyses of brown coals, wt% waf<sup>1</sup>

	Coal I <sup>2</sup>	Coal II <sup>3</sup>
C	64.9	66.1
H	4.8	5.3
N	0.7	0.8
S	0.9	0.6
O (diff.)	28.7	27.2

<sup>1</sup> dry and ash free<sup>2</sup> 15% moisture as received, dried to 1.5% moisture in vacuum at room temperature<sup>3</sup> 12% moisture as received, dried to 1% moisture in vacuum at room temperature**Table 2**Ash contents of brown coals, wt%, wf<sup>1</sup> and ash composition, wt%, oxidic ash

	Coal I	Coal II
Total	3.5	17.0
Na <sub>2</sub> O	4.0	— <sup>2</sup>
K <sub>2</sub> O	0.5	2.0
CaO	30.5	12.5
MgO	13.7	7.8
Al <sub>2</sub> O <sub>3</sub>	5.3	—
SiO <sub>2</sub>	15.5	60.0
Fe <sub>2</sub> O <sub>3</sub>	13.7	18.7
SO <sub>3</sub>	16.8	—

<sup>1</sup> dry<sup>2</sup> not determined*Gasification reactor and procedure*

Gasification studies were performed in a fixed bed flow reactor shown in Fig. 21. The pressure vessel consists of a high-dense, high-strength alumina ceramic tube. Pressures up to 5 MPa and temperatures up to 1200 °C are possible. The gas is preheated by flowing down through the gap between the outer and inner tube. In experiments with slow linear heating the sample (0.5 g) is fed to the reactor before starting the experiment. In isothermal experiments with shock heating the sample (0.1 g) is fed to the pressurized, preheated reactor

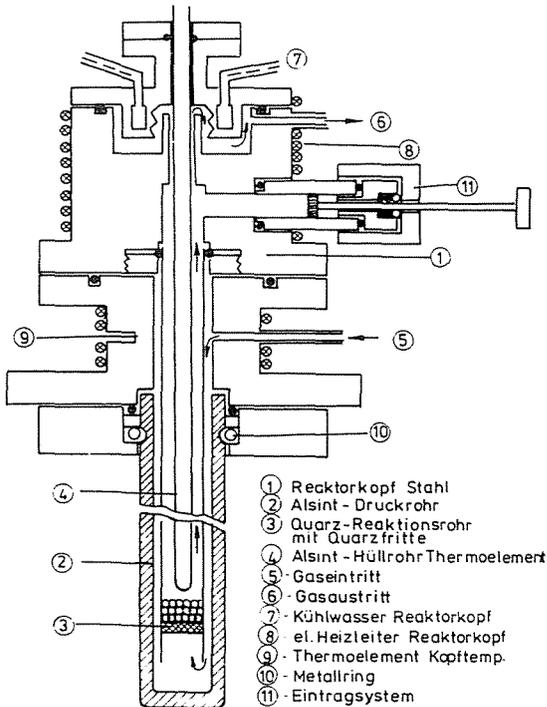


Fig. 21. Experimental reactor

with the aid of a piston at the head of the reactor. Gas analyses were performed on-line using i.r. analyzers, type BINOS, LEYBOLD-HERAEUS. In experiments with wet hydrogen or with hydrogen/water vapour mixtures the hydrogen was saturated with water vapour to the desired level in a saturator by adjusting the temperature. All experimental data (temperatures, gas concentrations) are stored in a computer. This type of experimental arrangement was successfully used in many gasification projects.

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