

INVESTIGATION OF THE HEATING UP PERIOD OF HYDROLIQUEFACTION

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INTRODUCTION

Earthy soft brown coals from deposits of GDR (Leipzig area) were found to be a highly reactive feedstock for slurry phase hydroliquefaction (1). The question arose as to whether short-contact-time hydrogenation may be an efficient process for hydroconversion of reactive coals (2). Rapid heating up of the slurry to the final reaction temperature may have a beneficial effect on product yields. Moreover, a more detailed study of the heating up period in hydrogenation is of importance for the explanation of the phenomenon of "coke" formation in the preheater sections of hydrogenation units.

EXPERIMENTAL

Experiments were carried out in dynamic 0.05 liter-microautoclaves, enabling a rapid heating up of the slurry to the desired reaction temperature within 1-2 minutes (figure 1).

After cooling down the autoclaves in air (3-8 minutes) component analysis of the solid and liquid hydrogenation product was performed by sequential soxhlet extraction with pentane, toluene and THF in order to determine oil, asphaltenes, preasphaltenes and the organic residue after ashing the whole residue. The gas constituents H₂S, CO₂, CO and hydrocarbons were analyzed by gas chromatography on several columns (3).

Parameters of the earthy brown coal feed are summarized in table 1.

Table 1: Ultimate and proximate analysis of coal Schleenhain

Moisture (%)	ash (% d)	bitumen (% daf)	C	H	O _D % (daf)	S _c	N
9,1	12,0	15,5	68,6	5,8	21,3	3,2	0,7

A comparative study of coal hydrogenation reactivity has shown that this coal should be contributed to the most reactive earthy brown coals (1).

Reaction conditions for the hydrogenation experiments are given in table 2.

Table 2: Reaction conditions

Final reaction temperature:	from 250 °C to 475 °C
pressure (H ₂ cold)	: 10 MPa
duration of the heating up:	approximately 90 - 100 sec
Input	: 2,5 g coal 2,5 g tetralene 0,16 g FeSO ₄ ·x7H ₂ O

Some of the typical temperature profiles measured are shown in figure 1. The rapid rocking of the microautoclaves within a molten salt bath (NaNO₃/KNO₃) has enabled a rapid heating up of the slurry to the reaction temperature. Cooling down in air occurred without any agitation.

Pseudocomponent formation versus final reaction temperature is illustrated in figure 2. A pronounced increase in oil formation was observed at T>400°C caused by an increase in conversion of the organic residue (rigid phase) at this temperature. Otherwise changes in asphaltene and preasphaltene yield with temperature were comparatively small. From this fact one may conclude that the degradation of the coal matrix under conditions of rapid heating up leads mainly to the formation of oil, water and gaseous components.

Up to 300°C the prevailing part of reaction gas consisted of carbon dioxide. The at T>300°C decarboxylation was accompanied by desulfurization, water formation (T>350°C) and carbon monoxide (T>375°C) and gaseous hydrocarbon formation (figure 3).

Results from ¹³C-CP-MAS-NMR measurements of the residues after hydrogenation were in a good agreement with these findings (figure 4). A decrease of signal intensity in the aliphatic region of the NMR-spectra was observed at T>350°C together with a steady decrease of the signal intensity of carboxylic groups.

Results from investigations of the texture properties of the THF-insoluble residues by Hg-porosimetry and CO₂-adsorption technique are summarized in table 3.

Table 3: Texture properties of hydrogenation residues

Property Temperature (°C)	Vp (Hg) cm ³ /g	Vp (micro) cm ³ /g	S (macro) m ² /g	S (micro) m ² /g
Coal residue	0,39	0,05	20	139
250	0,41	0,09	16	244
350	0,62	0,07	44	186
400	0,74	0,27	20	729
450	0,54	0,30	15	815

For the surface and volume of micropores a jump at 400°C was

measured, which probably was caused by an increase in C-C-bond cleavages occurring at this temperature. Otherwise, there was a decrease of macropore surface at $T > 350^{\circ}\text{C}$ and of macropore volume at $T > 400^{\circ}\text{C}$, which may be caused by the degradation of greater particles of the coal matrix.

The same conclusion of a remarkable bond cleavage at $T > 400^{\circ}\text{C}$ may be drawn from investigations of the oil composition by semi-preparative HPLC (4). Here, a so-called "dry" hydrogenation method was applied, described elsewhere (5).

Results from HPLC analyses are shown in figure 5.

At $T = 350^{\circ}\text{C}$ the prevailing components (80%) of the oil were neutral and acid hetero-compounds and only minor amounts of saturates were found.

The higher the final reaction temperature the more hydrocarbons were found in the oils. The fact that the yield of hetero-compounds decreased in the range from 400°C to 450°C indicates that hydrotreatment reactions of the oils formed occurred already under short contact time conditions.

LITERATURE

- (1) M. König, D. Radeck, M. Gutmann, H. Jancke:
Proc. 2nd symposium on carbochemistry, Rostock, 1988, vol. 1,
p. 100
- (2) C. Fehl, D. Radeck, M. König: to be published in Freiburger
Forschungshefte 1990
- (3) M. Gutmann, G. Keil, H. Klare, M. König, D. Radeck: Fuel
Processing Technology 15 (1987), 327
- (4) H. Zobel, H. Klare, M. Gutmann:
Freiburger Forschungshefte A 763 (1987), 72
- (5) M. König, M. Gutmann, D. Radeck, M. C. Mittelmeijer-Hazeleger
P. J. J. Tromp: to be published in Fuel Processing Technology

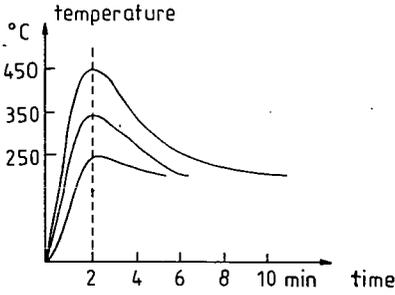


Figure 1: temperature profiles of the autoclaves measured

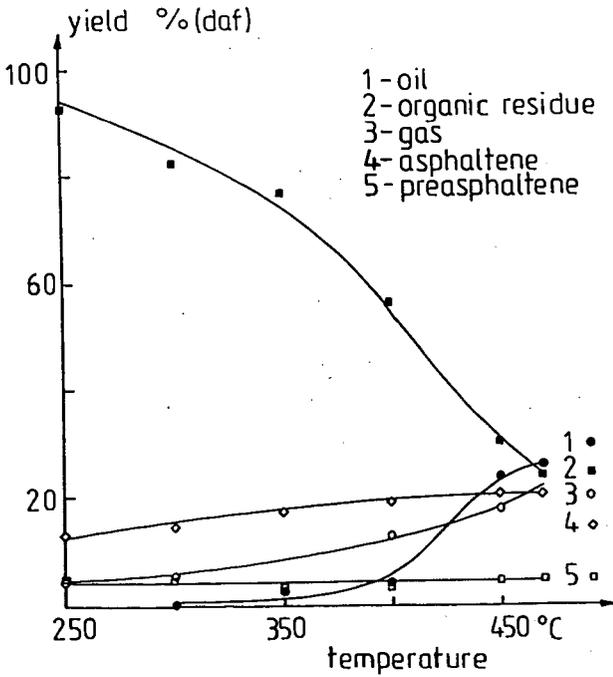


Figure 2: Dependence of component formation on final reaction temperature

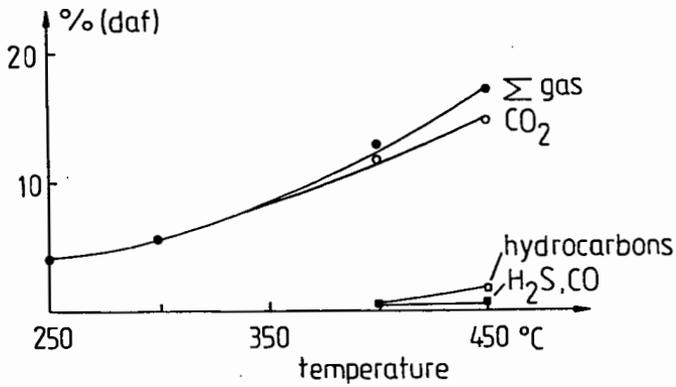


Figure 3: Formation of gases during short-contact-time hydrogenation

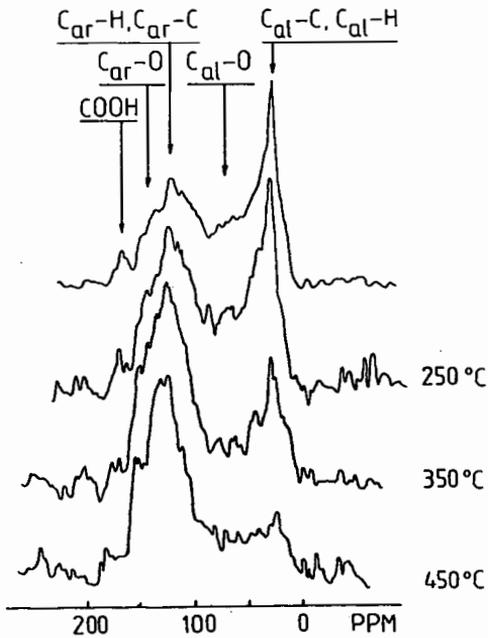


Figure 4: ¹³C-MAS-NMR measurements of the hydrogenation residues

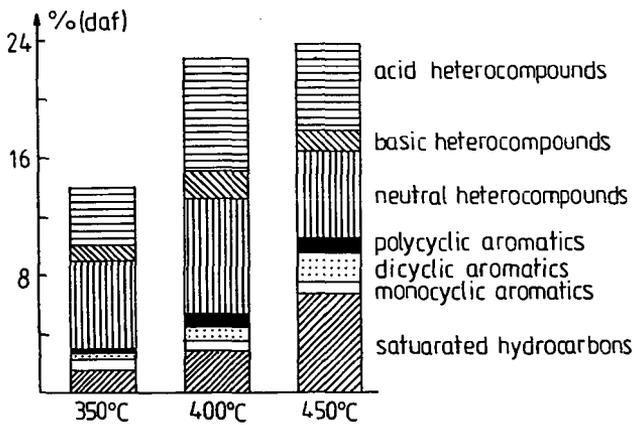


Figure 5: Analyses of oil composition by semipreparative HPLC