INVESTIGATION OF GASEOUS PRODUCT RELEASE PROCESS DURING PYROLYSIS OF COALS OF DIFFERENT CARBONIFICATION DEGREE

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In this thesis the effect of coal carbonification degree, heating rate and particle size on the quantity and quality of coal pyrolysis products was investigated. The pyrolysis process was investigated by thermogravimerty, mass spectrometry and fluidized bed experiments. Five coals from Yugoslavia: two lignite (Kolubara and Kostolac), two subbituminous coals (Soko and Bogovina) and bituminouse coal (Ibar) were used in experiments.

The objective of thermogravimetric experiments was to determine the effects of heating rate and coal type on the kinetics of pyrolysis process. Thermogravimetric analyses of coal pyrolysis were performed under an inert nitrogen atmosphere (coal particle size: 0,30–1,00 mm), in the temperature range 30–900 °C at constant heating rates of 20, 40, 80 and 160 °C/min. The weight losses as a function of temperature were recorded (TG-curve) and differential thermogravimetric curves (DTG-curve) were calculated from TG-curves. It was found that total volatile yield, maximal rate temperature and starting temperature of pyrolysis depends not only on carbonification degree, yet on applied heating rate. The heating rate has different influence on the behavior of coals of different carbonification degree.

Mass spectrometric analysis of gaseous coal pyrolysis products was performed using quadruple mass spectrometer EAI 210 (*Electronic Associates, California*) conected to the temperature programmed furnance. Coal samples (particle size: 0,30–1,00 mm) were placed in the pyrolysis chamber within the furnance and were heated by linearly increasing the temperature as a function of time (heating rate 10 °C/min; temperature range 400–900 °C). It was found that the main gaseous pyrolysis products of lignite coals, Kolubara and Kostolac, and subbituminous coal Soko, were water, carbon-dioxide and carbon-monoxide. The main gaseous pyrolysis products of subbituminous coal, Bogovina, and bituminous coal Ibar were light hydrocarbons.

In fluidized bed experiments coal samples (coal particle sizes: 1,00–2,00; 2,00–3,15; 3,15–4,75 mm) was dropped into the heated fluidized bed (temperature of FB: 500, 550, 600, 650, 700, 750 °C) under inert atmosphere of nitrogen. Gas samples were taken continuously and analyzed for carbon-dioxide (CO_2) and carbon-monoxide (CO). The objective of these experiments was to determine the effects of maximal temperature, particle size and coal type on the kinetics of CO_2 and CO evolution. It was found that the yields of the released CO_2 and CO were greater for lignite coals than for other coals, and the increase of coal carbonification degree caused the decrease in yield and molar ratio

of CO_2 and CO. Also, the participation of CO_2 and CO in the total volatile yield decreases with the increase of coal carbonification degree.

Complex set of pyrolysis reactions were analyzed using the distributed activation energy model. The distribution curve of the activation energies, f(E) and the activation energy dependent frequency factor, $k_o(E)$, were estimated, in both TGA and FB experiments. The results obtained by TG experiments signified that pyrolysis of different coals consists of multitude similar reactions that have similar rates, while k_o values were in the range 10^{-1}–10^{34} s^{-1}. Different shapes of activation energy distribution curves of different coals imply that different reactions were dominant for pyrolysis of different coals. As the carbonification degree of coals is higher the mean value of activation energy increases. The mean activation energy for the coal Kolubara was 160 kJ/mol, and for the coal Ibar 386 kJ/mol. The results obtained by FB experiments showed that the released CO_2 and CO were products of mainly two pyrolysis reation, since no activation energies distribution curve was noticed. The activation energies and frequency factors obtained for coals of different carbonification degree were similar ($E = 45 \pm 9$ kJ/mol, $k_o = 4$–65 s^{-1} and for CO_2 release and $E = 37 \pm 9$ kJ/mol, $k_o = 0{,}4$–$2{,}4$ s^{-1} for CO), which indicates that type of reaction which produced these gases is independent of coal rank.

Comparing the results for E and k_o obtained by different experimental techniques it might be concluded that coal pyrolysis reactions that produce CO_2 and CO were not main reactions. Good agreement of the results for k_o and E is the verification of the experimental method used for E and k_o estimation.