

Activation of Carbonized Maize with Carbon Dioxide

W. Klose and H. Wobig

FG Thermodynamik/Universität Gh Kassel, D-34109 Kassel, Germany

1 Introduction

Apart from direct combustion biomass can be used as an energy source by converting it into products of "higher-value" which can be used more flexibly. By pyrolyzing biomass one gets a solid product which is a suitable feedstock for activated carbon production, a pyrolysis oil useful as fuel oil, and a fuel gas. The kinetics of the pyrolysis of biomass are given elsewhere /1/. In this investigation the kinetics of the CO₂-activation of pellets made from the solid product and the oil of pyrolysis, and the porosity and apparent surface areas of the resulting activated carbons are studied.

2 Experimental

Air dried maize, chopped to a particle diameter below 1 cm, is pyrolyzed in a rotary kiln of semi-technical scale with a solid matter residence time of 20 min and a maximum temperature of 545 °C /2/. The solid product is pelletized with pyrolysis oil condensed at 25 °C at a mass rate of four to one to obtain an activated carbon with a sufficient mechanical strength. The pellets have a mass of 1.8 g, a thickness of 10 mm, and a diameter of 20 mm, the water content is 10 %, ash content of dry basis is 11.3 %, and the ultimate analysis gives values of $c_{daf} = 85.4$ %, $n_{daf} = 2.3$ %, $o_{daf} = 8.5$ %, and $h_{daf} = 3.8$ %.

The pellets are degraded again in a thermobalance purged with nitrogen (2 l/min, STP) to remove the residual volatiles. The outlet CO and CO₂ concentrations are measured with an infrared gas analyzer. The pellets are heated at a rate of 25 K/min to a final temperature 50 K above the activation temperature to ensure the separation of pyrolysis and activation. When reaching a constant mass signal ($dm/dt < 10^{-4}$ g/min) the gas flow is changed from inert to activation gas. Varied parameters are the final temperature, the burn-off,

and the CO and CO₂ concentrations in the N₂ flow at ambient pressure.

3 Theory

The assumption that the carbon gasification is separated in a sorption step and in an oxygen exchange mechanism as rate determining step leads with constant carbon true density to a Langmuir-Hinshelwood type for the reaction rate r as follows:

$$r = \frac{dm/dt}{A} = \frac{k_2 \cdot P_{CO_2}}{1 + K_1 \cdot P_{CO_2} + K_3 \cdot P_{CO}} \quad (1)$$

The intrinsic reaction rate is related to the active surface area which is very difficult to ascertain experimentally. Hence the BET apparent surface area is taken. It is determined with N₂-adsorption at 77 K evaluating the BET equation in a pressure range of $0.001 < P/P^S < 0.1$ because the linearity of the BET plot of activated carbons is not satisfying in the standard BET region.

4 Results and Discussion

Fig. 1 shows pellet mass, conversion, intrinsic reaction rate, CO concentration, and BET apparent surface area as functions of the burn-off for a gasification with pure CO₂ at 800 °C. After the start-up phase with low conversion but high reaction rate an almost steady state is reached at burn-offs between 0.2 and 0.7. At higher burn-offs conversion decreases while reaction rate increases. The differences in conversion and reaction rate at low and high burn-offs result from the low apparent surface area in this burn-off region.

According to the approach the intrinsic reaction rate is a pure temperature function with no influence of burn-off. The measured reaction rate in Fig. 1 shows that this fact is only

given in the burn-off range between 0.2 and 0.7 which is a limiting range for evaluating the coefficients in eq. (1) therefore.

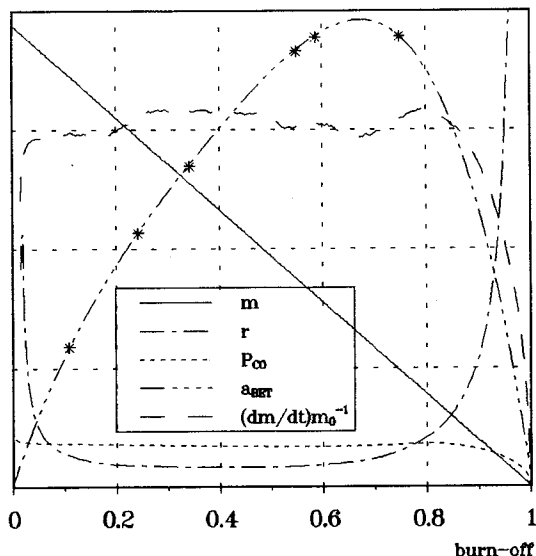


Fig. 1: Experimental values as functions of burn-off

The BET apparent surface area reaches remarkably high values clearly higher than 1000 m²/g at burn-offs about 0.65. Activation at 850 °C, 900 °C, and 950 °C with the same burn-off yields lower BET apparent surface areas decreasing from 970 m²/g to 560 m²/g at increasing temperature. This indicates that in this temperature range the gasification is not controlled kinetically solely but the influence of the pore diffusion is not negligible.

The distribution of pore radii is bimodal with one peak in the macropore and another in the micropore range with no significant influence of temperature and burn-off.

Rearrangement of eq. (1) gives:

$$\frac{1}{r} = \frac{1}{k_2 \cdot P_{CO_2}} + K_3 \cdot \frac{P_{CO}}{P_{CO_2}} + \frac{K_1}{k_2} \quad (2)$$

$$\stackrel{K_3 P_{CO} \ll P_{CO_2}}{=} \frac{1}{k_2} \cdot \frac{1}{P_{CO_2}} + \frac{K_1}{k_2}$$

so that one can evaluate K₁ and k₂ by varying the CO₂ partial pressure at low CO partial

pressure and K₃ by varying the CO/CO₂ ratio at constant CO₂ partial pressure, respectively. Fig. 2 shows a plot of eq. (2) for gasification with pure CO₂ at different concentrations at 800 °C and the burn-off as parameter. The variation of the CO/CO₂ ratio with constant CO₂ concentration at 800 °C is not given here but both plots according to eq. (2) give the expected straight lines with adequate accuracy. The calculated coefficients are K₁ = 2.4/bar, K₃ = 11.4/bar, k₂ = 3.1 · 10⁻⁷ g/(bar m² s). The results prove that the activation of carbonized maize can be described with the classical Langmuir-Hinshelwood approach like the activation of coal chars [3] but restricted to a limited burn-off range between 0.2 and 0.7.

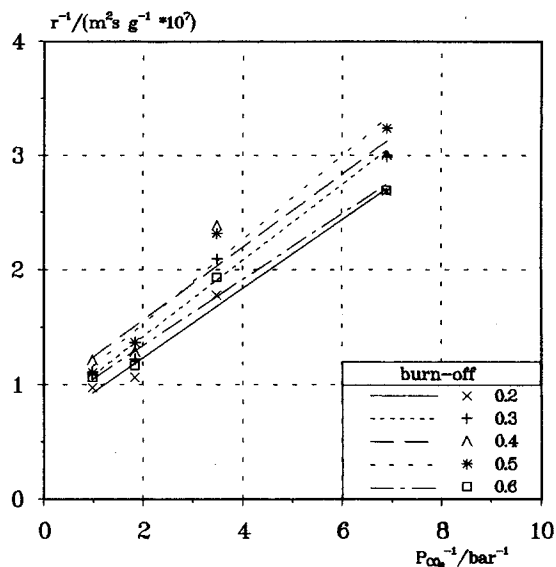


Fig. 2: Reaction rate at various burn-offs as function of CO₂ partial pressure

5 References

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