

REACTION KINETICS OF MISCANTHUS GASIFICATION WITH CARBON-DIOXIDE

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ABSTRACT

Gasification of *miscanthus* coke of different particle size was studied in the temperature range of 722°C to 870°C. Particular biomass can be regarded as a potential source of energy. The first stage of gasification up to conversion of 60% was described by a pseudo-first order rate equation. Rate constant and activation energy of particular reaction was determined. The particle size of the coke has no significant effect on the reaction rate in given conditions. Changes in reactivity were interpreted by studying the pore structure of the coke during gasification.

INTRODUCTION

More recently special attention has been devoted to renewable energy sources. Thus, municipal organic waste, and the wastes of forestry and agriculture have acquired a considerable significance. It is mainly attributed to the fact that processing of the various biomasses has limited environmental impact (greenhouse effect) and these waste materials are ubiquitous, as well.

Thermochemical transformations, such as gasification and pyrolysis are frequently applied to produce energy and chemical raw materials from biomasses. During gasification, various gases of different composition are evolved, and the energy content of gaseous products strongly depends on the quality (moisture, ash, alkali metal and volatile material content) and pretreatment of raw materials, and also on the gasification reagents (1-3).

In planning and operating a gasification process, it is important to know the reactivity of raw materials with given gasification reagents. Numerous papers have been published on reactivity of different carbon containing compounds during gasification (4-6). In most cases steam, oxygen, air, carbon-dioxide, or their mixtures were used as gasification reagents.

Our experiments focused on the gasification kinetics of a coke produce from *miscanthus* or chinese reed which is a promising source of energy.

METHODS OF INVESTIGATIONS

Reaction kinetic studies

The *miscanthus* was slowly pyrolysed at 500°C and the produced coke was separated to fractions of different particle size by sieving. To remove adsorbed moisture the samples were dried at 105°C. Samples of four different size range (>1.6 mm, 1.6-1.0 mm, 1.0-0.8 mm and 0.8-0.63 mm) and having mass of 0.5 to 1.0 g were gasified at four temperatures (722, 786, 822 and 870°C) in a large excess of carbon dioxide ($8 \text{ dm}^3 \cdot \text{h}^{-1}$) in the experimental set-up shown in Fig. 1. The mass change due to gasification was registered against reaction time.

Pore structure studies

- Studies on the fractured surfaces of coke samples by SEM (Jeol 50A)
- Determination of size distribution of mezopores from the desorption part of the adsorption isotherms of nitrogen; determination of the BET specific surface area by BET equation from the adsorption isotherms; determination of surface and volume of micropores from the range of $0,1 > p/p_s$ of the adsorption isotherms (ASAP equipment, liquid nitrogen)
- Determination of size distribution of macropores (Carlo Erba Mercury Porosimeter, 100-1000 bars)
- Measurement of apparent density (bulk density) of grains of total porosity (picnometer of Carlo Erba Mercury Porosimeter)

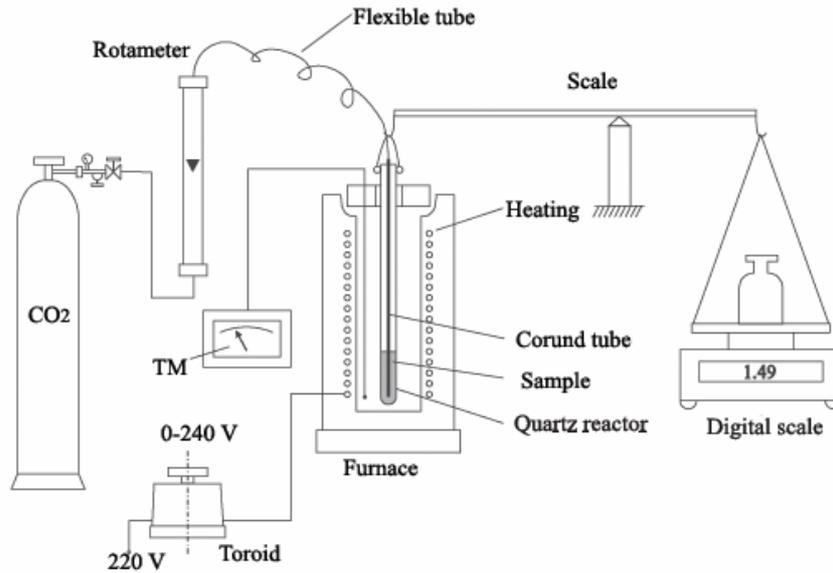


Fig. 1 Scheme of the experimental set-up

RESULTS AND DISCUSSIONS

Gasification of particular coke was described by a first order kinetic equation previously (7):

$$\frac{dm}{dt} = -km \quad (1)$$

By integrating Eq. (1) we arrive at the following equation:

$$\ln \frac{m}{m_0} = -kt \quad (2)$$

The $\ln(m/m_0)$ values were plotted against reaction time at 786°C for *miscanthus* coke fractions of different size ranges in Fig. 2. Run of $\ln(m/m_0)$ vs. t curves refers to more complicated kinetic equation than Eq. (2). However, the particle size of the coke has no significant effect on the mass loss during gasification. .

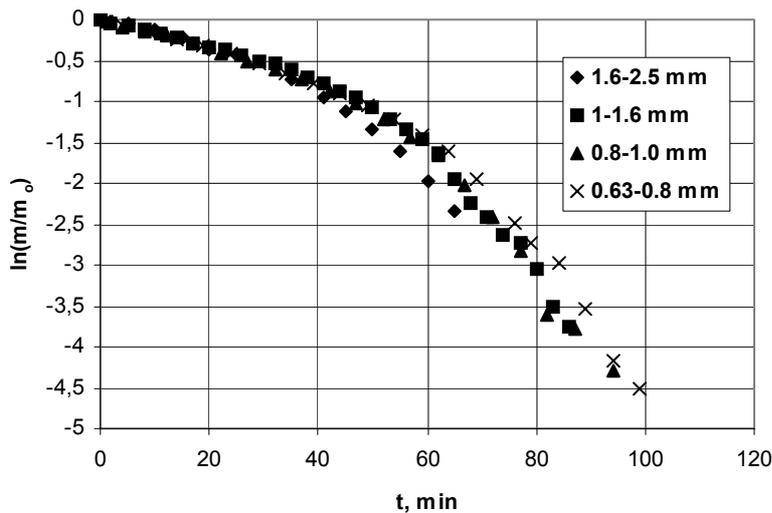


Fig. 2 The $\ln(m/m_0)$ values as plotted against reaction time ($T = 786^\circ\text{C}$, $p_{\text{CO}_2} = 749$ torr)

In order to have a deeper insight into the kinetics of gasification, change of reaction rate was plotted against conversion for the grain fraction of 1.0-1.6 mm in Fig. 3. The reaction rate was calculated from

mass changes measured at different temperatures. The conversion was defined as the actual mass loss referred to the initial mass of samples.

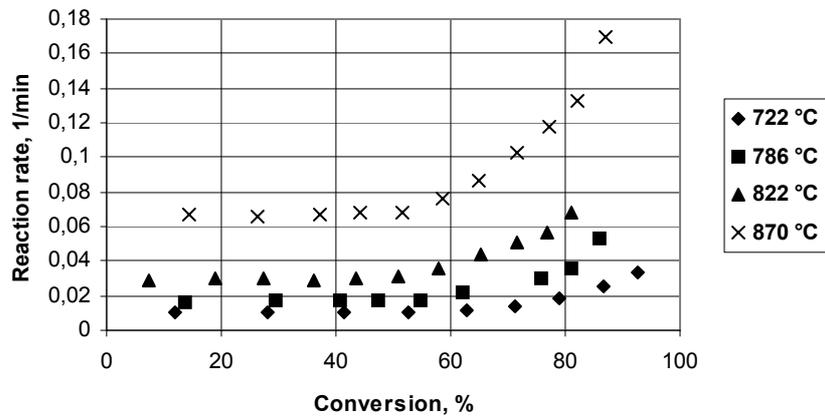


Fig. 3 Dependence of reaction rate on conversion at different temperatures

Fig 3 shows an actually constant reaction rate up to conversion of nearly 60%. It refers to first order kinetics in particular region. However over conversion of nearly 60%, the reaction rate increases rapidly depending on the gasification temperature. This result is in agreement with that of Marquez-Montesinos et al. (8), who studied the gasification of grapefruit peel by thermogravimetry. Hence, gasification of *miscanthus* coke up to conversion of about 60% can be described by a first order kinetics. The reaction rate constant can be determined from the slope of the first, straight section of $\ln(m/m_0)$ vs. t plot in Fig. 2. If we plot $\ln k$ values determined for different temperatures against $1/T$ (Fig. 4.) the activation energy can be calculated by the Arrhenius' equation. In particular case it was found to be $148,646 \text{ kJ}\cdot\text{mole}^{-1}$, in good agreement with data in the relevant literature.

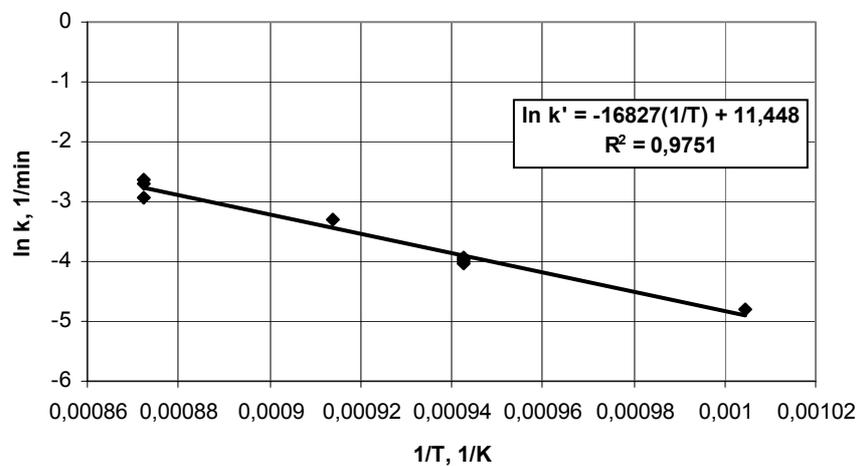


Fig. 4 Changes of the rate constant of *miscanthus* coke gasification with CO_2 against reaction temperature in the first order kinetic regime

Fig. 2 and results obtained for other temperatures, as well showed that the gasification rate hardly depended on the particle size of coke. It is possible only, if the quality of gasification reagent and its diffusion into the pores of solid material have no effect on the reaction rate.

However, increase of reaction rate above conversion of about 60% needs further explanation. To interpret changes in the reactivity at higher conversions the pore structure of coke samples for the size fraction of 1.0-1.6 mm was measured with forthcoming gasification.

SEM micrographs of coke grains subjected to gasification up to different conversions are shown in Figs. 5-8. At a conversion of 18% (Fig. 5) the grains have actually the same microstructure as the original ones. At a conversion of 64% (Fig. 6) an extensive through-burning of the tube walls can be

observed. At a conversion of 80% (Fig. 7) the original structure still can be recognized. However, there is some ash accumulated and partially melted on the surface of grains. At a conversion of 94% (Fig. 8) the material is completely melted and its structure resembles to that of volcanic stones.

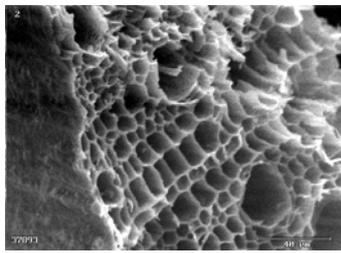


Fig. 5 SEM shot X=18%

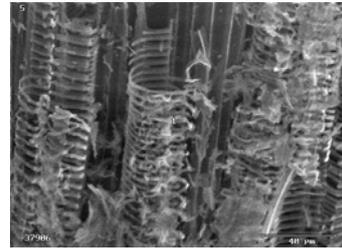


Fig. 6 SEM shot X=64%

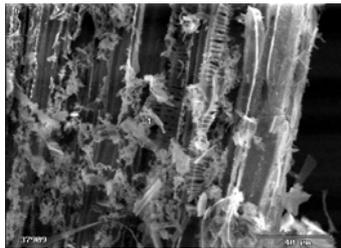


Fig. 7 SEM shot X=80%

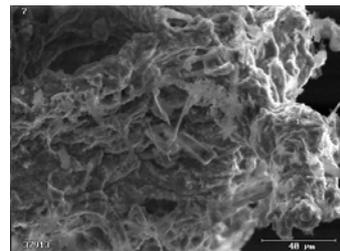


Fig. 8 SEM shot X=94%

Changes in the BET specific surface against conversion are presented in Fig. 9. The specific surface area has a maximum at the conversion of about 60%.

To interpret findings of morphological studies the surface area of micropores were plotted against the BET surface area in Fig. 10. It is quite clear that the micropores represent the greatest part of the specific surface area.

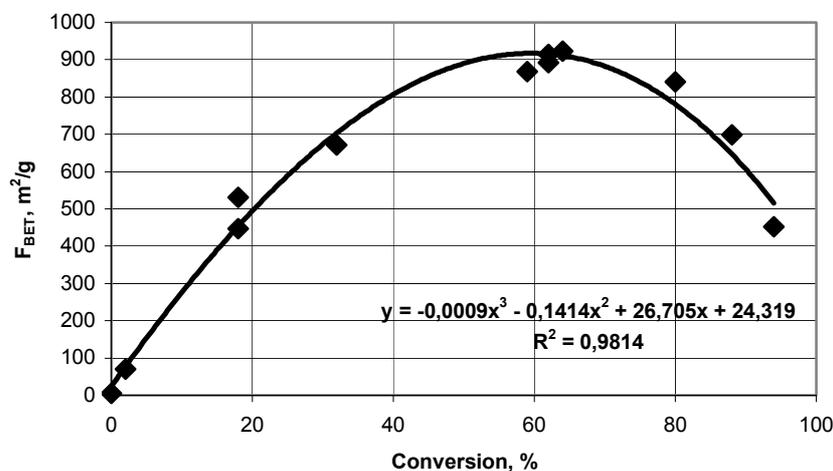


Fig. 9 Correlation between the conversion and the specific surface area

The missing effect of particle size on reaction rate can be explained by the pore structure of particular material. It can be assumed that the rate-determining step is the gasification on the surface of micropores. There is no mass transport hindrance in this case. However, growth in the surface of micropores (Fig. 9) stops at conversions of about 60%. Most probably, it is due to the deterioration of the walls of micropores. It is also supported by the further increase of conversion despite of the nearly linear decrease of specific surface area at higher conversions.

Interpretation of increase in reaction rate related to unit mass at conversions above 60% needs further studies. Finding of Marquez-Montesinos et al. [13] on the catalytic effect of alkali metals seem to be a possible reason. Moreover, the modified pore structure may have an important role, as well, assuming a considerable increase both in the size of transport pores and that of micropores.

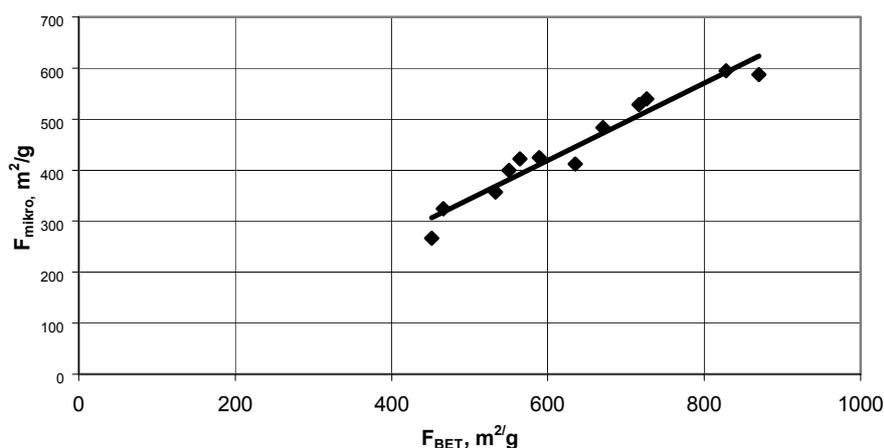


Fig. 10 The micropore surface area as plotted against BET surface area

CONCLUSIONS

- For *miscanthus* coke studied in this work its initial particle size has no significant effect on the gasification process in given conditions. The reaction is not hindered by diffusion.
- The kinetic equation for the *miscanthus* - CO₂ system up to a conversion of 60 % can be given as follows:

$$r = 93,713 \cdot e^{-139,899/RT} \cdot m \cdot p_{CO_2}$$
 During the progress of reaction there are no significant changes in the macropore network. However, significant changes occurred in the structure of micropores.

REFERENCES

- 1) A.V. Bridgewater, G. Grassi: Pyrolysis Liquid Upgrading and Utilization, Elsevier Applied Science, London, New York, (1991)
- 2) The Commission of the European Communities, R & D Programme, A. Strub, Energy from biomass. In: , A.V. Bridgewater, Editor, Thermochemical Processing Biomass, Butterworths, London (1984),.
- 3) A.V. Bridgewater, Editor, Advances in Thermochemical Biomass Conversion, Blackie Academic and Professional/Chapman & Hall, Glasgow/London (1993)
- 4) J.L. Johnson: Kinetics of Coal Gasification. New York: Wiley, (1979)
- 5) F. Kaptejin, J.A. Moulijn: Carbon and Coal Gasification, Dordrecht: Martinus Nijhoff Publishers, (1986).
- 6) J. Lahaye, P. Ehrburger: Fundamental Issues in Control of Carbon Gasification Reactivity. Dordrecht: Kluwer, 1991
- 7) Kutics Károly: Dióhéjból előállított aktív szenek adszorpciós és pórus szerkezeti tulajdonságainak vizsgálata, Műszaki doktori értekezés, Veszprémi Egyetem, (1984)
- 8) F. Marquez-Montesinos, T. Cordero, J. Rodriguez-Mirasol, J.J. Rodriguez: CO₂ and Steam Gasification of a Grapefruit Skin Char, Fuel, 81/4, 423, (2002)

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