

DETERMINATION OF FORMAL-KINETIC PARAMETERS FOR THE THERMAL DEGRADATION OF BIOMASS TARS

Wolfgang Klose, Arndt-Peter Schinkel
*University of Kassel, Institute of Thermal Engineering
Kurt-Wolters-Str. 3, D-34109 Kassel*

Corresponding author e-mail: klose@uni-kassel.de

Introduction

The use of biomass as a renewable energy source becomes more and more popular. To obtain high calorific and easy and long storable fuels an upgrading process like pyrolysis or gasification is reasonable. Therefore, a decoupling between crop and use is achieved.

The gaseous and solid products are favourable for fuel purposes. The tar fraction is undesirable in this context. The tars tend to oligomerise, and solids are formed in the feeding system of burners or gas engines. Hence, a costly gas cleaning has to be carried out. The aim is to design pyrolysis and gasification processes considering tar degradation by homogeneous and heterogeneous reactions. Measurements carried out by Klose and Wiest [1] at a laboratory-scale rotary kiln show a decreasing tar yield with an increasing bed depth. A mathematical simulation (Klose, Schinkel [2]) shows good agreements by considering a heterogeneous tar degradation reaction at fresh-formed char in the bed. The kinetic parameters have to be studied in detail to optimise tar degradation in situ of the pyrolysis or gasification reactor.

Therefore, wood tar degradation is studied in the temperature range between 450 °C and 800 °C. The tars are collected following the tar sampling guideline; worked out in the frame of the 5th European FP. It is essential to know the temperature distribution in the reactor up to the tar-collecting trap to obtain formal-kinetic parameters. Quartz glass is used to prevent catalytic reactions on the reactor walls. A mathematical model is developed considering the radiative and convective heat transfer to predict the temperature distribution. The deviation between the experimental data and the model results is in a range of 2 K.

Experimental Set-Up

Figure 1 shows the flow diagram of the experimental set-up. The unit consist of two consecutive reoccurs R1 and R2, a tar collecting device, an online gas analysis and a gas sampling device for post analysis. The primary reactor R1 can be equipped with two different reactor tubes:

Type 1 is used to locate the sample in a packed bed on a frit and type 2 is used to locate the sample in a crucible with a mounted balance.

- The type 1 consists of a quartz glass tube (9 mm ID x 1000 mm length) mounted in the centre of an electrical furnace. The stainless steel tube

(6 mm OD x 750 mm length) is mounted concentrically in the quartz glass tube to improve the heat transfer. Below the steel tube a frit is located as sample holder.

- Type 2 consists of a quartz glass tube showing a reduction in diameter right below the located crucible. The inner diameter of the tube is 41 mm at the reactor inlet. A stainless steel tube (38 mm OD x 750 mm length) is mounted co-axial with the quartz glass tube. Mounted baffles should improve the purge gas flow through the sample.

The pressure drop in a packed bed depends among others on the particle size distribution, and the particle shape. The application of pressure drop equations for packed biomass beds is not valid. Therefore, two types of primary reactors are needed to check if the purge gas flow is dominated via mal-distribution.

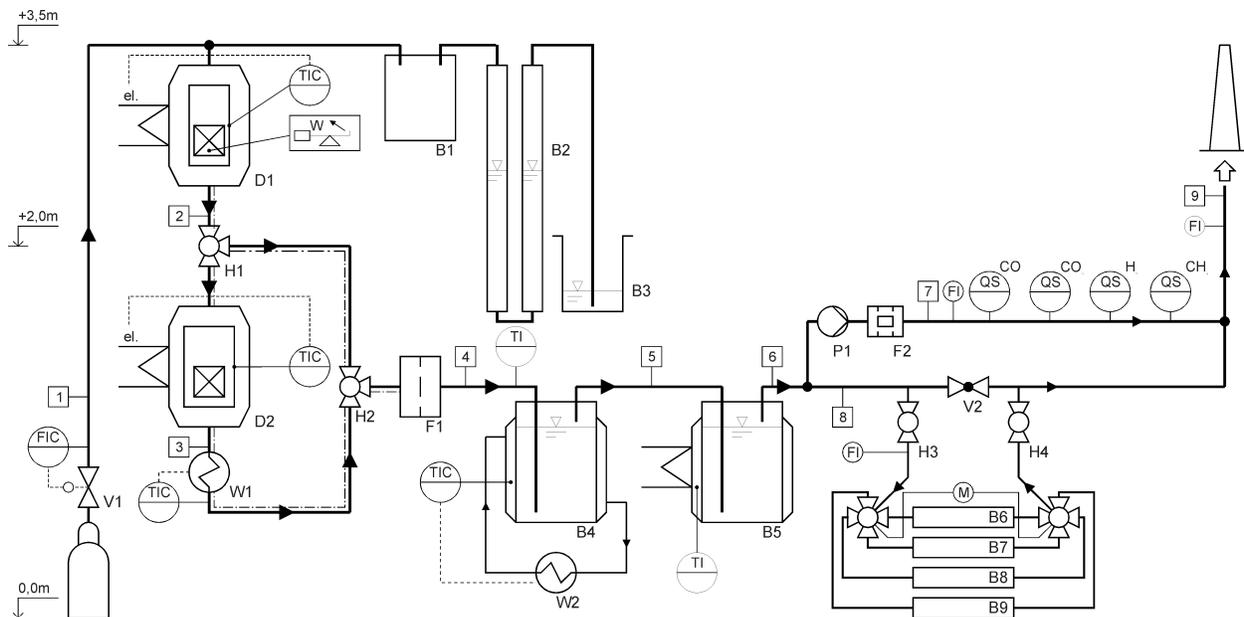


Figure 1. PI-diagram of the two-stage tar degradation system

The second reactor R2 consists of a quartz glass tube (9 mm ID x 1000 mm length) mounted in a furnace. A quartz glass tube filled with graphite powder is placed co-axial in the reactor tube to improve the heat transfer. The internal tube is mounted in a way to prevent contact between the gas and the carbonaceous filling of the tube. The reactor can be equipped with a frit to hold a packed bed of solids like char, activated carbon, or catalyst to investigate heterogeneous tar degradation.

The tar sampling follows the recommendations of the guideline elaborated by Neeft et al. [3] in the frame of the 5th European FP. It consists of 6 consecutive impinger bottles. The first 4 bottles are kept at a constant temperature of 20 °C; the last two are introduced in an ice-salt-water mixture. The first 5-impinger bottles are filled with 2- propanol.

Methane, hydrogen, carbon monoxide, carbon dioxide and oxygen are on-line analysed. Additionally, the gases are collected for a GC gas analysis.

Measuring and Modelling the Temperature Distribution

The temperature of the sample and the temperature distribution of the gas phase have to be well known to obtain kinetic parameters for the degradation of tars. Therefore, the heat transfer to the gas is modelled in detail considering thermal radiative heat transfer.

Mathematical Model of the Tube in Tube Configuration

Figure 2 shows the energy fluxes among the furnace, the quartz glass tube, the gas, and the stainless steel tube.

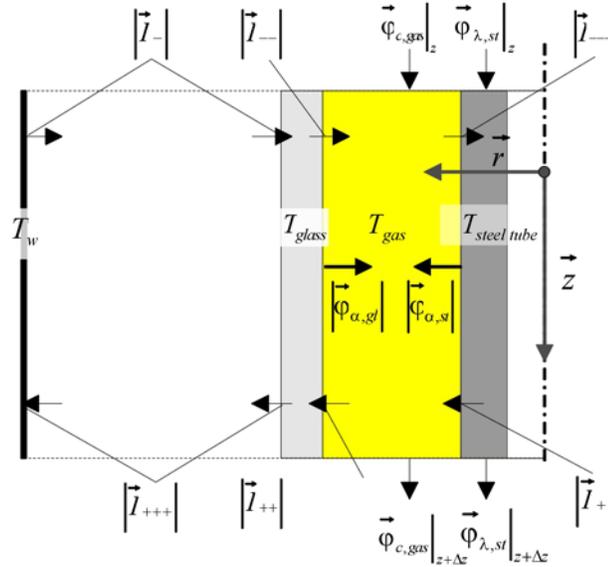


Figure 2. Radiate and convective energy fluxes

The thermal radiation balance using a 2-flux model suggested by [4,5] is given by

$$\frac{dI}{dr} = -aI + e\sigma T^4 \quad (1)$$

and is solved for the gas phase and the quartz glass. The boundary conditions at the furnace wall and at the inner tube are given by

$$\vec{I}_- = (1 - \alpha)I_{+++} + \varepsilon\sigma T_w^4 \quad (2)$$

and

$$\vec{I}_+ = (1 - \alpha)I_{---} + \varepsilon\sigma T_{steel\ tube}^4 \quad (3).$$

The tube thickness is small. Hence, a planar formulation of the balances is applicable. The balance equations are solved for this case. Additionally, the thermal energy balance for the gas

$$\frac{\partial \rho c_p T_{gas}}{\partial t} = -\frac{\partial w \rho c_p T_{gas}}{\partial z} + 2r_{steel\ tube} \frac{\alpha_{steel\ tube} (T_{steel\ tube} - T_{gas})}{(r_{i, glass}^2 - r_{steel\ tube}^2)} + 2r_{i, glass} \frac{\alpha_{glas} (T_{glas} - T_{gas})}{(r_{i, glass}^2 - r_{steel\ tube}^2)} \quad (4)$$

for the quartz glass tube

$$\frac{\partial \rho c_p \bar{T}_{glass}}{\partial t} = -2 r_{i,glass} \frac{\alpha_{glass} (T_{glass} - T_{gas})}{(r_{a,glass}^2 - r_{i,glass}^2)} + 2 r_{i,glass} \frac{(I_{++} - I_{--})}{(r_{a,glass}^2 - r_{i,glass}^2)} + 2 r_{a,glass} \frac{(I_- - I_{+++})}{(r_{a,glass}^2 - r_{i,glass}^2)} \quad (5)$$

and for the inner steel tube

$$\frac{\partial \rho c_p \bar{T}_{steel\ tube}}{\partial t} = \frac{\partial \lambda}{\partial z} \frac{\partial T_{steel\ tube}}{\partial z} - 2 r_{steel\ tube} \frac{\alpha_{steel\ tube} (T_{steel\ tube} - T_{gas})}{(r_{steel\ tube}^2 - r_{i,steel\ tube}^2)} - \frac{(I_+ - I_{---}) 2 r_{steel\ tube}}{(r_{steel\ tube}^2 - r_{i,steel\ tube}^2)} \quad (6)$$

are solved. Fig. 3 shows the measured and calculated temperatures. The simulation results are in very good agreement with the experimental data.

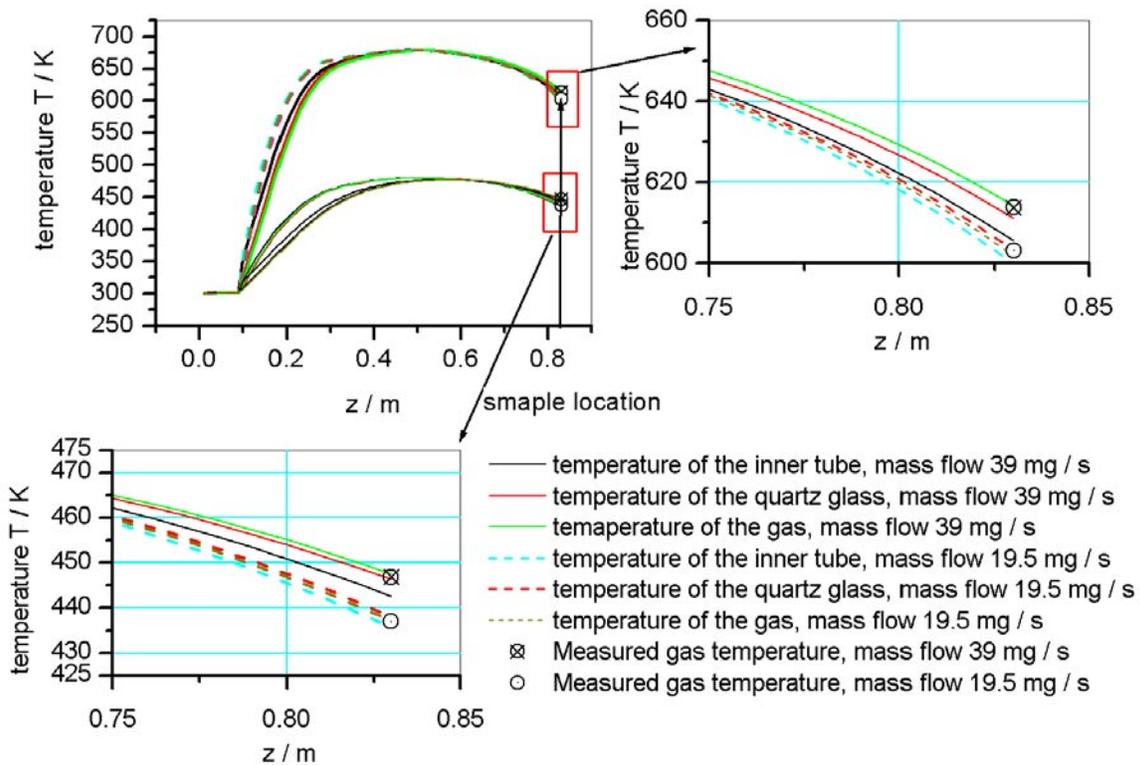


Fig. 3 Measured and calculated gas temperatures

Experimental Results

Beech wood chips ($2\text{ mm} < d < 3,125\text{ mm}$) are heated up with a heating rate of 6 K/min in the primary reactor D1. After approaching the temperature of $450\text{ }^\circ\text{C}$ the soaking time of 1800 s is applied. The gaseous and tarry products of the pyrolysis process are carried directly to the tar-sampling device and to the on-line gas analysis. In a second run the gaseous and tarry products enter the secondary reactor having a maximal temperature of $600\text{ }^\circ\text{C}$. Fig. 4 shows the total reaction rate attributed to the initial mass for both runs concerning carbon monoxide, carbon dioxide, and methane. The three reaction complexes can be assigned to the degradation of hemicellulose, cellulose, and lignin. The gas yield of the first run consists of 6.5% carbon dioxide, 3.6% carbon

monoxide, and 0.1 % methane. The yield of carbon dioxide is almost constant for the second run. The yield of carbon monoxide increases two times by the degradation of tars originated by the hemicellulose and cellulose. The tars produce from the lignin no carbon monoxide. The yield of methane shows the same behaviour. No methane is produced by the degradation of hemicellulose and cellulose in the first run. Only methane is detected in this run during the degradation of the lignin. In the second run the tars of cellulose and hemicellulose form methane. The tars originated by the degradation of lignin form no methane. The mean molar mass of the primary tar is 250 g/mol and increases in the second run up to 308 g/mol. Therefore, the tars formed by the cellulose and hemicellulose is partially degraded and the mean molar mass of the rest is increasing.

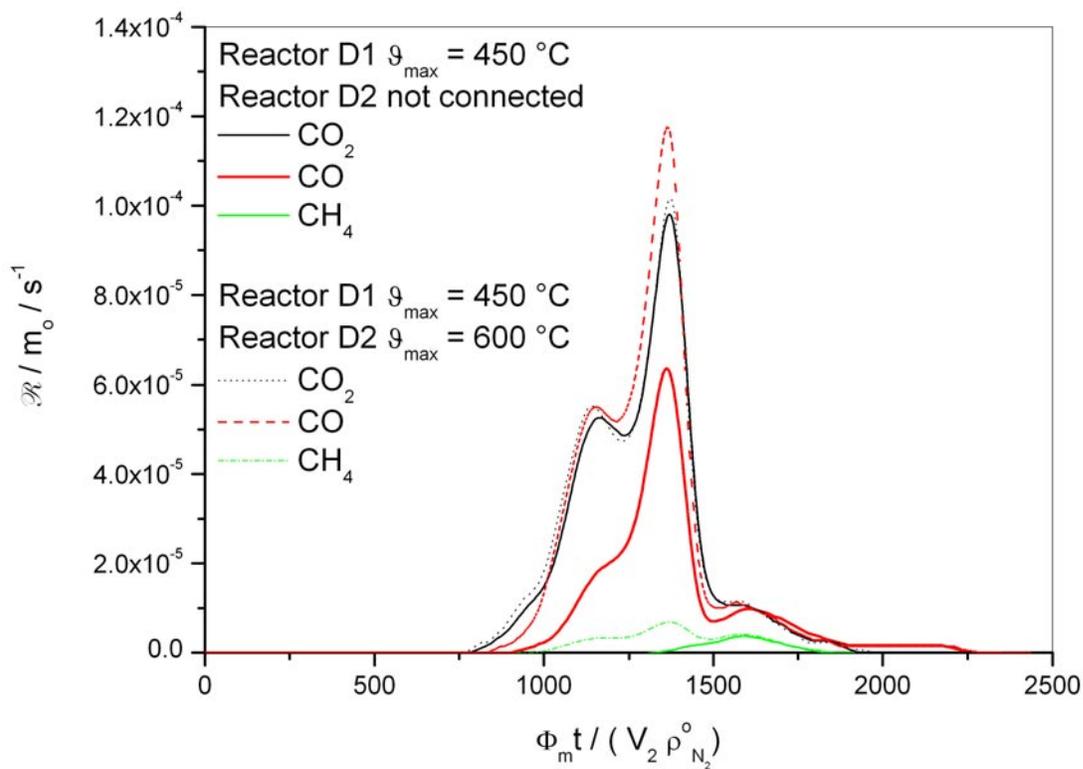


Fig. 4 Gas yield of the pyrolysis of beech wood and of the degradation of tars

Conclusion

The theoretical temperature distribution is in very good agreement with the experimental results. This fact is essential to obtain formal-kinetic parameters. The comparison of the results of the gas analysis shows no gas formation from the lignin-tars up to a temperature of $600 \text{ }^\circ\text{C}$. The degradation of tars forms cellulose and hemicellulose form methane and carbon monoxide. The yield of carbon dioxide remains constant.

References

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