MATHEMATICAL MODELING AND EXPERIMENTAL INVESTIGATION OF THE PYROLYSIS OF WASTE IN ROTARY KILNS

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ABSTRACT

Pyrolysis processes are used in the field of the thermal treatment of waste e.g. as a process unit in combination with a gasification or combustion unit realized in the RT21 process in Japan from Mitsui. Furthermore pyrolysis processes are used for specially prepared waste fractions as a thermal pre-treatment unit, e.g. before a power station in the Con-Therm process in Germany or in the steel and cement industry. In principle there is also the possibility to use pyrolysis for the direct recycling of materials such as Plexiglass or plastics reinforced with carbon fibres.

Often rotary kilns are used in the field of pyrolysis.

The lumpy starting material is mixed due to the rotation of the rotary kiln. The energy for the pyrolysis can be given to the starting material indirectly, e.g. through radiant tubes from an external heater, to the rotary kiln wall or directly through a hot gas flow. The starting material is converted through the steps of drying, release and conversion of volatile components to a pyrolysis coke and pyrolysis gas.

To optimize existing plants or to design new ones mathematical models are important tools to minimize the experimental effort.

In order to be able to describe the pyrolysis process in a rotary kiln using a mathematical model, the transport of the solid and the specific conversion processes dependent upon the constructive parameters such as diameter and length of the rotary kiln as well as operating parameters such as angle of inclination, rotational frequency, throughput and course of the temperature over the length in the rotary kiln must be described. For process models which describe such processes in a reactor, it can usually be distinguished between a reactor model and a so-called basic model. The behavior of the solid in the reactor (residence time behavior) is described using the reactor model and the material and heat transfer as well as the conversion process with the help of the basic model.

For the proposed paper a mathematical model which considers on the one hand side the residence time behaviour and on the other hand the heat and material transfer mechanisms (basic model), including unsteady behaviour, is presented. This paper shows a mathematical model and its validation for an homogenous material, such as sand, without and with solid conversion of polyethylene and the evaporation and drying process.

GENERAL PRINCIPLES

In order to be able to describe the pyrolysis process in a rotary kiln using a mathematical model, the transport of the solid and the specific conversion processes dependent upon the constructive and operating parameters (main influencing parameters) must be described.

The approaches to process modeling can be roughly categorized into balance models (see **Figure 1**) and maximum-gradient models (**Figure 2**) or models divided into sections as the case may be.

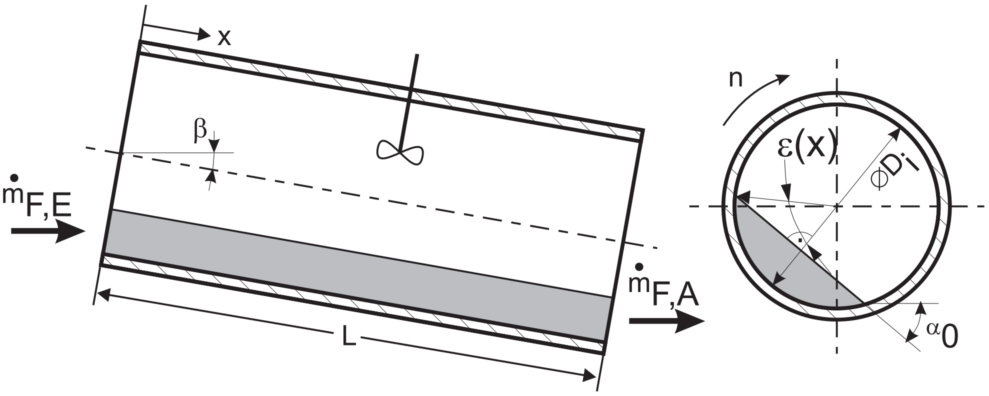

Fig. 1: Balance Model

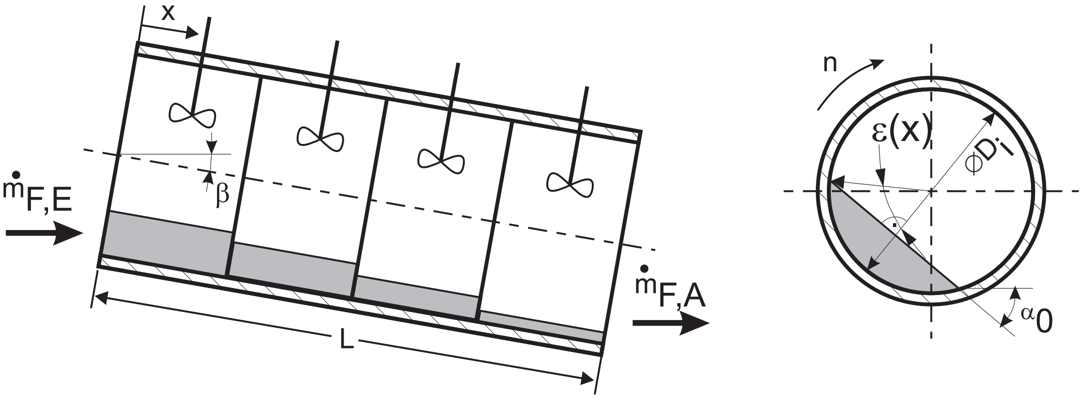

Fig. 2: Maximum-Gradient-Model

Balance models can generally be traced back to the basic element stirred vessel (abbreviated as SV in the remainder of this paper). Maximum-gradient models are obtained through the connection of several SV elements or zones (sections) in series. The model that is presented here uses a Maximum-Gradient-Model.

REACTOR MODEL

The behavior of the solid, also referred to as the residence time behavior or as reactor behavior in connection with the apparatus, has a significant influence on the course of the conversion over the reactor length. Therefore, the residence time behavior and the main influencing parameters for the control of the residence time behavior are of great importance for the optimization of the overall process. The description of the residence time behavior also forms a fundamental basis for the mathematical modeling of the solid conversion. In rotary kiln systems constructive parameters, such as rotary kiln radius R and kiln length L, and operating parameters, such as mass flow m_F, angle of inclination β, and rotary kiln speed n, are important with regard to the residence time behavior (**Figure 3**).

The residence time behavior is also influenced by the characteristics of the starting materials, e.g. composition, bulk density ρ_F, angle of repose α_o, particle-size distribution, etc.

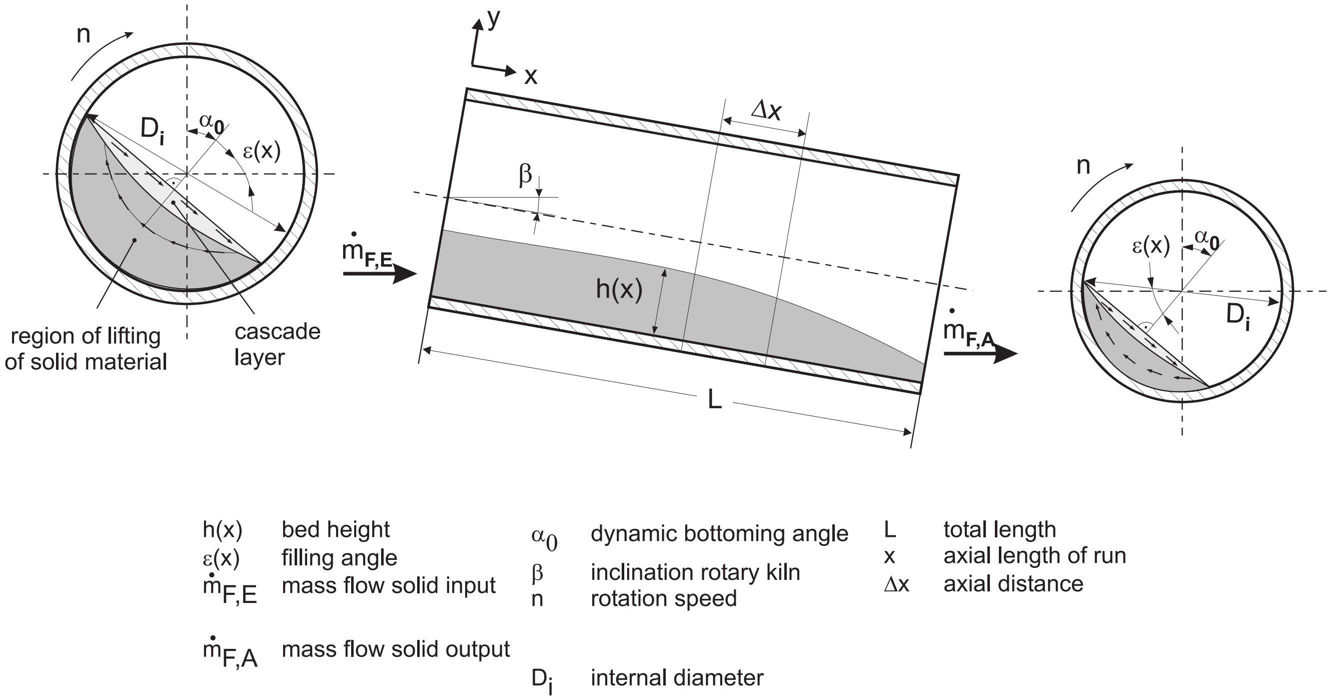

Fig.: 3: Main influencing parameters for the material transport

Generally, the residence time behavior is characterized through the residence time distribution E (Θ) [1] and the derived average residence time τ. In rotary kiln systems in particular, the residence time behavior can be described using path-dependent values such as filling height h (x), angle of bed inclination ψ (x) and the filling angle ε(x).

The residence time model delivers the following parameters for the total process model:

The course of the filling angle ε (z) (**Figure 3**) with the derived values of filling height h(x), degree of filling ϕ (x) and the corresponding portions of the area covered with solid, the surface of the solid facing the gas and the free wall area, which is necessary for the heat transfer as well as the average residence time τ, as well as individual residence times Δt_i for each SV element i.

The course of the filling angle for an unknown starting material can be determined according to the model from Hogg, Shoji and Austin [2] with few cold investigations of the residence time using the following equations:

$$\left(\frac{M \cdot z}{R}\right) = \int_{\varepsilon(z=0)}^{\varepsilon(z)} \frac{M^2 \cdot \sin\varepsilon \cdot d\varepsilon}{\sin^3\varepsilon - \left[\sin^6\varepsilon - M^2 \cdot \left(1 - \frac{2 \cdot C}{M} \cdot \sin^3\varepsilon\right)\right]^{0,5}} \qquad \text{(Eq.1),}$$

with $M = \left(\frac{2 \cdot \dot{m}_S}{K}\right)$ and (Eq.2),

$$C = \left(\frac{\tan\beta}{\cos\alpha_0}\right) \qquad \text{(Eq.3),}$$

as well as $K = 2/3 \cdot B \cdot \rho_s \cdot 2 \cdot \pi \cdot n \cdot R^3 \cdot \cot\alpha_0$ (Eq.4),

$\dot{m}_S$	mass flow of the solid [kg/h]
β	angle of inclination of the rotary kiln [°]
α_0	angle of repose [°]
ρ_S	bulk density of the solid [kg/m^3]
n	rotational frequency of the rotary kiln [min^{-1}]
R	radius of the rotary kiln [m]
ε	half of the filling angle [°rad]
z	variable over the length of the rotary kiln, starting at the discharge [m]
B	material factor, must be determined experimentally [-].

The equations (1) to (4) are only valid for low degrees of filling. The material factor B in this equation is an experimentally determined dimensionless material parameter which physically describes the ratio of the residence time of a particle on the surface to the total residence time for a cycle in the bed and on the surface. For sand a material factor B was determined to 0.70.

BASIC MODEL

In rotary kiln reactors the heat transfer to the bed takes place either

- directly through a combustion gas or
- indirectly through an external heater.

The type of energy input depends upon the respective process carried out. For example, the heat for the endothermic calcination of raw material is transferred through a hot gas. For process under inert atmosphere, such as pyrolysis, the energy is usually introduced from the outside, e.g. electrically or via internal gas-heated radiating pipes.

The partial processes radiation, convection and conduction are coupled with one another in the type of heat transfer. The material conversion processes also play a role in the energy balance. In order to couple the material conversion processes with the heat transfer and for the determination of heat transfer surfaces for gas, wall and solid, information concerning the solid transport and the residence time are required.

The basic model developed here is based on the mass- and energy balances (see **Figure 4** and equation 5 and 6).

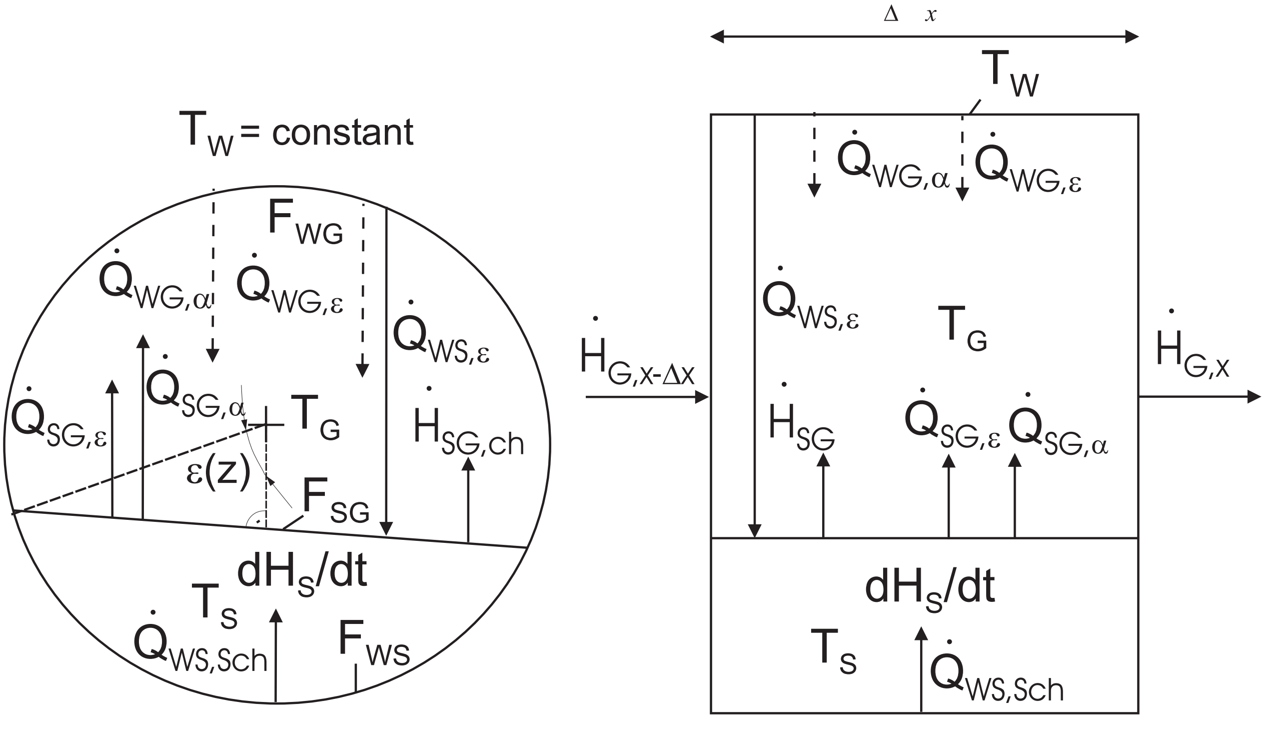

Fig.: 4: Heat flows in a stirred vessel element

The description of the solid transport gives rise to a maximum gradient model, i.e. only the change over the length of the rotary kiln is considered, not over the bed height. A small stirred vessel element with a volume dV from the point of view of an “observer riding along” is regarded for the conversion processes. The stirred vessel element is situated at a certain position z along the longitudinal direction of the rotary kiln after a certain residence time dt. At this position, the stirred vessel element undergoes material and energy exchange with the gas atmosphere flowing above and energy exchange with the wall of the rotary kiln. Dependent upon the temperature, the mass dm_s is transferred from the surface to the gas flowing above it in a certain time period dt in the stirred vessel element dV. The changing of the solid’s enthalpy is equal to the sum input and discharge as well as formation/consumption.

$$\frac{dH_S}{dt} = \frac{dm_S \cdot c_{S,0S} \cdot (T_S - T_0)}{dt} + \frac{d(T_S - T_0) \cdot m_S \cdot c_{S,0S}}{dt} = \dot{Q}_{WS,Sch} + \dot{Q}_{WS,\varepsilon} - \dot{Q}_{SG,\alpha} - \dot{Q}_{SG,\varepsilon} - \frac{dm_S}{dt} \cdot \left| \Delta h_R \right| \qquad \text{(Eq.5)}$$

$\dot{Q}_{\mathrm{WS,Sch}}$	Heat flow from the wall on the side of the bulk material into the solid due to radiation and conduction [W],
$\dot{Q}_{\mathrm{WS},\varepsilon}$	Heat flow from the wall opposite the solid due to radiation under consideration of the secondary radiation of the gas [W],

$\dot{Q}_{SG,\varepsilon}$	Heat flow from the solid into the gas due to radiation under consideration of the secondary radiation of the opposite wall [W],
$\dot{Q}_{SG,\alpha}$	Heat flow from the solid into the gas through convection [W],
$dm_S/dt*\Delta h_R$	consumption of heat due to material conversion, evaporation and drying [W].

The gas mass flow is assumed to be as steady-state:

$$\frac{dH_G}{dt} = 0 = \dot{H}_{G,x-\Delta x} + \dot{H}_{SG} + \dot{Q}_{SG,\varepsilon} + \dot{Q}_{SG,\alpha} + \dot{Q}_{WG,\alpha+\varepsilon} - \dot{H}_{G,x} \qquad \text{(Eq.6)},$$

with

$\dot{H}_{G,x-\Delta x}$	enthalpy flow from the last SV [W],
$\dot{H}_{G,x}$	enthalpy flow from the actual SV [W],
$\dot{H}_{SG}$	enthalpy flow from conversion, evaporation and drying [W],
$\dot{Q}_{WG,\alpha+\varepsilon}$	Heat flow from the wall into the gas due to radiation and conduction [W].

The evaporation of water during the heating of the solid is modelled with the formulars according to the analogy of heat and material transport mechanism. The drying process is calculated with the help of Gauss error- function [3].

With the reactor model from Austin and the described basic model a calculation for the solid temperatures for sand at 300 °C, 400 °C and 500 °C wall temperature was performed.

Figure 5 shows the calculated and measured solid temperature profiles for sand without conversion.

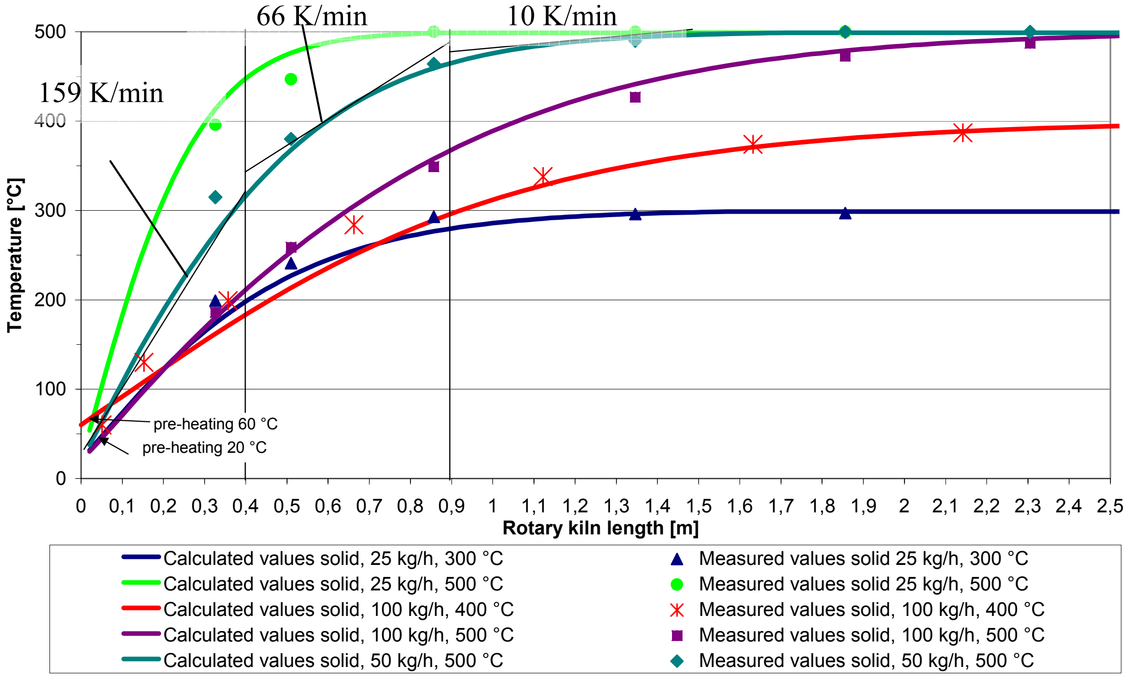

Fig. 5: Solid temperature profile without conversion ($dm_s/dt = 0$)

The gas flow at the rotary entrance is about 1 Nm^3/h.

The courses of calculated and measured temperatures show a good accordance.

DESCRIPTION OF THE KINETICS

For the presented model the conversion processes proceed dependent upon the process conditions (temperature, concentration) in the SV element. The determination of kinetic data for mixed waste materials is not recommended for the mathematical modeling due to the heterogeneous and frequent changes in composition. The use of so-called effective kinetic data is more suitable. In Gehrmann [4] the course of conversion for a waste material or mixture of wastes is determined through experiments using a thermobalance. The heating function ϑ = f(L) over the length, important for the pyrolysis processes under inert atmosphere, is assumed at first and then underlies the corresponding residence time behavior as the heating function ϑ = f(t) for the investigation of each waste or waste mixture using a thermobalance.

The results from the thermogravimetric investigations are inserted into the model and a corresponding heating function ϑ = f(L) over the length of the rotary kiln results. If this does not coincide with the curve specified by the thermogravimetric investigations, then the procedure must be repeated. For example for a continuous heating rate of about 10 °K/min the curve of decomposition of polyethylene (PE) (**Figure 6**) was measured.

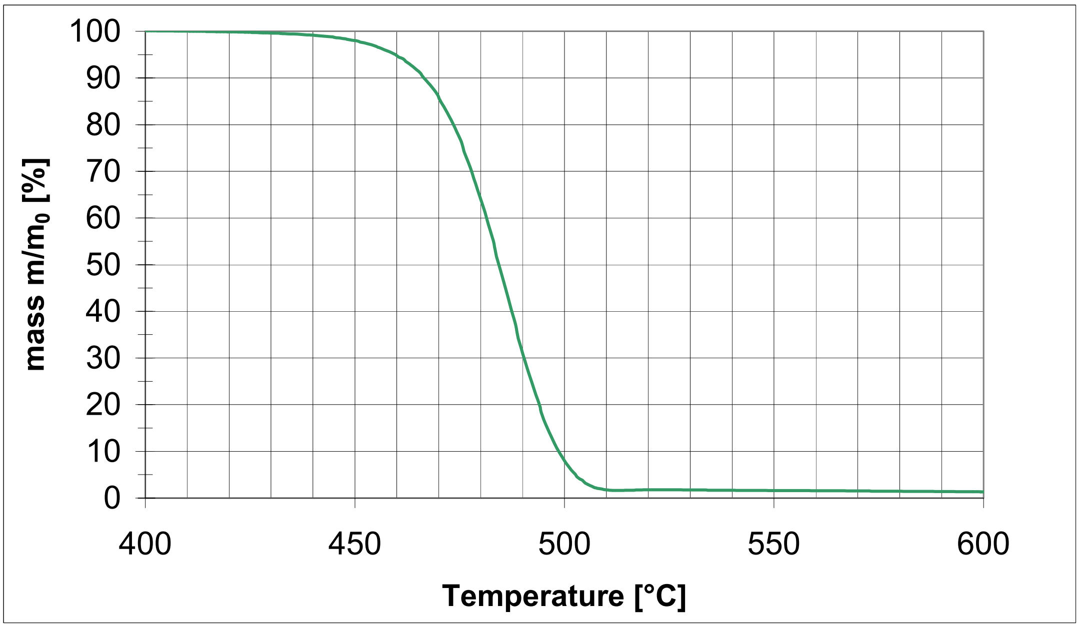

Fig. 6: Result from an investigation with the thermobalance with PE at a heating rate of 10 K/min

These curve could be approached by these function:

$$\frac{d\alpha}{dt} = k_{\infty} \cdot \exp\left[(-\frac{E}{R \cdot T})\right] \cdot (1-\alpha)^n \text{ [1/s], [5]} \qquad \text{(Eq.7),}$$

with $\alpha = \frac{m_0 - m(t)}{m_0 - m_\infty}$ [-] (Eq.8).

The determined values from Fig. 6 are:

n = 0.77, E = 261 kJ/mol, $k_\infty = 9.11 \cdot 10^{15}$ [1/s].

m_0 mass at the time t = 0,

m(t) actual mass at the time t and

m_∞ mass at the time t = t_{finish}.

Then follows for the material conversion $\Delta m_S/\Delta t$ with the mass flow m_0 as actual mass flow into the first stirred vessel element and m_∞ as mass flow out of the rotary kiln:

$$\frac{\Delta m_S}{\Delta t} = (\dot{m}_0 \cdot \Delta t_0 - \dot{m}_\infty \cdot \Delta t_\infty) \cdot k_\infty \cdot \exp\left[(-\frac{E}{R*T}\right] \cdot \left[1 - \frac{(\dot{m}_0 \cdot \Delta t_0 - \dot{m}_S(t) \cdot \Delta t)}{(\dot{m}_0 \cdot \Delta t_0 - \dot{m}_\infty \cdot \Delta t_\infty)}\right]^n \text{ [kg/s]} \qquad \text{(Eq.9)}$$

With regard to the equations (5) the courses of the solid and the gas during conversion of PE 10 kg/h and sand 90 kg/h could be calculated as it is shown in **Figure 7**.

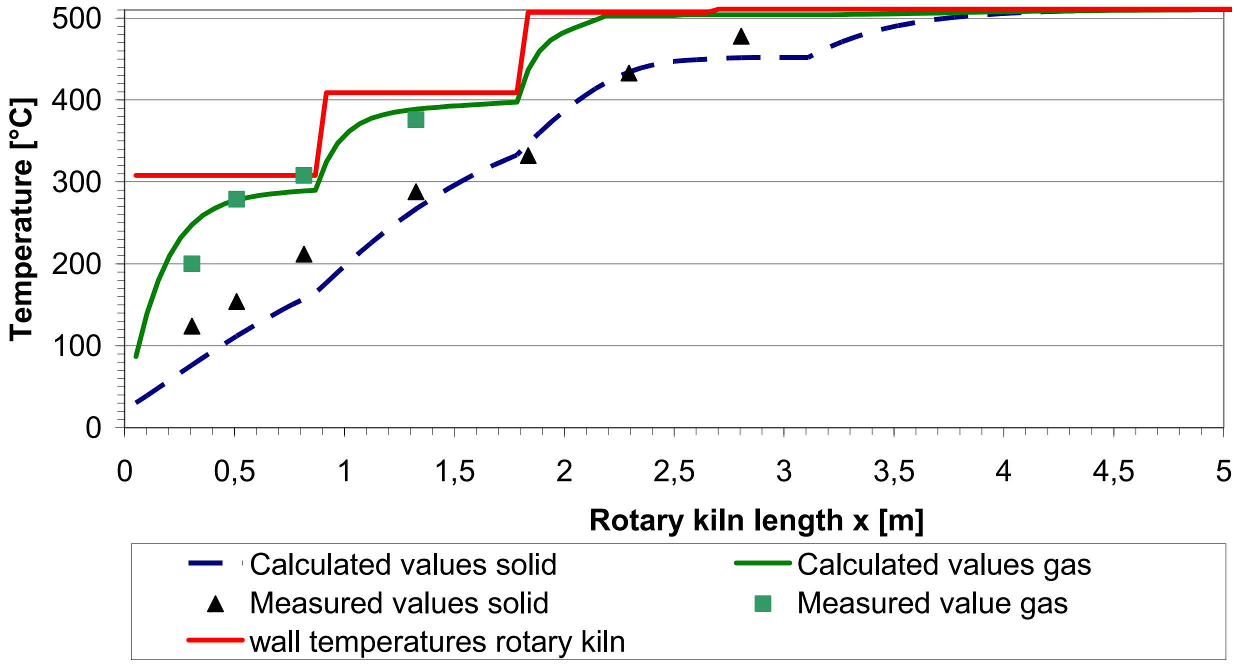

Fig. 7: Calculated and measured temperature profiles of solid and gas phase with a staging of the wall temperatures of 308/ 405/ 507/ 511 °C with 90 kg/h sand and 10 kg/h PE

The gas flow (nitrogen) at the rotary entrance is about 0.8 Nm^3/h. The reaction enthalpy $\Delta_R h$ was assumed with 400 kJ/kg, Δt_0 = 11 s, Δt_∞ = 4 s for 100 SV and a length about 5.1 m. A carbon dioxide- concentration was measured to 1.7 Vol.-%.

The results show that the model can describe the residence time behavior and heat transfer (Figure 5) as well as the thermal conversion of homogeneous material (Figure 6) already plausible in comparison with experimental results. With this mathematical model for the description of pyrolysis processes a determination of the dependence on the main constructive and operational parameters in a rotary kiln is possible.

For a mixture polyethylene, water and sand a calculation and an experiment were done as it is shown in **Figure 8**.

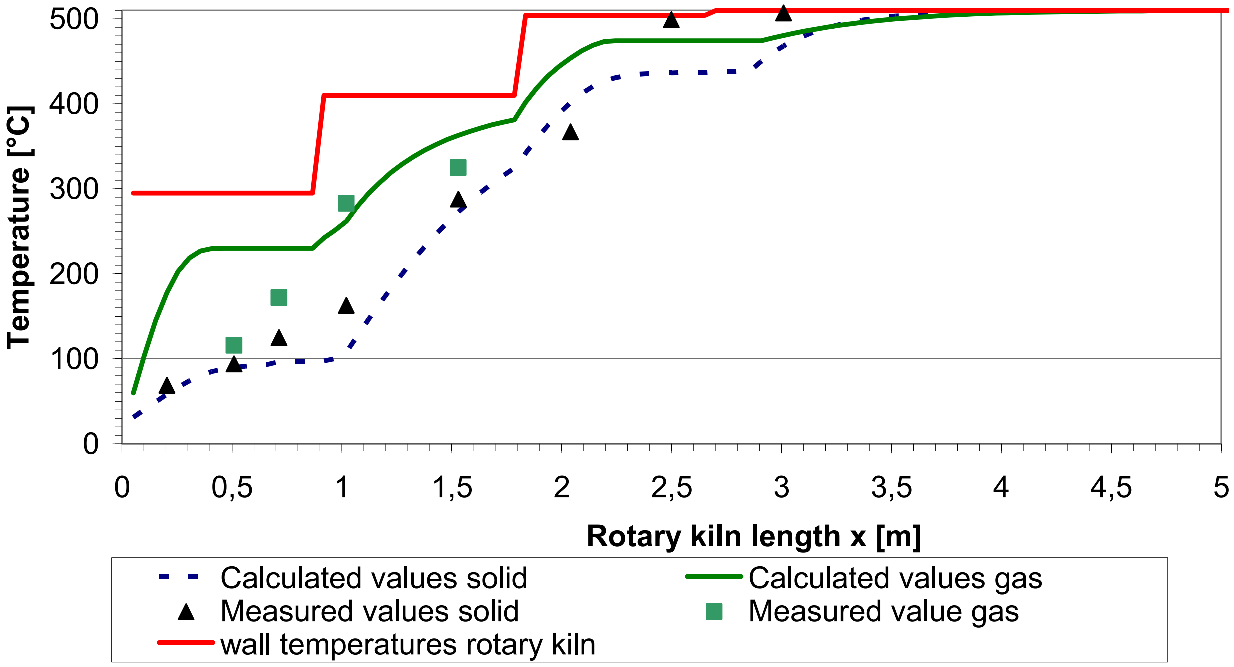

Fig. 8: Calculated and measured temperature profiles of solid and gas phase with a staging of the wall temperatures of 308/ 405/ 507/ 511 °C with 59 kg/h sand, 6 kg/h water and 10 kg/h of PE

The gas flow (nitrogen) at the rotary entrance is about 1 Nm^3/h. The reaction enthalpy $\Delta_R h$ was assumed with 400 kJ/kg, $\Delta t_0 = 31$ s, $\Delta t_\infty = 4$ s for 100 SV and a length about 5.1 m. A carbon dioxide- concentration was measured to 0.8 Vol.-%.

With exception of the gas temperatures in the range of evaporation and drying phase the profiles show a good accordance between calculated and measured values.

The modeling of the gas composition and the validation for heterogeneous waste material is currently under development.

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