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Gasification Kinetics of Low-Grade Waste Under High-Pressure Entrained-Flow Conditions

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Motivation

The utilization of biogenic residues, refuse-derived fuels (RDF) and waste via advanced gasification technologies is a very promising solution enabling waste-to-X routes to produce value added chemicals, sustainable liquid fuels or power generation [1]. Especially entrained-flow gasification provides a high-quality synthesis gas from low-grade biogenic residues or heterogeneous waste streams. Moreover, pressurized systems benefit the thermo-dynamic equilibria in subsequent synthesis and provide more cost advantages. Hence, it is essential to deeply understand the gasification conversion of biomass and plastic waste under high-pressure entrained-flow conditions. Herein, we report on a systematic analysis by individual investigation of devolatilization kinetics and char gasification kinetics of biogenic residues, RDF and waste under entrained-flow conditions.

Methods & Materials

While many studies on pyrolysis kinetics employ a thermogravimetric analyzer (TGA), high heating rates like entrained-flow conditions cannot be replicated in a TGA, which influences the pyrolysis product distribution. In contrast, we outline a Pressurized Wired-Mesh Reactor (PWMR), which enables sample heating rates up to 5000 K/s. Pulverized raw fuel <300 µm are examined on their temperature- (1) and pressure-dependent (2) as well as on their time-resolved devolatilization behavior.

Fig. 1: Pressurized Wired-Mesh-Reactor (PWMR) provides kinetic devolatilization data for accurate entrained-flow gasification modelling and CFD studies.

Hence, kinetic data using Single-First-Order-Reaction Model (SFOR) can be obtained by applying equation (3) under the same characteristic conditions as in an entrained-flow gasifier up to 1600 °C and 50 bar [2].

$$Y_V(T) = Y_{V,Tset} + (Y_{V,Tmax} - Y_{V,Tset}) \cdot (1 - \exp(-\nu(T - T_{set})) \quad (1)$$

$$Y_V(p) = Y_{V,pset} \cdot \frac{\left(\frac{p}{p_{set}}\right)}{\rho} \quad (2)$$

$$Y_V(t) = A_V \cdot \exp\left(-\frac{E_A}{RT}\right) \cdot (Y_{V,Tmax} - Y_{V,Tset}) \quad (3)$$

Char preparation is performed in an electrically heated and Pressurized High-Temperature Entrained-Flow Reactor (PiTER) operating up to 1800 °C, 50 bar, particle residence times up to 2.4 s, which are comparable to industrial scale. The reaction zone is designed to a inner diameter of 70 mm and a length of 2200 mm. Validation tests are used to show the suitability of the SFOR model. Moreover, chars can be collected by a height-adjustable sampler at different residence times in order to study the consequence of pyrolysis conditions on structure and gasification reactivity.

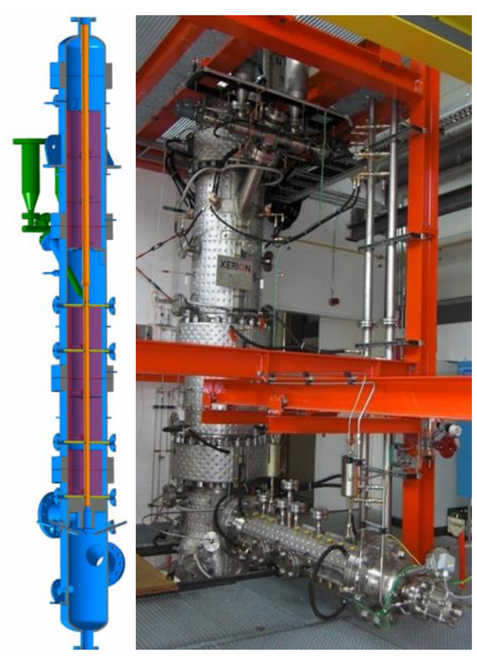

Fig. 2: Pressurized High-Temperature Entrained-Flow Reactor (PiTER) is applied for pyrolysis char preparation, validation experiments and O_2/CO_2/H_2O-gasification of pulverized fuels.

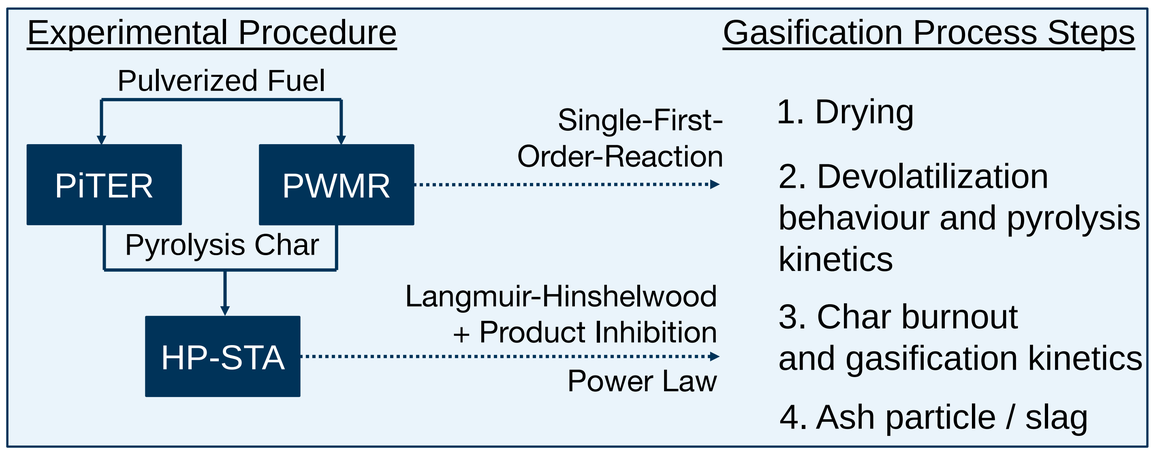

Fig. 3: Scheme of experimental procedure for determination of highly-needed pyrolysis and gasification kinetics under entrained-flow conditions.

Chars derived from PWMR and PiTER are subsequently further characterized for their reactivity in a High-Pressure Thermogravimetric Analyzer (HP-TGA). Herein, 10 mg of char sample is converted isothermal up to 1000 °C and by varying partial pressures of the gasifying agents. Prior, heating rate experiments at 5 K/s are conducted in order to identify rate-limiting reaction temperatures by chemical kinetics.

$$r_i = k_i(T) \cdot p_i^n = k_{0,i} \cdot \exp\left(-\frac{E_{A,i}}{RT}\right) \cdot p_i^n \quad (4)$$

$$r_{ij} = \frac{k_{1,i} \cdot p_i}{1 + (k_{A,i} \cdot p_i) + (k_{B,j} \cdot p_j)} = \frac{k_{0,1} \cdot \exp\left(-\frac{E_{A,1}}{RT}\right) \cdot p_i}{1 + k_{0,A} \cdot \exp\left(-\frac{E_{A,A}}{RT}\right) \cdot p_i + k_{0,B} \cdot \exp\left(-\frac{E_{A,B}}{RT}\right) \cdot p_j} \quad (5)$$

By using the Power Law (4) and Langmuir-Hinshelwood equation including H_2 and CO product inhibition (5) highly necessary kinetic data for char gasification can be determined. Herein, partial oxidation using O_2, Boudouard reaction using CO_2 and heterogeneous water-gas shift reaction applying H_2O are studied. Moreover, gas mixtures of the gasifying agents are further investigated.

Fig. 4: Initial char reactivity and kinetic char gasification parameters are derived by applying High-Pressure Thermogravimetric Analyzer (HP-TGA) by Linseis GmbH, Selb, Germany.

Results

Pyrolysis kinetics are not to be neglected due to high-volatile content in investigated feedstocks. Entrained-flow pyrolysis conditions show high influence on chemical and physical char structure resulting in structure dependent gasification reactivity leading to thermal deactivation with higher temperatures. Adequate O_2/CO_2/H_2O-char gasification kinetics can be determined under high-pressure conditions to provide crucial modelling parameters for entrained-flow gasification at industrial scale. Both, devolatilization and char gasification kinetics are highlighted to be essential for 1D-simulations and accurate computational fluid dynamic studies, summarized in a solid fuel database [3]. Therefore, this work contributes to the realization of an entrained-flow gasification plant under industrial conditions opening sustainable synthesis routes towards chemicals or liquid fuels from biogenic residues, RDF and waste.

Literature

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