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Research paper

Experimental study of wood char gasification kinetics in fluidized beds

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ABSTRACT

During gasification two steps take place. The first one is pyrolysis and the second one is gasification of the char that remains back after pyrolysis. The second step is slower than the first one, so this step is the limiting factor in designing fluidized beds. Kinetic data for designing fluidized beds are necessary. The paper describes gravimetric measurements directly applied to fluidized bed with large sample sizes. The samples are char of 6 mm wood pellets and 10–40 mm wood cubes in order to directly measure ”apparent kinetics”. The parameters examined in this paper are particle size, product gases (= hydrogen) in the gasification medium, type of wood and differences in CO_2/steam gasification. The results are presented as Arrhenius diagrams and half-value period diagrams. The most important parameters are the temperature and product gases (hydrogen) in the gasification agent. The particle size seems to be less important for large wood particles as the measurements do not show significant differences for gasifying char of wood cubes 10–40 mm. The half-value periods for gasification of char from wood cubes (10 mm - 40 mm) with 100% steam at atmospheric pressure lie between 1000 s at 1023 K and 300 s at 1173 K. For char of 6 mm wood pellets the half-value periods lie between 1900 s at 1023 K and 250 s at 1173 K. The reaction is most likely in pore diffusion regime.

1. Introduction

To be able to use biomass fuels in efficient processes a refinement is necessary. Therefore, gasification is a way to get a gaseous fuel that can be burned in gas engines or gas turbines. There are two kinds of gasification, allothermal and autothermal gasification. The autothermal gasification works with air as gasification agent and thus gets the process heat by partly oxidation of the fuel. In contrast allothermal gasification needs an external energy source for the process, because gasification with the most used gasification agents steam and carbon dioxide is endothermic. For heating of an allothermal gasification reactor, it is possible e.g. to have an external combustion chamber, which includes heat pipes for the transportation of heat into the reactor, like it takes place in the so-called heat pipe reformer [1,2]. Advantage of the allothermal gasification is that the produced gas is higher calorific, because there is no nitrogen that would dillute the produced gas and thus reduce the heating value.

As wood is one of the most used biomass fuels this paper focuses on that kind of fuel. For designing new wood gasification reactors it is necessary to know, how fast the reaction takes place. While pyrolysis, with instant gasification of the pyrolysis gases, takes place in comparable short time, the gasification of the residual char needs much more time [3]. So this is the limiting step in gasification process [4].

As reactor concept the fluidized bed has turned out as useful. The fluidized bed concept is based on a reactor that is filled with sand and fluidized with the gasification agent. Most sand materials are inert and do not affect the reaction in any way. An example for an inert material sand is the widely used quartz sand. Olivine sand has a catalytic influence on the reaction [5].

When looking at a fluidized bed as reactor concept, it is important to keep in mind that in fluidized beds there are special conditions that do not occure in other types of reactors. This is especially the comminution of wood char particles through forces on the particles by the sand.But not only while gasification of the char, the special conditions of a fluidized bed are important. As literature shows, it is also important, under which conditions the pyrolysis took place before gasification. A fuel that was pyrolyzed with a high heating rate delivers an other char than a low pyrolyzed

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List of symbols

Notations

A	preexponential factor $[s^{-1}]$
c_{H_2O}	molar concentration of steam $[mol \cdot m^{-3}]$
C_{RF}	reactivity factor$[-]$
D	diffusivity $[m^2 \cdot s^{-1}]$
d	particle diameter $[m]$
E_A	activation energy $[J]$
k	rate constant $[s^{-1}]$
k_0	preexponential factor $[s^{-1}]$
K_{eq}	equilibrium constant $[-]$
k_V	volumetric rate constant $[s^{-1}]$
m	mass $[g]$
n	number of measurements $[-]$
p	pressure $[Pa]$
R	universal gas constant $[J \cdot mol^{-1} \cdot K^{-1}]$
r	reactivity $[s^{-1}]$
ρ	density $[kg \cdot m^{-3}]$
ρ_{50}	density at t_{50} $[kg \cdot m^{-3}]$
T	temperature $[K]$
$T_{surface}$	surface temperature $[K]$
t	time $[s]$
t_{50}	half value period $[s]$
u	superficial gas velocity $[m \cdot s^{-1}]$
u_0	superficial gas velocity at $[m \cdot s^{-1}]$

Loosening point

y	molar mass fraction $[-]$
η	effectiveness factor $[-]$
ϕ	Thiele modulus $[-]$

Subscripts

0	initial condition
real	industrial conditions (e.g. large sample sizes)
labscale	labscale conditions (e.g. small sample sizes)
t	at time-point t

fuel [6]. It is more reactive than one that was pyrolyzed under low heating rates [7,8]. So it is important that the pyrolysis takes place under conditions that are comparable to industrial gasification plants. In fluidized beds the heating rates are high [9] and limited by heat conduction within the sample, because the external heat transfer coefficient from the bed to the sample is extraordinary high. So the (internal) pyrolysis number, which is the relationship between the heat conduction rate and the reaction rate, indicates a limitation even for pellets of 6 mm diameter from about 550 K to 700 K on [10].

Reactivities for the wood char gasification process with steam and carbon dioxide have been widely studied in literature (e.g. Refs. [11–18], review available in Refs. [19,20]). But it is questionable, if the results of these measurements are applicable on fluidized bed reactors. Most of the measurements were conducted on sample sizes that are very small and thus do not include transport phenomena. Also the pyrolysis conditions are often not comparable to that of fluidized beds.

Out of these reasons this paper picks up the gasification of wood char in fluidized beds as topic. The aim of this paper is to determine the influences on the gasification kinetics and to present kinetic data that are realistic for industrial fluidized bed gasifiers.

2. Basics of char gasification

2.1. Chemical reactions

As char pyrolyzed at temperatures > 1000 K consists mainly (> 85%) of carbon [21], it is a sufficient approach to treat the char chemically as it would consist just of carbon and ash. So for the formulation of the overall reaction, it is possible to write (adapted from Ref. [1]):

- Gasification with steam:

$$C + H_2O \rightleftharpoons CO + H_2 \tag{1}$$

- Gasification with carbon dioxide:

$$C + CO_2 \rightleftharpoons 2CO \tag{2}$$

When looking at the gasification products of char gasification with steam, one could assume that also a reaction of hydrogen with carbon could play a role. The reaction is:

$$C + 2H_2 \rightleftharpoons CH_4 \tag{3}$$

In gasifiers this reaction takes place of course. However this reaction is not relevant for gasification under atmospheric conditions, as it is slow compared to the reaction in Eq. (1) [22]. So this reaction should not be discussed further.

2.2. Limitation by physical processes

As gasification of char is a heterogeneous process, the diffusion of the gasification agent to the active cells of the carbon is necessary. So diffusion can be the limiting factor for the gasification of char. When looking at radial conversion profiles presented by Gómez-Barea and Leckner [22], more or less the complete particle reacts simultaneously, so that there is just a small radial gradient in the conversion degree of the particle. For combustion in opposite the reaction mainly takes place just near to the surface of the char. The explanation is that gasification is much slower than combustion. As a consequence of that, the gasification agent can diffuse deeper into the particle.

It seems that there is an influence of the pore size or porosity of the char, because measurements in literature show higher reactivity of char that had been pyrolyzed under high heating rates [8]. This effect occurs, because the high heating rates lead to lower shrinkage than it would be at low heating rates, because the devolatilization rate is higher. So it is important that the pyrolysis conditions are comparable to industrial gasifiers.

[22] says that gasification of char in fluidized beds is usually limited by pore diffusion. So the pores are important for reaction rates.

2.3. Modeling of gasification process

2.3.1. Overview

The models in literature are dividable into different kinds of models:

- Particle models.
- Effectiveness factor.
- (Quasi-)equilibrium models.
- Numerical models.