Kinetic Modelling of a Pyrolysis – Gasification Reactor

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Biomass is of growing interest as a secondary energy source. Biomass could be converted to energy especially by pyrolysis or gasification. Understanding the mechanism and the kinetics of biomass pyrolysis and gasification could be the key to the design of industrial devices capable of processing vast amounts of biomass feedstock. There are multiple reactions describing the decomposition of biomass to gaseous products and it is difficult to identify each of the reactions. Therefore reactions must be simplified; in general well identified reagents and products with different states (feedstock, tar, gas) are used for calculations, instead of using different compounds of real products. In our work real product compounds obtained from pyrolysis were used, and the kinetic constants for biomass pyrolysis and gasification were identified.

A laboratory scale reactor was used for the physical experiments containing consecutive fast pyrolysis and gasification stages.

The main aim of this research was to create a detailed and validated first principle model for the reactor system. In this study, a compartment modelling approach was used, where all compartments facilitate different reactions (pyrolysis, thermal, and catalytic gasification). With the identification of the model parameters (using PSO algorithm) a stable and validated model was created, which can be used for further optimisation studies. MATLAB was used for the creation of the compartment model, and Particle Swarm Optimisation was used for the kinetic parameter identification.

1. Introduction

To ensure the sustainability of our life and planet new technologies are developed every day. Due to the limitations of fossil fuels there are multiple on-going researches to facilitate the use of biomass plants and renewable resources, as substitute fuels. One possible resource is the cellulose derived from different types of plant biomass. With the proper treatment these feedstock could be converted to hydrogen, or synthesis gas which could be a good feedstock for industry, and could also be used as fuel. These processes are often called biomass to transportation liquid processes (BTL), which consist of pyrolysis, gasification, CO_2 capture, and other processes. Sun et al. (2014) used a flow sheeting simulator to optimise the BTL production. Their study uses a barley straw conversion to transport fuel process as an illustration of the optimisation methodology.

There are multiple options for feedstock, and efficient technologies for biomass processing. Suzdalenko et al. (2011) used wood, and wheat straw pellets as feedstock. They used one reaction for pyrolysis, two additional equations for carbon, resulting in CO and hydrogen.

Yang et al. (2007) calculated the yields of three component feedstock in the case of pyrolysis. Different temperatures from 160 to 900 °C were examined. They found cellulose gave a higher CO, while hemicellulose produced higher CO_2, and lignin gave a higher H_2 and CH_4 yield. Panepinto and Genon (2011) used municipal solid waste as a feedstock. They compared the pyrolysis/gasification process to waste combustion, and examined the influence of the most important model parameters. They found the combustion was more energy efficient; however the pyrolysis/gasification methods have much lesser environmental impact.

Xiong et al. (2014) created an open source CFD simulation model for calculating pyrolysis reactions in a fluidised bed reactor. There are four chemical reaction considered in this case (modified Broido–Shafizadeh mechanism),

the activation of biomass from virgin biomass, the production of tar from active biomass, the production of biochar and syngas, while the fourth reaction is the production of biochar and syngas from tar.

Wang et al. (2016) use the same three materials as feedstock. They used multiple steps for calculating the kinetic parameters for hemicellulose and lignin; however they only used single step kinetics for the pyrolysis of cellulose. They identified a kinetic model for the three biomass components, and they used experimental data to calculate the activation energies from thermogravimetric (TG) measurements.

Lin et al. (2009) uses the same approach. They use TG to characterise the products, and calculate activation energies. Their research shows a single step kinetic mechanism for cellulose pyrolysis, and shows kinetic parameters for various temperature ranges and reaction conditions.

Lédé (2012) discusses the role of intermediate active cellulose and pointed out that despite the large number of publications in the field of cellulose pyrolysis there is no consensus according to the kinetics of cellulose pyrolysis.

After the pyrolysis step is completed, the next step is the gasification of the pyrolysis compounds and the reactions between the product gases. These reactions start without a catalyst, but the process can be significantly increased by adding a catalyst to the system. Lobo and Carabineiro (2016) summarise the kinetics and mechanisms for carbon gasification. Three major processes were considered, carbon dissolution, bulk diffusion and the surface reaction. The use of potassium ions was proved to have a synergic effect for the gasification of carbon. Kaushal and Tyagi (2017) use a model to calculate a larger number of reactions for the gasification of tar. They use a process simulator, and different types of models to calculate the gasification process. The gasification took place at 820 °C, and uses literature data for model validation. The results are in good agreement at different temperatures.

There are different modelling methods that can be used to build a detailed model for biomass pyrolysis and gasification. Most of the researches do not take into account the hydrodynamics, and use only TG measurements, or a simplified model (perfectly mixed reactors or plug flow reactors) to calculate the component balances inside a reactor. Simplified models can be used for preliminary design, and development processes, but have limited capability to describe systems with complex hydrodynamics. The other approach is the use of a CFD simulator and detailed hydrodynamics. Halama and Spliethoff (2015) use a detailed CFD simulator of an entrained gasifier implemented in ANSYS Fluent. They used Eulerian-Lagrangian method, and user defined functions which was implemented including all particle sub models

The third approach is the use of compartment models. These models use simplified models as building blocks. Compartment models can be used efficiently, even with multiple reactions, and complex hydrodynamics. The model parameters (volumes, distribution ratios) can be derived from the real system, or from CFD model (Egedy et al., 2016), or with the help of some identification algorithm (Egedy et al., 2012).

In our study, a mechanistic approach is used to model the pyrolysis gasification process using cellulose as feedstock. Kinetic parameters were identified for the pyrolysis and gasification reaction steps, while have a modifiable framework for further development. This paper shows the model building steps of a two-step pyrolysis-gasification reactor, and the identification of the kinetic parameters for the reactions of pyrolysis, and catalytic gasification. A compartment model was used for the calculation implemented in MATLAB environment.

2. Model description

A two stage pyrolysis/gasification system was modelled in this study. The schematic representation of the system is shown in Figure 1. The experimental procedures and results are discussed in detail in Zou et al. (2016). The geometry of the reactor and the parameters are shown in Figure 1(a) (800°C was the reaction temperature).

There are multiple reactions during pyrolysis and gasification. The first step of the pyrolysis is the hydrolysation of the cellulose into cellobiose, and the formation of glucose (Lin et al., 2009). The glucose formation was not calculated within this study. The biomass used in this study was cellulose, placed in the upper sample boat. There are two gas inlets; nitrogen is the inert gas and in this case not participating in any of the reactions. The role is more like to be as a carrier gas in this case. The other gas (water steam) is fed below the pyrolysis boat, so participates only in the reaction for the steam reforming. Figure 1(b) shows the structure of the compartment model, and the reactions that take place.
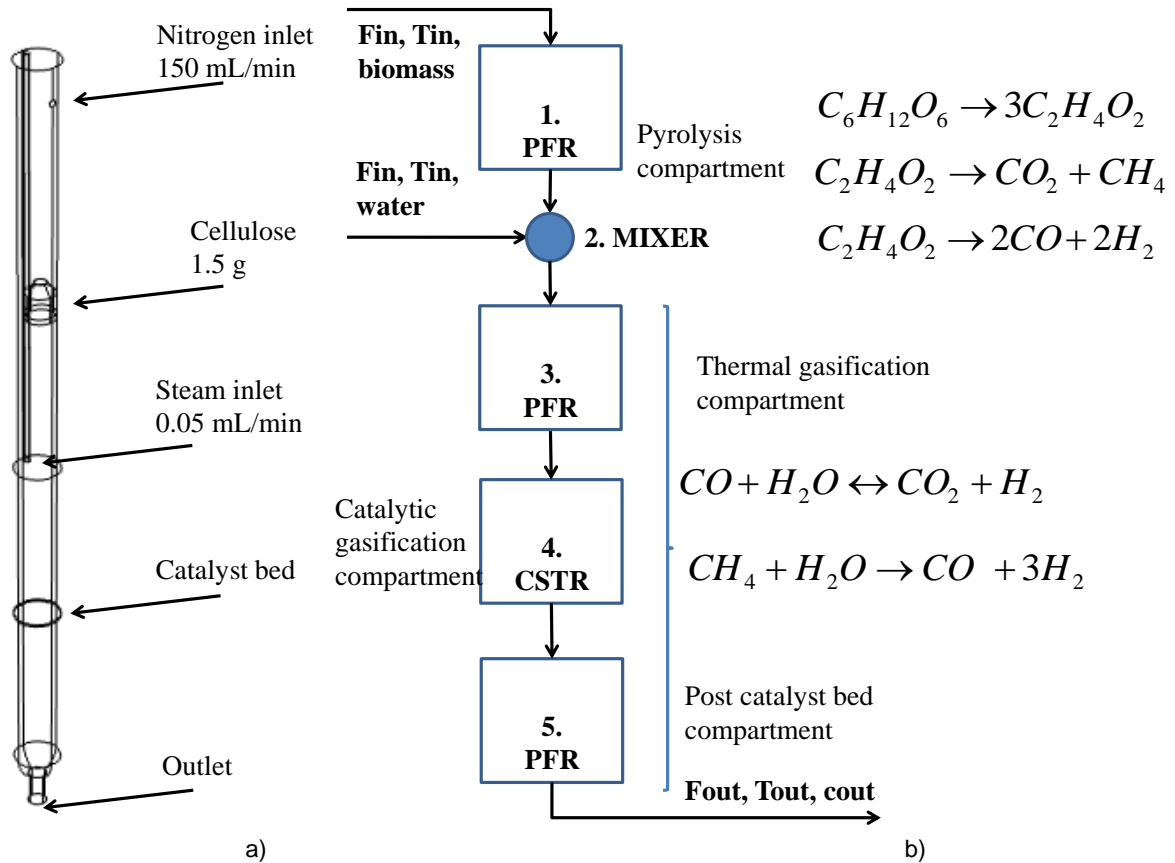
$$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$$

$$C_2H_4O_2 \rightarrow CO_2 + CH_4$$

$$C_2H_4O_2 \rightarrow 2CO + 2H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Figure 1: (a) The reactor, and the parameters (b) the proposed a compartment model

The first three reactions show the pyrolysis stage. The other two reactions show the reactions considered in the gasification stage. The physical system has multiple stages with different reactions. A compartment model containing five zones was proposed. The first compartment (Pyrolysis) facilitates the first three reactions, while the third (Thermal gasification) and fifth (Post catalyst bed) compartment, only thermal gasification took place. The three reactions were modelled as a plug flow reactor (PFR because the tube like geometry of the vessel. The second compartment is the mixer where the water inlet took place. The fourth compartment is the catalyst bed facilitating the catalytic gasification reactions.

The catalyst bed compartment (4. CSTR showed in Figure 1 b)) was modelled as a continuous stirred tank reactor (CSTR). In this model there are two inlets, and one outlet.

The PFR compartment was modelled as a consecutive cascade of 10 CSTR compartments. Based on the reactions took place the reaction rates for the pyrolysis and gasification are the following, Eq(1) - Eq(9). r_i are the reaction rates, k_i refers to the rate constants, while c_i are concentrations [mol/m^3], k_{0i} is the pre-exponential constant, while Ea_i R and T are the activation energy [J/mol], gas constant [J/mol/K], and temperature [K] respectively. f_l –s are the dimensionless multiplication factors for the catalyst bed. The rate constants are calculated as Arrhenius type equations Eq(10), except r_4-r_6, where the exponent does not contain the gas constant.

$$r_1 = k_1 \cdot c_{C6H12O6} \tag{1}$$

$$r_2 = k_2 \cdot c_{C2H4O2} \tag{2}$$

$$r_3 = k_3 \cdot c_{C6H10O6} \tag{3}$$

$$r_4 = k_4 \cdot c_{CO} \cdot c_{H2O} \tag{4}$$

$$r_5 = k_5 \cdot c_{CO2} \cdot c_{H2} \tag{5}$$

$$r_6 = k_6 \cdot c_{CH4} \cdot c_{H2O} \tag{6}$$

$$r_7 = f_1 k_4 \cdot c_{CO} \cdot c_{H2O} \tag{7}$$

$$r_8 = f_2 k_5 \cdot c_{CO2} \cdot c_{H2} \tag{8}$$

$$r_9 = f_3 k_6 \cdot c_{CH4} \cdot c_{H2O} \tag{9}$$

$$k_i = k_{0i} \cdot \exp\left(\frac{-Ea_i}{RT}\right) \tag{10}$$

And the source terms for each of the components are the following, Eq(11) – Eq(17). R_i refers to the component source terms for each component.

$$R_{C6H12O6} = -r_1 \tag{11}$$

$$R_{C2H4O2} = 3 * r_1 - r_2 - r_3 \tag{12}$$

$$R_{H2O} = -r_4 + r_5 - r_6 - r_7 + r_8 - r_9 \tag{13}$$

$$R_{CO2} = r_2 + r_4 - r_5 + r_7 - r_8 \tag{14}$$

$$R_{H2} = 2 * r_3 + r_4 - r_5 + 3 * r_6 + r_7 - r_8 + 3 * r_9 \tag{15}$$

$$R_{CO} = 2 * r_3 - r_4 + r_5 + r_6 - r_7 + r_8 + r_9 \tag{16}$$

$$R_{CH4} = r_2 - r_6 - r_9 \tag{17}$$

The first step was the definition of the boundaries for the model parameters, followed by the fine tuning of the parameters using Particle Swarm Optimisation (PSO). PSO algorithm is a computation technique which uses a fixed number of populations to calculate possible solutions with using different parameter sets. The initial parameters are defined using a uniform distribution of the parameters in each direction. The population in this algorithm are called swarm, and the candidate solutions are called particles. There is an objective function which should be minimised. The objective function in this study was defined as the minimum of the absolute difference between the measured and simulated gas yields, Eq(15). (1-4 is the four gas component, which concentrations were measured CO, H_2, CO_2, CH_4.).

$$\sum_{i=1}^{4} |n_{measured} - n_{simulated}| \tag{18}$$

The best solutions in each generation are carried out further, while the worst solutions are discarded in every generation. This makes sure the global optimum are found, however the time until reaching this optimum are strongly depend on the boundaries of the parameters defined. The simulation time was 40 min, and an Euler solver (fixed step 0.1 s) was used in MATLAB to solve the differential equations. The pre-exponential constants and activation energies were identified for the first three reactions, while literature values were applied for the thermal gasification (Yan et al., 2016). The catalytic reactions were modelled with a multiplication factor of the thermal gasification reactions.

3. Results and discussion

In this section the results of the simulation and model validation are shown. The first step was to determine the parameter boundaries for our system, to make the work of the optimisation algorithm easier. The algorithm will set initial values based on the boundaries, so shorter, and better parameters can be calculated if feasible initial conditions are set. The parameter intervals were calculated one-by one. The lower boundary was decided to be valid if it is a small and positive value (almost 100 conversion). The upper boundary was chosen where the conversion is almost 0, but a slight change from that boundary concludes a conversion change.

The pre-exponential constant interval for reaction 1 was calculated, leaving the other parameters constant (in the case of activation energy for reaction 1). All the other parameters were neglected. The cellulose conversion is almost 1, so a parameter which can lead to almost full conversion should be obtained. The pre-exponential constant interval for the first reaction found between 1 and 3 m^3/mol/s. In the next step a constant was used for this reaction, and the effect of the pre-exponential constant for reaction 2 and reaction 3 were examined. All the other reactions were ignored. The pre-exponential constants limits were found between 1 and 5.

Rate of reaction 4 and 5 was multiplied by 1/1,000 based on the preliminary investigation. These parameters were used for the thermal gasification steps. As It was mentioned before the catalytic gasification steps were calculated by using multiplication factors. 1 and 100 was used as boundaries for the multiplication factors. After the boundaries were calculated, the next step was the identification of the kinetic parameters. PSO was used for the calculation of the kinetic parameters.

Reaction parameters for reactions Eq(4) – Eq(6) were already known. In the next step, the multiplication factors interval for reactions Eq(7) – Eq(9) were calculated which are found as 99.689, 57.813 and 66.218. Then the simulated and the measured gas product yield were compared to each other.

Figure 2 shows the results, the differences between the measured and simulated values, and Table 1 shows the reaction parameters.

The absolute error is 3.1 which mean our simulated results are in a good agreement with the measured values, despite the higher differences in the case of CO and CH_4.
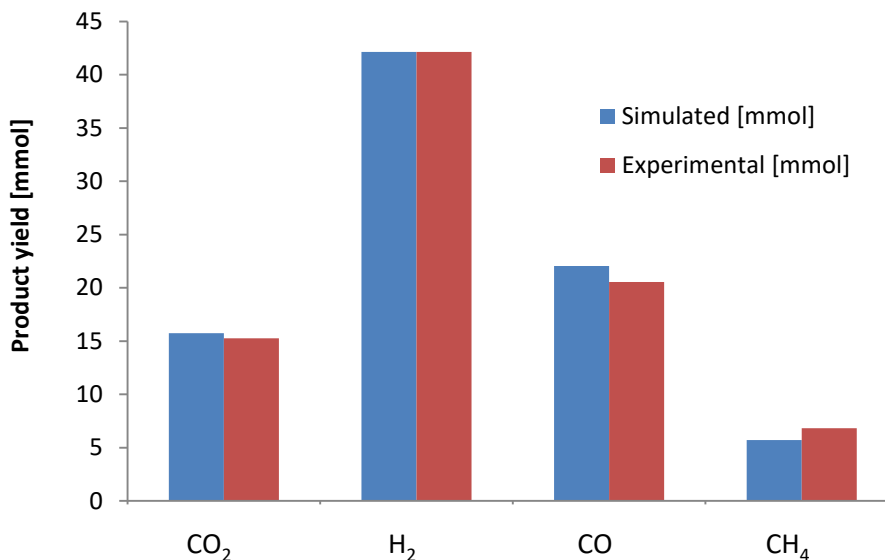

Figure 2. The comparison of the experimental and the simulated values

Table 1: Reaction parameters

Reaction	r1	r2	r3	r4	r5	r6	r7	r8	r9
Pre-exponential constant [varies]	1.3848	1.5175	1.4295	2.5e5	9.4e6	0.312	n/a	n/a	n/a
Activation energy [J/mol]	26,675	51,024	41,255	16,597	20,563	15,098	n/a	n/a	n/a
Multiplication factor [1]	n/a	n/a	n/a	n/a	n/a	n/a	99.689	57.813	66.218

The pre-exponential constant of reaction 1-3 is in almost the same magnitude, while the activation energy is higher (almost double) in the case of reaction 2, and 50% higher than reaction 1. The multiplication factors of reaction 7 is the highest of the three, which mean the catalyst gasification for reaction 7 (f_1) is a hundred times faster than in the thermal water-gas shift reaction of this system. The multiplication factor for reaction 8 (f_2) and 9 (f_3) is lower; however it is more than fifty times faster than the thermal gasification reactions. The reaction rate constant for reaction 7-9 is 3.88e6, 5.4e7 and 3.4 respectively, which means the backwards reaction rate for water gas shift is one magnitude larger than the forwards reaction, while reaction 9 is 7 magnitudes slower.

4. Conclusions

In this study the detailed model of a biomass pyrolysis/gasification reactor was created. Compartment modelling was used for the calculation of the hydrodynamic conditions of the reactor. In addition, kinetic parameters were identified for the reactions that took place. In the future the reaction scheme could be extended to facilitate more reactions, and reagents, and these modelling approaches could serve as a framework for further investigation with different catalysts, and feedstock. The measured and the simulated yields are in good agreement, and based on the comparison of the measured and the simulated values, the model was validated. In the next step the simulator can be used to perform more detailed studies, using different feed concentration, and different parameters. In the future this simulator can be used even to test different type of catalyst, and activities. With

the help of the simulator even scale-up studies can be calculated, and industrial scale systems can be optimised, which can lead to environmentally and economically feasible technologies.

Acknowledgments

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