A Mathematical Model For Pyrolysis Of Biomass

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Abstract—**Biomass is recently gaining popularity in industry as a promising source of renewable energy. Thermal conversion of biomass is recently gaining increased attention of researchers as a way of improving the efficiency of raw biomass fuel due to higher advantages it gives as compared to direct biomass combustion. These conversion methods are well studied using mathematical models and computer simulations based on them. The present paper focuses on developing a Pyrolysis model which will be sensitive to type of wood subjected to pyrolysis. In present approach, pyrolysis reaction is represented by a one-step global reaction. The stoichiometric coefficients of this reaction are assumed to be dependent on the type of wood species subjected to pyrolysis, thus making it possible to include the dependency on wood species to mathematical model. The stoichiometric coefficients are then determined using experimental data obtained from ultimate and proximate analysis of biomass. Computational Fluid Dynamic Simulations are then run for pyrolysis of *Gliricidia*, Coconut shells and Mango shells.**

Keywords—Pyrolysis; Mathematical mode; Global reaction scheme

I. INTRODUCTION

As fossil fuels are depleting, renewable energy sources are beginning to gain attention as possible ways of supplying world's energy demand. Biomass is one such energy source to produce renewable, green energy. There are three main ways of conversion of biomass i.e thermo-chemical, bio-chemical and extraction. There are three main ways of conversion of biomass thermo-chemically; i.e combustion, gasification and pyrolysis [1], [2]. The direct combustion of biomass has limited applications in process industry due to several drawbacks it introduces. One such problem is that direct combustion of biomass cannot produce high temperature flames required by certain applications and the versatility of biomass is also low. Because of these drawbacks, thermal conversion of biomass into secondary fuels is gaining attention. Syngas and bio oil are two widely used fuels derived using biomass. Syngas is produced by subjecting biomass to gasification process, in which biomass is partially combusted to produce a mixture of carbon monoxide and hydrogen [2]. Unlike raw biomass, this gas mixture can be combusted to produce high temperature flames. The production of Syngas is carried out in a special gasification reactor called a gasifier.

The design optimization of gasifiers is mainly done usingcomputer models. Many such approaches can be observed in literature [3]-[5].The simulation based approach minimizes the cost, time requirement and any potential risks that will be presentin actual experimental analysis.

The modeling of gasification process requires development of models to represent sub processes taking place in gasification process. Pyrolysis is one such important sub processes and is dependent on wood species. Several approaches are used to represent pyrolysis reaction. One step global reaction schemes, two stage schemes, competing parallel reactions schemes are among such approaches [3],[4],[6]. The present model introduces a global reaction scheme whose stoichiometric coefficients can be evaluated by experimental data, and this reaction scheme is included in a Computational fluid dynamics model of pyrolysis process. Such a species dependent model has the advantage of having capability to predict the effects of wood species on final efficiency of conversion process. Simulations are run to analyse the composition of product gases produced by three different raw materials. These are Mango pit, Coconut shell and *Gliricidia*. However the model can be applied to other biomass types as well provided the ultimate and proximate analysis data are available.

II. MATHEMATICAL MODEL

A. Governing Transport Equations

Biomass pyrolysis process of a packed bed consists of a multiphase system of solid and gas phases. The computational domain of the two phase system is shown in Fig. 1.
For modeling of such systems two approaches of mathematical models are used in the literature [3], [7]. These are;

1. Euler-Euler models

2. Euler - Lagrange models

In Euler-Euler models both phases are represented as continuums and gas flow through the packed bed is modeled as a flow through a porous media [8]. This approach is used in many CFD simulations of gasification and its sub processes [3]-[5], [8].

In Euler-Lagrange models the motion of individual particles are considered in approaches such as discrete element method and only the gas phase is modeled as a continuum with CFD.

The final model is expressed as a sum of individual contributions of each particle and their interaction with surrounding gas phase [7].

These models are more accurate in simulating packed beds. As a result they require expensive computing facilities and considerably longer times to simulate.

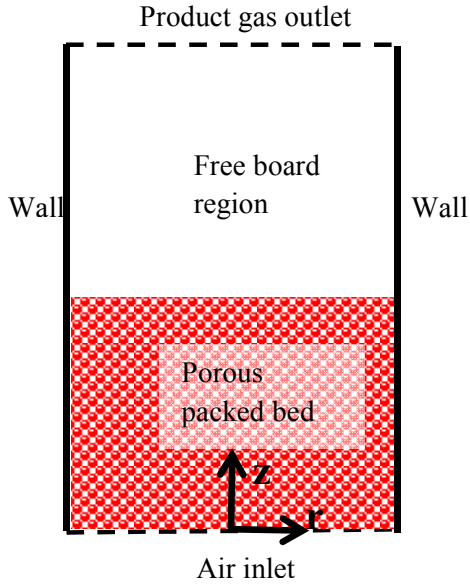As a result, the Euler-Euler approach is used by majority of researchers to simulate packed bed processes.

Fig. 1. Computational domain of the two phase packed bed.

The resulting transport equations for gas and solid phases are given in following equations.

Gas phase equations:

Energy conservation equation

$$\frac{\partial(\epsilon_g T_g)}{\partial t} + \nabla.(\epsilon_g U_g T_g) - \nabla.\left(\frac{\epsilon_g k_g}{\rho_g C_g}\nabla T_g\right) = hA_p(T_s - T_g) \qquad (1)$$

Where, subscript g represents the gas phase quantities and subscript s represents solid phase quantities. ε is the porosity, U – velocity, T – temperature, ρ – density, k – thermal conductivity, C – specific heat capacity, h – heat transfer coefficient, A_p specific surface area of porous bed.

Species conservation equations of product and inert gases

$$\frac{\partial(\epsilon_g \rho_g Y_i)}{\partial t} + \nabla.(\epsilon_g \rho_g U_g Y_i) - \nabla.(\epsilon_g \rho_g D_{g,i}\nabla Y_i) = a_i.r \qquad (2)$$

Where i = CO, CO_2, CH_4, H_2, N_2 and a_i is the respective stoichiometric coefficient of gas species as given in section II.B.

For N_2 a_i is taken as zero. Y – mass fraction, $D_{g,i}$-diffusion coefficient of ith species. r – reaction rate of pyrolysis reaction.

Solid phase equations:

In the present study, the packed bed is assumed to be fixed. Hence connective term is neglected when developing equations for solid phase.

Energy conservation equation

$$\frac{\partial(\epsilon_s T_s)}{\partial t} - \nabla.\left(\frac{\epsilon_s k_s}{\rho_s C_s}\nabla T_s\right) = -hA_p(T_s - T_g) \qquad (3)$$

Species conservation equations for solid products and reactants

$$\frac{\partial(\epsilon_s \rho_s Y_j)}{\partial t} - \nabla.(\epsilon_s \rho_s D_{s,j}\nabla Y_j) = -a_j r \qquad (4)$$

Where j = Wood, Char , Ash and a_j represents the respective stoichiometric coefficient of jth species in pyrolysis reaction. $D_{s,j}$ is the diffusion coefficient of jth solid component.

B. Global Reaction Model for Pyrolysis

In the present work, a global reaction scheme for pyrolysis is assumed. This is given in following equation.

$$Wood \rightarrow aC + bCO + cCO_2 + dH_2 + eCH_4 + fAsh \qquad (5)$$
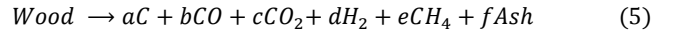
It is assumed that the stoichiometric coefficients are dependent on the species of wood. This gives the overall mathematical model the ability to analyze different wood species.

The coefficients are determined using experimental data obtained by proximate analysis and an assumed distribution of volatiles gases based on previous literature.

The coefficients for carbon and ash are directly determined by the fraction of free carbon and ash content given by proximate analysis. For gas species, each coefficient is determined by following equation.

$$a_i = \alpha(T_g)_i VF \qquad (6)$$

Where, a_i represents a, b, c etc for different values of i. The temperature dependent factor α describes the distribution of gases in the volatile fraction and VF is the volatile fraction of wood species under interest. For present study values for α is calculated using data given in [9].

The thermal conductivity of gas phase is calculated by [3]

$$k_g = 4.8 \times 10^{-4} T_g^{0.717} \qquad (7)$$

The thermal conductivity of biomass packed bed is evaluated using a correlation developed for thermal conductivity of a quiescent bed corrected for the effect of gas flow, as proposed in [10]. This correlation is presented in equation (8).

$$k_s = 0.8 k_g + 0.5 Re. Pr. k_g \qquad (8)$$

Where, Re and Pr represent Reynolds and Prandtl numbers respectively. Biomass particle diameter is used as the characteristic length in evaluating the Reynolds number.

Individual heat capacities of solid and gas species are not considered. An overall temperature dependent heat capacity for each phase is assumed. Heat capacity of solid and gas phases are assumed to vary according to the relations given in equations (9) and (10). These correlations are taken from [10].

$$C_s = 420 + 2.09 T_s + 6.85 \times 10^4 T_s^{-2} \qquad (9)$$

$$C_g = 990 + 0.122 T_g - 5680 \times 10^3 T_g^{-2} \qquad (10)$$

The porosity of bed is considered to be varying as Pyrolysis progresses. Porosity is expressed as a function of mass fractions of raw biomass, char and ash as indicated in equations (11) and (12)

$$\epsilon_s = \frac{mWood}{\rho_{wood}} + \frac{mChar}{\rho_{char}} + \frac{mAsh}{\rho_{ash}} \qquad (11)$$

$$\epsilon_g = 1 - \epsilon_s \qquad (12)$$

$mWood$, $mChar$ and $mAsh$ represent the mass of wood, char and Ash present in a unit volume.

Heat transfer coefficient h between solid and gas phase is evaluated using [11],

$$Nu = (0.35 + 0.34 Re^{0.5} + 0.15 Re^{0.58}) Pr^{0.3} \qquad (13)$$

Where, Nu is the Nusselt number.

It is assumed in the present model that biomass particles are spherical. The specific surface area of a biomass particle is calculated by equation (14) taken from [10],

$$A_p = \frac{\epsilon_s d}{6} \qquad (14)$$

Where, d is the diameter of biomass particle.

Diffusion coefficients are evaluated using equation (15) [12]. These are calculated as binary diffusion coefficients based on diffusion of a specific component in air.

$$D_{i,air} = 0.0018583 \sqrt{T_g^3 \left(\frac{1}{M_i} + \frac{1}{M_{air}} \right)} \frac{1}{p \sigma_{i,air}^2 \Omega_{i,air}} \qquad (15)$$

Where, M-molar mass, p – pressure, σ − average collision diameter, Ω - diffusion collision integral.

The gas phase is assumed to be incompressible. The incompressibility of gas phase is a common assumption among many packed bed gasification models.

Pyrolysis rate is evaluated using an Arrhenius reaction rate expression given by equation (16) [6].

$$r = \rho_s Y_{wood}. A exp \left(\frac{-E_p}{RT_s} \right) \qquad (16)$$

IV.EXPERIMENTAL SET UP

Methodology

Proximate analysis was performed on samples of three different wood species. *Gliricidia*, Coconut shells and mango shells. The samples are prepared in size range of 15 − 25 mm. Following steps are performed.

Determination of Ash

Samples were weighted accurately after moisture determination in crucibles. It is then introduced in muffle furnace the temperature of which was maintained at about 700 °C for 1 hour. It is then cooled in desiccator & weighted.

Determination of volatile matters

Samples were weighted accurately after moisture determination in crucibles. It is then introduced in muffle furnace the temperature of which was maintained at about 700 °C for 7 minutes. It is then cooled in desiccator & weighted. Crucibles were covered with lid.

Determination of fixed carbon

Fixed carbon amount is calculated by subtracting weight of ash from the weight of residue obtained after VM.

The results of analysis of wood samples are presented in table 1.

TABLE I. RESULTS OF PROXIMATE ANALYSIS

Wood Species	Proximate Analysis (dry basis percentage)		
	Free Carbon	Volatiles	Ash
Mango pit	22.6	77.3	0.1
Coconut Shells	14.1	85.83	0.07
Gliricidia	17.8	82.16	0.04

V. COMPUTATIONAL FLUID DYNAMIC SIMULATION

A. Computational domain and Numerical Solution

The open source CFD software OpenFOAM was used to develop a numerical solution to differential equations governing pyrolysis as presented in sections II and III. The equations are numerically solved using finite volume method. Convective terms are discretized using Gauss Upwind scheme. The computational domain of solution is presented in figure 1.The pressure velocity coupling was handled using the PISO (pressure implicit with splitting of operator) algorithm. The overall solution procedure of the transport equations is presented in figure 2.

B. Initial and Boundary conditions

It is assumed that the pyrolysis process is carried out in a cylindrical reactor using an oxygen free external hot gas stream of constant temperature. This gas stream is supplied at constant flow rate from bottom of the reactor. The solution domain is two dimensional and consists of radial and axial dimensions only. This is because the reactor is axisymmetric in geometry, initial and boundary fields and as a result the solution is effectively two dimensional.

The initial velocity field within the reactor is taken as zero. Pressure is set to atmospheric pressure. The initial temperatures of gas and solid phases are taken as 300 K. Initial compositions of product gases are taken as zero. And inert gas is assumed to be oxygen free and consists of carbon dioxide and Nitrogen. Boundary conditions for velocity, pressure, temperature and species mole fractions are indicated in following equations.

Inlet boundary conditions

$$U = U_{in} \ , P = P_{in} \ , \ T_g = T_{g,in} \ , \ T_s = 300 \, K \ , \ Y_i = Y_{i,in}$$

Wall boundary conditions

$$U = 0 \quad , \quad \frac{\partial P}{\partial r} = 0 \quad , \quad \frac{\partial T_g}{\partial r} = 0 \quad , \quad \frac{\partial T_s}{\partial r} = 0 \quad , \quad \frac{\partial Y_i}{\partial r} = 0$$

Outlet boundary conditions

$$\frac{\partial U}{\partial z} = 0 \ , \quad \frac{\partial P}{\partial z} = 0 \quad , \quad \frac{\partial T_g}{\partial z} = 0 \quad , \quad \frac{\partial T_s}{\partial z} = 0 \ , \quad \frac{\partial Y_i}{\partial z} = 0$$
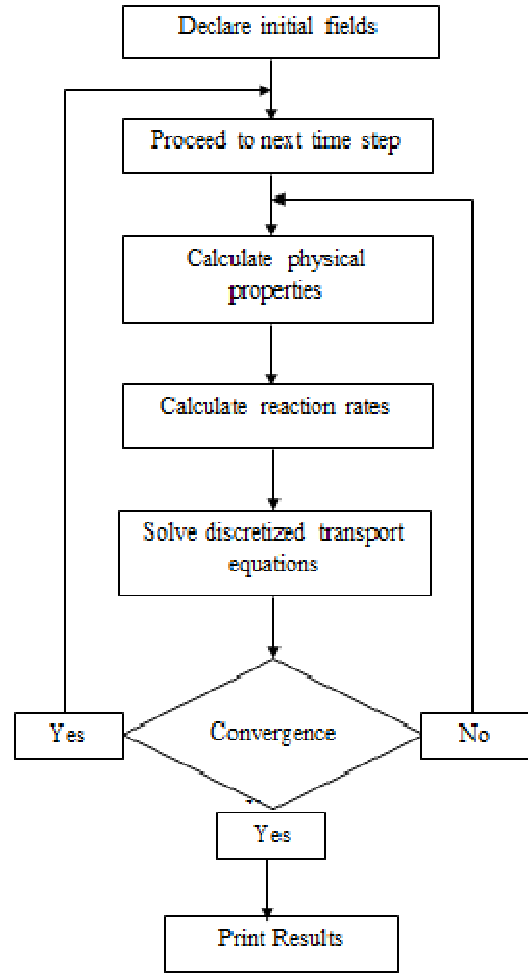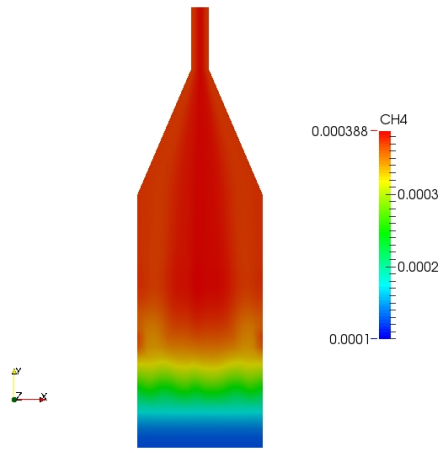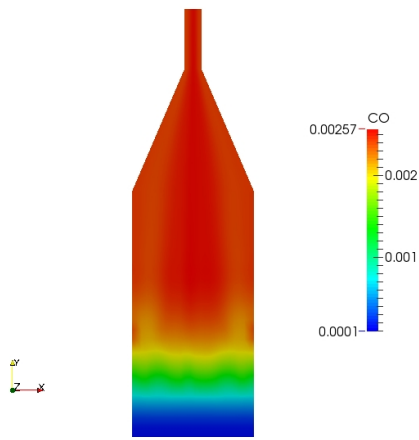

Fig. 2. Iterative solution algorithm
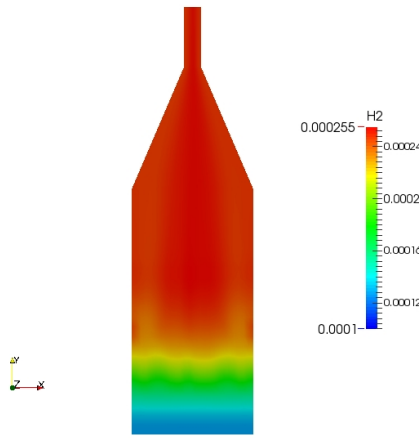
VI. SIMULATION RESULTS

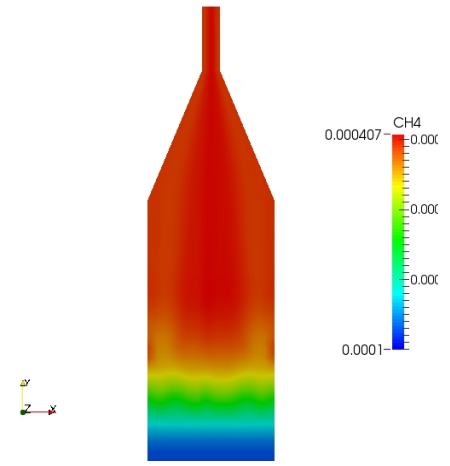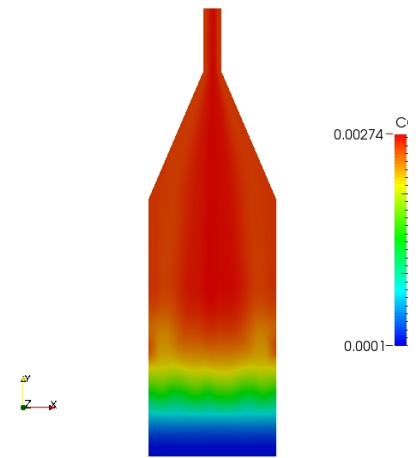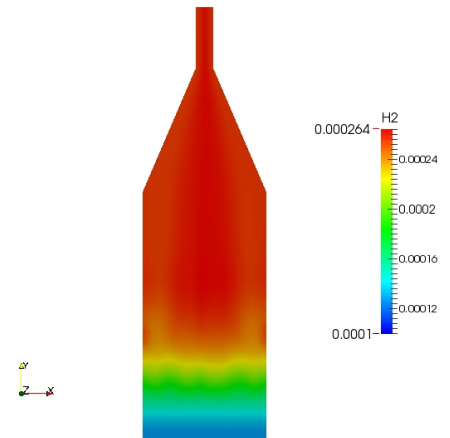The distributions of mass fractions are indicated in following figures.

Fig. 3. Pyrolysis of Mango pit using an oxygen free gas stream at 614 K. Bed dimensions: diameter 0.5m height 0.6 m. Inlet gas velocity 0.3 m/s. Simulation time 9000 s. (a) CH_4 mass fraction (b) CO mass fraction (c) H_2 mass fraction.

Fig. 4. Pyrolysis of Gliricidia using an oxygen free gas stream at 614 K. Bed dimensions: diameter 0.5m height 0.6 m. Inlet gas velocity 0.3 m/s. Simulation time 9000 s. (a) CH_4 mass fraction (b) CO mass fraction (c) H_2 mass fraction.
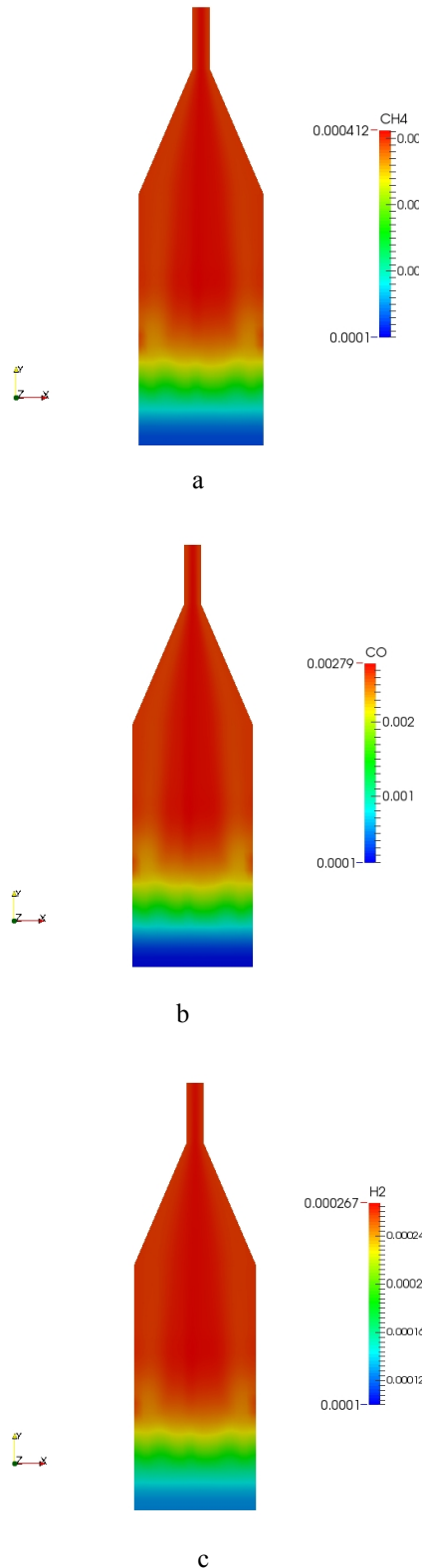
Fig. 5. Pyrolysis of Coconut shells using an oxygen free gas stream at 614 K. Bed dimensions: diameter 0.5m height 0.6 m. Inlet gas velocity 0.3 m/s. Simulation time 9000 s. (a) CH_4 mass fraction (b) CO mass fraction (c) H_2 mass fraction.

VII. CONCLUSION

A computational fluid dynamic model of a packed bed pyrolysis process is developed. Pyrolysis reaction is represented by a one-step global reaction. The stoichiometric coefficients of the reaction are assumed to be dependent on the wood species subjected to pyrolysis. The coefficients are determined by experimental data found by proximate analysis of three wood species. Coconut shells, mango pits and *Gliricidia*. Based on the simulation results it can be observed that emission characteristics of all wood species are almost same. Similar behavior of different biomass types can be observed in other research work as well [13], [14].

VIII. AKNOWLEGDMENT

IX. REFERENCES

[1] P. McKendry, "Energy production from biomass (part 2): conversion technologies," *Bioresour. Technol.*, vol. 83, no. 1, pp. 47–54, May 2002.

[2] P. McKendry, "Energy production from biomass (part 3): gasification technologies," *Bioresour. Technol.*, vol. 83, no. 1, pp. 55–63, May 2002.

[3] M. A. Masmoudi, M. Sahraoui, N. Grioui, and K. Halouani, "2-D Modeling of thermo-kinetics coupled with heat and mass transfer in the reduction zone of a fixed bed downdraft biomass gasifier," *Renew. Energy*, vol. 66, pp. 288–298, Jun. 2014.

[4] K. Umeki, T. Namioka, and K. Yoshikawa, "Analysis of an updraft biomass gasifier with high temperature steam using a numerical model," *Appl. Energy*, vol. 90, no. 1, pp. 38–45, Feb. 2012.

[5] C. Mandl, I. Obernberger, and F. Biedermann, "Modelling of an updraft fixed-bed gasifier operated with softwood pellets," *Fuel*, vol. 89, no. 12, pp. 3795–3806, Dec. 2010.

[6] S. Sinha, A. Jhalani, M. R. Ravi, and A. Ray, "Modelling of pyrolysis in wood: A review," *SESI J.*, vol. 10, no. 1, pp. 41–62, 2000.

[7] A. H. Mahmoudi, F. Hoffmann, and B. Peters, "Application of XDEM as a novel approach to predict drying of a packed bed," *Int. J. Therm. Sci.*, vol. 75, pp. 65–75, Jan. 2014.

[8] Y. Wu, Q. Zhang, W. Yang, and W. Blasiak, "Two-Dimensional Computational Fluid Dynamics Simulation of Biomass Gasification in a Downdraft Fixed-Bed Gasifier with Highly Preheated Air and Steam," *Energy Fuels*, vol. 27, no. 6, pp. 3274–3282, 2013.

[9] P. J. Ż. Kamil Kwiatkowski, "Biomass gasification solver based on OpenFOAM," 2013.

[10] Tomas Jurena, "Numerical modelling of grate combustion," Brno University of Technology, Brno, 2012.

[11] *Mass-Transfer Operations, 3rd Edition 3rd (third) edition by Treybal, Robert E. published by McGraw-Hill Book Company (1980) Hardcover*. McGraw-Hill Book Company, 1000.

[12] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena, 2nd Edition*, 2 edition. New York: Wiley, 2001.

[13] S. Fournel, B. Marcos, S. Godbout, and M. Heitz, "Predicting gaseous emissions from small-scale combustion of agricultural biomass fuels," *Bioresour. Technol.*, vol. 179, pp. 165–172, Mar. 2015.

[14] H. Sefidari, N. Razmjoo, and M. Strand, "An experimental study of combustion and emissions of two types of woody biomass in a 12-MW reciprocating-grate boiler," *Fuel*, vol. 135, pp. 120–129, Nov. 2014.