Pyrolysis and gasification of single biomass particle - new openFoam solver

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Abstract. We present a new solver \textit{biomassGasificationFoam} that extended the functionalities of the well-supported open-source CFD code OpenFOAM. The main goal of this development is to provide a comprehensive computational environment for a wide range of applications involving reacting gases and solids. The \textit{biomassGasificationFoam} is an integrated solver capable of modelling thermal conversion, including evaporation, pyrolysis, gasification, and combustion, of various solid materials.

In the paper we show that the gas is hotter than the solid except at the centre of the sample, where the temperature of the solid is higher. This effect is expected because the thermal conductivity of the porous matrix of the solid phase is higher than the thermal conductivity of the gases. This effect, which cannot be considered if thermal equilibrium between the gas and solid is assumed, leads to precise description of heat transfer into wood particles.

1. Introduction

The complex nature of gasification, wide range of available feedstocks together with an extensive process parameter space, and various types of reactors and possible reaction paths impede the development of a comprehensive and rigorous description of the process from a numerical perspective.

The process of biomass gasification and its subprocesses are well fitted in the fields that may be simulated within the Computational Fluid Dynamics (CFD) framework, and particularly with open-source CFD code OpenFOAM \cite{1}. The solvers embedded in the standard OpenFOAM distributions for modelling pyrolysis (\textit{fireFoam}) and chemical reactions (\textit{reactingFoam}) or gasification in fluidised bed (\textit{coalChemistryFoam}) are not suitable for modelling gasification of thick biomass particles. Currently available approaches do not consider the mutual influence of the reacting flow and gasified solid and volumetric reactions within porous material.

In this work, we present the new solver \textit{biomassGasificationFoam} and the complementary library \textit{biomassGasificationMedia} \cite{2} developed to simulate a wide range of processes and applications related to the gasification of thin and thick biomass particle and, after further development, to simulate fixed bed gasification.
In this code, we implemented the following:
- volumetric reactions within porous material,
- homogeneous and heterogeneous reactions with the heat of reaction defined directly or derived from enthalpies of formations,
- a flexible definition of biomass and its thermochemical properties,
- customisable kinetic mechanisms of pyrolysis and gasification,
- heat and mass transfer between gases and solids around and within porous medium,
- transient flow within and around porous medium,
- separate energy equations for gas and solid phases for thermal non-equilibrium effects.

2. biomass Gasification Foam solver
2.1. Mathematical model
In figure 1, we present typical considered processes when one or more biomass fragments is pyrolysing or gasifying surrounded by inert or reactive gases. The gas phase is composed of a mixture of gases with different origins: gas that initially filled the reactor, gas supplied to the process, water vapour evaporated while the biomass is drying, and gases produced during thermal conversion of the solid. The potential liquid phase (water and liquid hydrocarbons) is considered vapour. This assumption is well satisfied for most of the considered processes.

The other assumptions are as follows:
- In current implementation the movement of porous medium is neglected.
- The moisture is embedded within this porous structure. Moisture released from the solid evaporates immediately.
- Gas flows according to Darcy’s Law inside the porous medium.
- Radiative transfer from domain walls to solid surfaces is available.
- Chemical reaction and thermal processes may lead to thermal non-equilibrium.
- The porous medium loses mass via homogeneous and heterogeneous processes.
- The volume fraction of the gas phase $\gamma$ is determined for the entire domain as $\gamma = \frac{V - V^S}{V}$ ($\gamma = 0$ when only the solid phase is present and as $\gamma = 1$ if there is no solid).
The three-dimensional, time-dependent mathematical model of the thermal conversion of biomass is based on conservation laws that are determined for both gaseous and solid phases. The solid is an isotropic or anisotropic porous medium with a porosity \( \gamma \), which may change slowly during thermal conversion.

The governing equations for the gaseous phase are as follows: momentum conservation, continuity, species conservation, and energy conservation. The set of species typically involves water vapour, \( CO \), \( CO_2 \), \( O_2 \), \( N_2 \), and \( CH_4 \). The solid-phase equations involve conservation of solid components and the energy conservation equation. Details of the governing equations are presented in [3] and [2].

2.2. Volumetric reactions
To allow the volumetric implementation of thermal processes, we propose to introduce porous medium inside the main computational domain as a volumetric porous field, as shown in figure 1. In the current approach the equations inside and outside the porous medium are the same and the boundary has no extra dynamics of its own.

The boundary of the porous material is the surface where the physical parameters present in those equations are discontinuous. In the momentum equation, for example, both the d’Arcy term and the usual viscous term of a Newtonian fluid, as in the Navier-Stokes equation, are formally present on both sides, but the associated coefficients have a jump across the interface.

2.3. Heat transfer
The thermal equilibrium between a gas and solid vanishes when chemical reactions or thermal conversions take place [4]. Our first analysis confirmed that during the thermal conversion of a single thermally thick wood particle, the gases (both outside and inside the particle) are not in equilibrium with the solid [5] and separate energy equations for the gas and solid are required.

The early analysis performed by [6] and repeated recently by [7] suggested that within the microscopic pores of single wood particles, the gases and solid are in thermal equilibrium. Investigations into the miniaturisation of heat exchangers independently led to the same conclusion: the assumption of thermal equilibrium is reasonable for micrometre-sized pores. In such case, the temperatures of the gas (in the pores) and solid phases are always equal and only one energy equation has to be solved within the computational domain. This assumption is common in the numerical modelling of pyrolysis and gasification. However, the above-mentioned analysis did not consider energy fluxes due to chemical reactions.

The withdrawal of the assumption of thermal equilibrium requires that energy transfer between the gas and solid is considered within the entire porous medium according to the source term.

\[
\alpha \Sigma (T^G - T^S)
\]

where: \( \alpha \) - heat transfer coefficient (per surface), \( \Sigma \) - total surface area of pores per solid state volume.

2.4. Implementation
The new set of libraries that we implemented introduces thermal, chemical, and radiation properties of such defined porous field and determines their interactions with the gas phase flowing through and around these fields. Essentially, the libraries handle biomass as a collection of additional scalar and tensor fields within the computational domain, e.g., the mass fraction of cellulose, the thermal conductivity of the porous medium, and the absolute density.

The \textit{biomassGasificationFoam} solver is based on the algorithm used in the unsteady solver \textit{reactingFoam} for reacting flows available in the OpenFOAM standard distribution.
A schematic illustration of the main PIMPLE loop of the *biomassGasificationFoam* solver is provided in figure 2. The main loop contains two inner corrections for solving the pressure-momentum coupling influenced by energy and species distributions. The mass conservation equation is solved and the source terms calculated once per each main loop term.

![Figure 2. Scheme of the main loop of the *biomassGasificationFoam* solver based on the PIMPLE algorithm. New development in the solver is in bold.](image)

The model of the thermal conversion of biomass, as presented in figure 3, is constructed from three main elements:

- the definition of a porous medium and its mechanical properties - *porousReactingMedia* library, with the *setPorosity* utility;
- definitions of thermal, chemical, and radiation properties of solids - *thermophysicalModels* libraries;
- class linking the above libraries to the biomass gasification model - *pyrolysisModels*.

3. Validation and results

TGA, through a detailed measurement of mass loss, quantifies the thermal decomposition of wood under well-controlled conditions. The experiment was performed using the Q500 (TA Instrument, New Castle, Delaware, US) thermogravimeter with an initial temperature of 300 K and a constant heating rate of 10 K/min. The experiment was carried out until the temperature reached 1,300 K. Because we provided a nitrogen environment, only the processes of drying and pyrolysis took place. The heating protocol and process environment were introduced through the initial and boundary conditions, which are summarised in table 1.

The solver was validated with the case of pyrolysis of a preprocessed isotropic wood sample with an initial mass of 24 mg. The test calculations were performed with simplified geometry...
Figure 3. Structure of the developed code: the solver and collection of libraries.

Table 1. Initial and boundary conditions used in the simulations.

|                     | Initial condition | Boundary condition walls | outlet |
|---------------------|-------------------|--------------------------|--------|
| Inert species       | nitrogen          | nitrogen                 | -      |
| Temperature         | 300 K             | 300 K + 10 \cdot t K/min| 300 K + 10 \cdot t K/min |
| Velocity            | 0 m/s             | 0.3 m/s                  | 0 m/s  |
| Pressure            | 101300 Pa         | 101300 Pa                | -      |

for the TGA reactor and sample, both of which are modelled as cubes (figure 4). The edge of the reactor is 12 mm. The entire computational domain was composed of 20 x 20 x 20 cells. The porous zone was distributed over 10 x 10 x 10 cells.

Figure 4. A simplified TGA reactor with cubic geometry and a hexagonal wood sample placed in the centre. In a diagonal plane cross-section of the sample, five points are marked (centre (C), top (T), bottom (B), top-corner (TC), and bottom-corner (BC)) in order to probe results.

In this paper, we use the mechanism of wood biomass pyrolysis, where cellulose, hemicellulose,
and lignin decompose into a set of gases: $H_2$, $CO$, $CO_2$, and $CH_4$ [8]. The heat of pyrolysis was determined from enthalpies of formation of substrates and products. The parameters of kinetics are summarised in table 2.

| Table 2. Pyrolysis parameters and kinetics constants used in the simulation. |
|-----------------|-------------|-------------|-------------|-------------|
| Moisture        | Cellulose   | Hemicellulose | Lignin      | Ref.        |
| Initial mass fraction [kg/kg] | 0.07 | 0.359 | 0.276 | 0.285 | [8] |
| Pre-exponential factor [1/s]    | $1.4 \cdot 10^{14}$ | $2.1 \cdot 10^{7}$ | $5.8 \cdot 10^{13}$ | $1.06 \cdot 10^{3}$ |
| Activation energy [J/mol]       | $1.35 \cdot 10^{4}$ | $1.34 \cdot 10^{4}$ | $1.94 \cdot 10^{4}$ | $8.95 \cdot 10^{3}$ |
| Minimum temperature [K]         | 300 | 450 | 400 | 500 |
| Enthalpy of formation [J/kg]    | $-15.9 \cdot 10^{6}$ | $-1.0 \cdot 10^{6}$ | $-8.5 \cdot 10^{5}$ | $-9.2 \cdot 10^{5}$ | [9] |

The experimentally determined material properties of wood are typically 'effective', combining the effects of gas and solid phases. Such properties depend strongly on the origin of the wood, the structure of the porosity, and the selected experimental procedures. In the solver presented here, we have introduced separate equations for the solid state that requires parameters for a 'pure solid'. A good example of such a material property is thermal conductivity. Measured effective values vary from 0.1 to 1 W/m/K, but the thermal conductivity of a solid is an order of magnitude higher, approximately 10 W/m/K. The set of material properties are presented in table 3.

| Table 3. Physical and material properties of lignocellulose material used in the simulation. |
|-----------------|-------------|-------------|-------------|
| Moisture        | Wood components | Char       | Ash         | Ref.        |
| Absolute density [kg/m$^3$] | 1000 | 1480 | 1957 | 2500 | [10] |
| Initial void fraction [-] | — | 0.55 | 0.91 | - | [11] |
| Initial pore diameter [m] | — | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-4}$ | - | [12] |
| Permeability [m$^2$] | — | $1 \cdot 10^{-14}$ | $1 \cdot 10^{-11}$ | - | [7] |
| Thermal conductivity [W/m/K] | 0.58 | 0.20 | 0.1$^a$ | 0.17 | [10] |
| Heat capacity [J/kg/K] | 4200 | 1380 | 1100 | 840 | [10] |

The comparison of mass loss during evaporation and pyrolysis in the TGA experiment and the corresponding simulation is presented in figure 5. The results are in qualitative agreement, but discrepancies are visible. The main reasons for these discrepancies are the imperfect, oversimplified kinetics of pyrolysis and the variability of wood composition, that cannot be exactly determined.

The subsequent peaks of the inverse of the mass loss rate presented in figure 6 correspond to the processes of evaporation and pyrolysis of hemicellulose, cellulose, and lignin, respectively. All processes stop at approximately 800 K, when only char remains. In reality, as it is shown in figure 5, a small amount of char is still volatilising at higher temperatures. This effect is not included in the selected pyrolysis kinetics. The mass loss rates shown in figure 6 are plotted for five different locations within the wood sample, as we marked in figure 4. The rates of mass loss at the bottom, centre, and top are similar. Only the rates at the corners (top and bottom) are slightly distinguished.

Figure 7 illustrates how the densities (mass) of solid components, embedded moisture, hemicellulose, cellulose, and lignin are decreasing while the density (mass) of char is increasing.
Reproducing this well-known sequence of decomposition is possible with separate kinetics constants for individual solid components, which is straightforward in the presented solver.

Figure 8 presents the composition of the produced gases. Because the process takes place in a reactor filled with nitrogen, the presented values are relative. However, the solver with the selected kinetics adequately reproduces the composition of gases and the peaks of the processes.

Figure 9 illustrates the increase in the temperature of the gas phase at five selected points inside the wood: the centre, the bottom, the top, the bottom-corner, and the top-corner. The differences between points are now small. This result corresponds well with the expectation that temperature gradients should be negligible in such a small sample [13]. The included thermal processes are endothermic and, as noted in figure 9, the gas temperature decreases slightly when these processes occur. As expected, this decrease is most pronounced in the centre of the sample.

In figure 10, we present the difference between the gas- and solid-phase temperatures, plotted for the same points. First, we can see that the temperatures of the gas and solid are close, which is expected for such a small sample. As expected, this difference is negligible when no reaction takes place but increases when thermal processes are present. The subsequent peaks visible in figure 10 are due to the evaporation and pyrolysis of the solid components.

In general, the gas is hotter than the solid except at the centre of the sample (black line in figure 10), where the temperature of the solid is higher. This effect is expected because
the thermal conductivity of the porous matrix of the solid phase is higher than the thermal conductivity of the gases. This effect cannot be considered if thermal equilibrium between the gas and solid is assumed.

Figure 9. Temperature of gas phase.

Figure 10. Difference between the temperature of the gas and solid.

4. Conclusion
As demonstrated here, the developed model, with simplified kinetics, reproduces the experimental results of the TGA experiment with an acceptable degree of uncertainty. Moreover, the solver reproduces several expected effects that are difficult for direct measurement and comparison.

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