ACCURACY AND POTENTIAL USE OF A DEVELOPED CFD-PYROLYSIS MODEL USED FOR SIMULATING LAB-SCALE BIO OIL PRODUCTION

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ABSTRACT: The paper describes development of a CFD-pyrolysis model using an Eularian-Eularian framework with an implemented pyrolysis reaction model. The CFD-pyrolysis model is used to simulate the bubbling fluidized bed reactor integrated in a new experimental fast pyrolysis process for bio oil production. The model is compared to experiments in aspect of outlet gas composition, temperature and bed height. Tar behavior and yield of bio oil are illustrated and a parametric study investigates impact of flow rate and temperature on bio oil yield. The results show a tolerable fit compared to measurements and reasonable tendencies in the parametric study.

Keywords: Fast pyrolysis, pyrolysis oil, fluidized bed, modeling.

1 INTRODUCTION

Awareness on consequences of fossil fuel use, opt for a change in fuel types. Evidence of climate change and rising social conflicts due the diminishing availability gives strength to this cause. In democratic countries, public opinion reflects the awareness and gives politicians mandate to impose regulations in favor of renewable fuel types.

The renewable fuel types will naturally inherit the applications of the fossil counterparts. Apart from the sheer volume of fuel needed; one important challenge for renewable fuel types are the properties which will differ by feedstock, refining method, and country of origin. Fossil fuels are indeed much more homogenous throughout the world compared to the existing renewable fuel types. This puts focus on refining methods, as the key for achieving consistent properties and generic solutions.

2 BACKGROUND

2.1 Bio oil

Bio oil is a term describing the thick brown liquid formed during fast pyrolysis and subsequent condensation of the pyrolysis vapors. The bio oil consists of condensable compounds referred to as Tars and also water. Corrosiveness, chemical instability and a low heating value per unit weight have troubled this fuel for quite some time.

However, some applications of bio oil have become reality in recent years. Some chemical compounds are cost-efficiently produced in this process, for example benzoic acid. Boilers fueled with bio oil exist, though in quite limited numbers.

The opportunities of bio oil is disputed, however no one can deny such advantages as the CO$_2$ reduction potential and aggregate form which permits efficient transportation.

2.2 Pyrolysis kinetics

Kinetic modeling and understanding of the pyrolysis process is challenging but nevertheless useful when developing technology for combustion, gasification and pyrolysis. The comprehensive models that emerged throughout recent years are covered by Di Blasi [1].

2.3 CFD modeling

Computational Fluid Dynamics (CFD) has developed rapidly along the availability of computational resources.

The integration of different sub-models with a CFD model have proven to be a powerful resource in analyzing chemical processes, most notably larger scale plants like boilers and furnaces.

3 PURPOSE

The purpose of this publication is two-fold. Most notably is the matter of almost non-existing verification and validation of comparable CFD-pyrolysis models (high-lighted by [2], for example). This has raised questions about the predictability of such models. This publication aims to contribute in this area by evaluating the accuracy of a newly developed CFD-pyrolysis model.

Secondly the potential use of such models is not discussed as much as it should. Indeed many aspects of a process could be simulated with aid of such models; however the reliability of the results is not always clear.

4 METHOD

4.1 Experimental setup

The system as a flow chart is shown in Fig. 1. The developed model only simulates the bubbling fluidized bed (BFB) reactor, which is located leftmost in the figure and constitutes the first stage in the process.

The condensable compounds are separated from the gaseous species in a scrubber. Prior to that, a cyclone removes any entrained sand and char particles.

Figure 1: Process flow diagram of experimental setup
The fluidizing agent is $\text{N}_2$, with an inflow rate 0.25 m/s which is equivalent to $4.146 \times 10^4 \text{Nm}^3/\text{s}$.

Heating elements, reaching up 65 cm from the distributor plate heat the walls. A temperature set point is maintained and an integrated system monitors temperature readings from thermocouples (TC) inserted below inlet, 5 cm, 25 cm, 45 cm, 65 cm and 85 cm above the distributor plate. The TCs were placed as close as possible to the centerline in the horizontal direction, i.e. at distance of 3.6 cm from the wall.

The biomass is a mix of pine and spruce with an assumed component weight-percentage of 43% cellulose, 29.4% hemi-cellulose and 27.6% lignin (data from Demirbas [3] for Spruce). The moisture content of the wood is an assumed number of 7% by weight. Particle size of the wood is roughly 600 µm.

In molecular terms, wood is assumed to be equivalent to $\text{CH}_2\text{O}_{0.6}$, with a subsequent molar weight of 23 kg/kmol.

4.2 Model development

The commercial code of ANSYS Fluent v. 13.1 is utilized in the development and running of the 3D CFD pyrolysis model.

A transient solution is preferred since steady-state simulations do not represent a fluidized bed very well.

User defined functions (UDF) is developed for describing the rate of reactions, as well as the wall boundary conditions and drag force between solid granules and gas.

The mesh is constructed with aid of ICEM CFD v.13.0. The cylindrical domain is composed of 64640 hexagonal cells and 58968 nodes. The fitting of a quadratic mesh to a circular horizontal cross-section is achieved by constructing an o-grid.

The computation resources supplied by the Swedish National Infrastructure for Computing were utilized for longer computations

4.3 Fluid dynamics

An Eularian-Eularian multiphase framework was utilized in order to describe the fluid motion and distinguish the fluid and the granular phases. The granular phase was defined as a mixture of chemical components, one being the sand initially in place. The other components are absorbed moisture, volatiles and char.

For taking into account the turbulence, the standard $k$-$\varepsilon$ model is applied to the fluid phase.

For accurate simulation of the bubbling fluidization, the drag force between particle and fluid had to be estimated.

For this purpose, the Syamlal O’Brien drag law [4] was implemented. It is customized according to the procedure explained by [4]. For the ease considered in this paper, the constants referred to as $C_1$ and $C_2$ are found to be 5.386778 and 0.513026, given a minimum fluidization of 0.08 m/s and an estimated void fraction of 0.5 at minimum fluidization. Nearly the same procedure is described by [5]; however the constants are instead referred to as $Q$ and $P$ respectively.

The bed height when fluidized is one parameter that is directly tied to the drag force between particle and fluid; as such it is important to determine.
4.4 Reactions

The reactions defined in the model correspond to the pyrolysis model defined by Miller and Bellan [6]. The chemical pathways are shown in Fig. 4.

An advantage of this pyrolysis model is that the elemental balance of the already ill-defined lumped reactions can be fairly closed. In fact, this model among similar models (compiled and discussed by Di Blasi [1]) is more based on the aggregate state of the end product, than the chemical components themselves.

Figure 4: Reaction pathways for pyrolysis sub-model.

Previous researchers (e.g. Xue et al [7]), modeling pyrolysis mechanisms in fluidized beds, have considered GAS (shown in Fig. 4) as a lumped uniform specie. However, in this work the composition of the named GAS has been estimated with aid of data from Boroson [8]. So has the char yield (X in Fig. 4), which in this case have been recalculated based on the assumed weight percentages of cellulose (43 %), hemi-cellulose (29.4 %), lignin (27.6 %) and the respective char yields for each component given by Miller and Bellan [10], i.e. $X_{\text{Cellulose}} = 0.35$, $X_{\text{Hemicellulose}} = 0.60$ and $X_{\text{Lignin}} = 0.75$.

Furthermore, the reactions; originally three for each component and pyrolysis reaction step (except R4), has been lumped together in order to decrease computation time and constraints on the system. The end result with stoichiometric coefficients is given by Fig. 5.

- R1: Vol $\rightarrow$ Vol$_A$
- R2: Vol$_A$ $\rightarrow$ 0.882 Char + 0.046 CO + 0.062 CO$_2$ + 0.01 CH$_4$ + 0.364 H$_2$ + 0.526 C$_2$H$_4$
- R3: Vol$_A$ $\rightarrow$ 0.16 Tar
- R4: Tar $\rightarrow$ 0.233 C$_6$H$_6$ + 2.69 CO + 0.397 CO$_2$ + 0.869 CH$_4$ + 2.223 H$_2$ + 0.526 C$_2$H$_4$
- R5: H$_2$O(l) $\rightarrow$ H$_2$O(g)

Figure 5: Reactions with stoichiometric coefficients.

The standard state enthalpy of Vol, Vol$_A$, Tar and C$_6$H$_6$ (light tar) were fitted in order to correspond with measured heat of reaction found by Rath et al [9] (for R2 and R3) and Di Blasi [1] (for R4). Standard state enthalpy for all other species was collected from [10].

The rates of the lumped reactions has been averaged based on the weight percentages of the components. The rate expressions are shown in Table V.

A close fit in terms of temperature by the model is desirable since the kinetic rate constants differ by several orders of magnitude, for a small difference in temperature.

Table I: Reaction rates

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression, r (mol m$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$(0.430 \cdot k_C + 0.294 \cdot k_H + 0.276 \cdot k_L) \cdot [\text{vol}]$</td>
</tr>
<tr>
<td>R2</td>
<td>$(0.430 \cdot k_C + 0.294 \cdot k_H + 0.276 \cdot k_L) \cdot [\text{vol}_A]$</td>
</tr>
<tr>
<td>R3</td>
<td>$(0.430 \cdot k_C + 0.294 \cdot k_H + 0.276 \cdot k_L) \cdot [\text{vol}_A]$</td>
</tr>
<tr>
<td>R4</td>
<td>$A \cdot e^{-\frac{E}{RT}} \cdot [\text{Tar}]$</td>
</tr>
<tr>
<td>R5</td>
<td>Heat transfer controlled</td>
</tr>
</tbody>
</table>

Table II: Kinetic rate constants [1], A (s$^{-1}$), E (kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_C$</th>
<th>$k_H$</th>
<th>$k_L$</th>
<th>$A_C$</th>
<th>$E_C$</th>
<th>$A_H$</th>
<th>$E_H$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$2.8 \cdot 10^{19}$</td>
<td>$2.1 \cdot 10^{16}$</td>
<td>186.7</td>
<td>$9.6 \cdot 10^8$</td>
<td>107.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>$1.3 \cdot 10^{10}$</td>
<td>$2.6 \cdot 10^{11}$</td>
<td>145.7</td>
<td>$7.7 \cdot 10^6$</td>
<td>111.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>$3.3 \cdot 10^{14}$</td>
<td>$8.8 \cdot 10^{15}$</td>
<td>202.4</td>
<td>$1.5 \cdot 10^9$</td>
<td>143.8</td>
<td></td>
<td></td>
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<td>R4</td>
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5 RESULTS

5.1 Experimental comparison of model results

The experimental case which is compared to the model, are run with an inlet temperature of 397.7°C and a wall set point temperature of 510°C. However setting a wall boundary condition of 510°C does not represent reality well since the bed is constantly cooling the wall. For the comparison a 30°C lower wall temperature was chosen.

After 200 seconds of real time, the time-averaged model results are compared to the thermocouple measurements gathered at stable conditions, See Fig. 6.

Figure 6: Time-averaged temperature profile along the centerline after 200 s, compared to measurements.

Fig. 7 The measured bed-height is shown next to the predicted volume fraction of solids as function of height.

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The gas composition was measured after removal of condensable compounds; molar percentages are indicated in Table III. The composition of the model is time-averaged after 200 seconds of actual time.

Table III: Gas compositions

<table>
<thead>
<tr>
<th></th>
<th>Model, %mol</th>
<th>Model*, %mol</th>
<th>Measured, %mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4.27</td>
<td>5.66</td>
<td>4.72</td>
</tr>
<tr>
<td>H₂</td>
<td>2.36</td>
<td>3.13</td>
<td>0.44</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.23</td>
<td>1.63</td>
<td>1.14</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.39</td>
<td>3.17</td>
<td>2.77</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.55</td>
<td>0.73</td>
<td>0.13</td>
</tr>
<tr>
<td>N₂</td>
<td>64.65</td>
<td>85.69</td>
<td>90.76</td>
</tr>
<tr>
<td>Tar</td>
<td>5.71</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>18.61</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
* After removal of condensable compounds

5.2 Composition and tar behavior in the freeboard

Fig. 8 shows the development of tar at different instances, since the start of the process.

The reactions occur mostly on top of the bed, and the tar distributes quite evenly along the horizontal cross section.

The total mass of different species, inside the reactor, as function of time is indicated in Fig. 9. The gas phase compounds stabilize after around 200 seconds. The 200 seconds needed for stabilization is consistent with comparable modeling work, carried out by for example Xue et al [7].

After this lap of time, the feeding rate is stabilized versus the reactions and the flow rate at the outlet. As indicated in the Fig. 9, a small total mass of vapors resides in the reactor. This is positive since a long residence time otherwise would suggest an unsteady or problematic operation. Furthermore, a high bio oil yield can be achieved as a long duration in high temperature conditions will otherwise cause extensive tar cracking.

Fig. 10 shows the instantaneous cross-sectional average composition (after 200 s) of the fluid phase, as function of height in the reactor. The tar cracking is visible in the upper second half of the reactor. The tar cracking produces a number of chemical compounds according to R4 in Fig. 5. This dilutes the N₂ slightly, which is visible as a drop of N₂ near the top of the reactor.

Fig. 9 shows the stabilization of tar yield at the outlet, as a function of time. At stable conditions the tar yield is roughly 45 % by weight.

Fig. 11 shows the yield of Tar at the outlet, as function of time.
5.4 Temperature in freeboard

As is shown the time-averaged temperature profiles of the model along the centerline (Fig. 6) are not precisely correct. The reactions are hardly the cause since a relatively small amount of heat is consumed by the endothermic reactions. Instead the discrepancy is likely caused by insufficient heat transport in the horizontal direction in the model. See Fig. 12 (for the same graph as in Fig. 6) with the horizontal mass-averaged temperature shown. This temperature shows a considerable drop near the exit, which is consistent with the measurements.

**Figure 12:** Mass of species development with time.

Fig. 13 displays the temperature, over a cross section of the whole model, at different instances. The figure shows the development of temperature in the reactor and also the non-symmetric profile which is particularly pronounced close to the exit. This clearly shows why shape of the profile in Fig. 12 shows a large drop in temperature.

**Figure 13:** Displays the temperature, over a cross section of the whole model, at 0, 2, 7 and 17 seconds.

5.2 Fluidized bed dynamics

Fig. 14 and 15 shows cross-sections of the lower section in the reactor. The biomass inlet is visible to the right. As may be seen in Fig. 14, bubbles form and the biomass and N₂ from the feeding system pushes the bed up slightly against the wall. The flow of the bubbling fluidized bed flow is fully developed after 2 seconds.

**Figure 14:** Instantaneous volume fraction of the granular phase.
The slight impact on yield of temperature is explainable by the small amount of heat actually carried by the fluidizing gas. See Fig. 16, comparing the temperature profile of case 2, 7 and 5.

![Figure 15: Instantaneous volume fraction of biomass.](image)

As visible in Fig. 15, where the volume fraction of biomass is displayed, the biomass floats upwards and do not spread out into the bed. This naturally gives you the impression of a poor mixing in the horizontal direction, which is quite typical for a BFB reactor. But remember that the feeding rate in this case is slow and reactions occur very fast, so the biomass are rapidly consumed and do not have enough time to spread out.

However, in a succeeding iteration of the setup where a higher feeding rate of biomass is desired, the model will be able to point out insufficient mixing and aid in constructing a new feeding system.

### 5.5 Effect of temperature and flow rate on tar yield

A parametric study was launched in order to see the effect two parameters, inlet temperature and flow rate of fluidizing gas. The parametric study is shown in Table IV; 12 seconds were calculated for each case in order to distinguish the trends.

<table>
<thead>
<tr>
<th>Case</th>
<th>Inlet temperature °C</th>
<th>N₂ flow-rate m/s</th>
<th>Bio oil yield* % by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>398</td>
<td>0.15</td>
<td>50.6</td>
</tr>
<tr>
<td>2</td>
<td>398</td>
<td>0.25</td>
<td>47.2</td>
</tr>
<tr>
<td>3</td>
<td>398</td>
<td>0.40</td>
<td>47.3</td>
</tr>
<tr>
<td>4</td>
<td>498</td>
<td>0.15</td>
<td>46.9</td>
</tr>
<tr>
<td>5</td>
<td>498</td>
<td>0.25</td>
<td>48.7</td>
</tr>
<tr>
<td>6</td>
<td>498</td>
<td>0.40</td>
<td>47.2</td>
</tr>
<tr>
<td>7</td>
<td>448</td>
<td>0.25</td>
<td>48.5</td>
</tr>
</tbody>
</table>

* Includes light tars, i.e. C₆H₆

![Figure 16: Temperature at 12 seconds for cases.](image)

The slight difference in temperature is noticeable in the figure. The heat supplied by the walls and the heat contained in the bed is large compared to the heat supplied by the fluidizing gas.

With increasing flow rate in the low-temperature cases (1-3) the yield goes down, while the yield goes up in the high temperature cases (4-6) and then down. It is clear that the higher flow rate in the cold cases lowers the temperature in the bed while the opposite is true for the high temperature.

It is well known that yield of bio oil is temperature dependent and reaches its peak in the vicinity of 450°C, of course depending on other parameters. Too much heat carried by the fluidizing gas lowers the yield which is evident from case 6.

### 6 COMMENTS

The BFB reactor is complex with many phenomena involved. The vastly different physical phenomena in the bed compared to the freeboard are challenge in this type of modeling. In fact, the choice of implementing a turbulence model favors accuracy in the freeboard, however not in the bed. These kinds of considerations are a necessity if the freeboard and the bed are not to be treated separately in different CFD models.

Several improvements of the model are possible, one being the depiction of the outlet. In the real case, the gas is channeled through a smaller orifice to the cyclone, which will produce a pressure build-up and a slightly
longer residence time. This should give the temperature some more time to distribute evenly in the horizontal direction.

The boundary conditions of the wall and the wall-to-bed heat transfer could be improved as the heating from the walls supply are large portion of the total heat. Also the pyrolysis model could be improved which would increase the predictability outside the present temperature range.

7 CONCLUSIONS

Given the present circumstances the accuracy of model is tolerable and there is significant room for improvement. The trends shown by the parametric study is promising and largely agrees with well-known trends of tar yield versus temperature. The potential use of the model is indeed interesting since a lot of parameters may be studied and evaluated. The same computational framework may be applied to a next-iteration experimental setup, in order to determine the most efficient design.

8 REFERENCES


9 ACKNOWLEDGEMENTS

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