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Comprehensive secondary pyrolysis in fluidized-bed fast pyrolysis of biomass, a fluid dynamics based modelling effort

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Abstract

Homogenous secondary pyrolysis is category of reactions following the primary pyrolysis and presumed important for fast pyrolysis. For the comprehensive chemistry and fluid dynamics, a probability density functional (PDF) approach is used; with a kinetic scheme comprising 134 species and 4169 reactions being implemented. With aid of acceleration techniques, most importantly Dimension Reduction, Chemistry Agglomeration and In-situ Tabulation (ISAT), a solution within reasonable time was obtained. More work is required; however, a solution for levoglucosan ($C_6H_{10}O_5$) being fed through the inlet with fluidizing gas at 500 °C, has been obtained. 88.6 % of the levoglucosan remained non-decomposed, and 19 different decomposition product species were found above 0.01 % by weight. A homogenous secondary pyrolysis scheme proposed can thus be implemented in a CFD environment and acceleration techniques can speed-up the calculation for application in engineering settings.

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Keywords: Secondary Pyrolysis, Fast pyrolysis, CFD, Bio oil, Biomass

1. Introduction

The fast pyrolysis process seems promising but the complexity of underlying chemistry is vast and understanding it is challenging to say the least. We aim however, to model this with the present means and understanding including CFD coupled with comprehensive kinetic schemes. The starting approach is to simulate primary pyrolysis, as the bed-material supplies heat and interact with the solid decomposition. As such, a model for primary pyrolysis has been devised to estimate the primary products, which emerge from the solid particles – this has been done with steam and nitrogen as fluidizing agent, to see the differences due to the physical properties of steam [1]. However, once the primary products form a liquid and evaporate from the particle, secondary pyrolysis takes place and we assume the fluidizing agent will provide *chemical* effects. This is the focus of this paper, where again the case of steam is investigated.

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2. Background

Primary tar, are originally formed from solid biomass via primary pyrolysis. With continuous exposure to a heated environment, primary tar can undergo secondary tar reactions (STR), which alters both mass and composition of the resulting liquid [2]. STR, as a term, includes all reactions after primary pyrolysis; however in the context of such work as Morf et al [2], reactions important for gasification are primarily considered. If instead STR are defined according to Milne et al [3], the first secondary reactions starts inside the pyrolyzing biomass particle or close—in the vapour phase—at relatively low temperatures.

Tar composition clearly changes in a vapour stream, especially via STR, but in CFD models it is rarely considered. In fact, secondary pyrolysis is generally considered lumped, see (1) from [4, 5], as such the actual composition is disregarded. In that case the stoichiometric coefficients of non-condensable gases (NCG) are tailored to fit experiments; for gasification, the reaction represents the cracking of problematic tar to syngas while in fast pyrolysis it represents the liquid yield loss.

$$\mathrm{Tar} \rightarrow \mathrm{CO} + \mathrm{CO_2} + \mathrm{CH_4} + \mathrm{H_2} + \mathrm{Tar_{inert}} + \mathrm{char} \quad (1)$$

A notable exception is Elfadakhany [6] who developed a functional group model for CFD modelling of STR. In the for this paper the secondary pyrolysis is considered as a step in the commonly accepted tar maturation scheme previously introduced by Milne et al. [3], see Figure 1. As the tar matures—assumed to occur in three stages—the composition changes while temperature being a prominent factor.

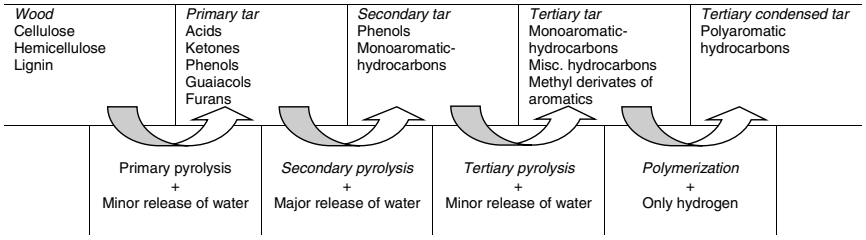

Figure 1. The tar maturation adopted from Milne et al. [3] shown alongside the different pyrolysis stages with formed amount of water.

According to the phase involved, STR is categorized into two classes: homogenous and heterogeneous reaction. Homogeneous STR has been widely studied [e.g. 2, 7 and 8]. Long contact time between tar vapour obtained from pyrolysis process and solid char surface can cause a reduction of tar component, which was originally found several decades ago [9, 10]. It was found to be an effective catalyst for tar removal in gasification process [11, 12]. In this paper, no heterogeneous reactions are considered, despite their importance. This is an obvious limitation which should be addressed in future work.

3. Methodology

In the attempt to model pyrolysis, see Mellin et al. [13], it was found that too little pyrolytic water formed due to missing secondary reactions (presumed to contribute with a major part of pyrolytic water, see Figure 1). A comprehensive kinetic model might better predict this critical part for fast pyrolysis. This paper describes the effort to implement these homogenous gas phase reactions in a CFD framework. For solving the comprehensive chemistry and fluid dynamics, a probability density functional (PDF) approach is used. The PDF approach simulates the flow as stochastic *fluid particles* and is advantageous in treatment of complex chemistry, which saves computational cost. A comprehensive understanding of the theoretical foundations of the pdf approach can be found in Bope [14]. Wang and Yan [15] have mentioned PDF method as one of the available CFD models for solving turbulent-chemistry interaction.

Table 1. Species formed due to primary pyrolysis in Mellin et al [1].

Gas			Liquid								Solid
CO	CH_4	H_2	$C_3H_4O_2$	C_3H_6O	CH_3HCO	CH_3OH	$C_2H_2O_2$	$C_2H_4O_2$	$C_9H_{10}O_2$	H_2O	C
CO_2	C_2H_4		$C_5H_8O_4$	CH_2O	C_6H_5OH	$C_6H_6O_3$	$C_6H_{10}O_5$	C_2H_5OH	$C_{11}H_{12}O_4$		

In this model, primary products form; which are stated in Table 1. These further decompose and interact according to a kinetic scheme, comprising 134 species, and 4169 reactions [16] (version 1311, November 2013), is implemented in the CFD environment of ANSYS Fluent 14.5. The kinetic scheme was previously used in Calonaci et al [17] to study fast pyrolysis at the particle level. When implement the scheme it is reduced to 100 species using a Dimension Reduction algorithm. Chemistry Agglomeration and In-situ Tabulation (ISAT) is in addition used to accelerate the computation. Figure 2 shows the geometry (left) and the modelling approach (right); time-averaged results are transferred from a transient model describing primary pyrolysis to a model for secondary pyrolysis. Levoglucosan formation is shown as an example in Figure 2 (right), which is used as input i.e. source term, to the secondary pyrolysis model. Steam is in addition used as the fluidizing media, which interacts with the vapours.

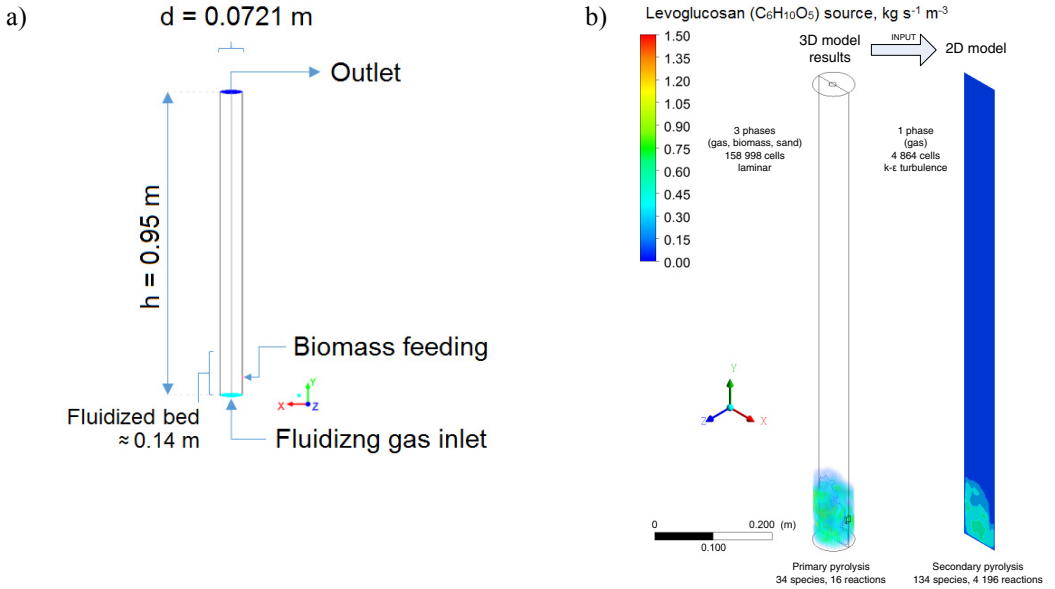

Figure 2. a) the geometry, inlets and outlet; b) layout of the modelling approach, time-averaged results are transferred from a transient model describing primary pyrolysis to a model for secondary pyrolysis.

4. Example results

A sample result is shown here as analysis of the results is time-consuming and requires space. In this simulation, 1 %wt of levoglucosan ($C_6H_{10}O_5$) was fed through the inlet together with the fluidizing gas. Convergence was achieved after about 4250 iterations, (2 weeks time). Table 2 represents the largest occurring species at the outlet, and together constitute almost all the decomposed levoglucosan.

Table 2.Yield by weight of secondary products from levoglucosan pyrolysis, at the outlet of the reactor.

Gas			Liquid						
CO	CH_4	H_2	$C_3H_4O_3$	$C_3H_6O_2$	CH_3CHO	$C_2H_2O_2$	$C_5H_4O_2$	$C_4H_6O_2$	H_2O
15.63	4.67	0.76	34.45	0.01	0.13	4.50	0.13	4.94	2.59
CO_2	C_2H_4	C_2H_6	CH_2CO	CH_2O	$C_6H_8O_4$	$C_6H_6O_3$	C_2H_3CHO	CH_3COOH	
0.19	0.02	0.03	6.80	13.86	10.41	1.78	0.09	0.01	

For results along the reactor height, see Figure 3, where water forms alongside anhydrous levoglucosan.

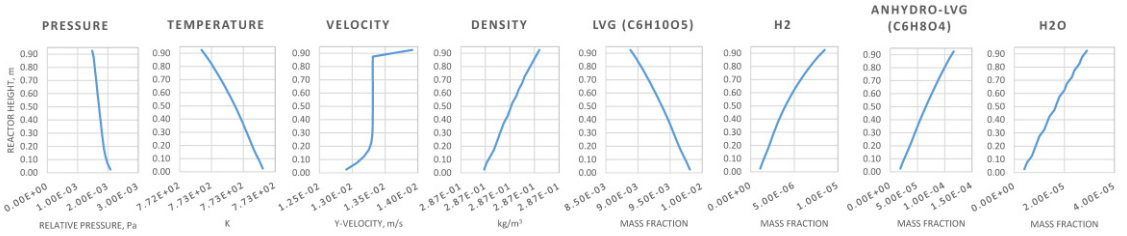

Figure 3. Along the reactor height, mass-averaged Pressure, temperature, Y-velocity, Density and Mass fraction of Levoglucosan, Hydogen. Anhydro-Levoglucosan ($C_6H_8O_4$) and Pyrolytic Water.

5. Conclusions

The homogenous secondary pyrolysis scheme proposed by Ranzi and co-workers, is possible to implement in a CFD environment. Acceleration techniques provided in the software package ANSYS Fluent can speed-up the calculation and make it feasible for application in an engineering setting.

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