Modeling Gas Effects in a Bubbling Fluidized Bed Reactor for Biomass Pyrolysis

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Contents

Abstract

Fast pyrolysis of biomass in a fluidized bed reactor is typically conducted in a nitrogen gas environment. Recycling product gas can improve the economics of operating such a system by reducing reliance on pure process streams.

1 Introduction

Fast pyrolysis is a versatile method for thermochemical conversion of solid biomass into liquid bio-oil which can be used for bio-fuel and high-value chemical production. Bio-oil is commonly generated in bubbling fluidized bed and

circulating fluidized bed reactor systems in which biomass particles rapidly devolatilize in the absence of oxygen into mixtures of light gases, condensable bio-oil vapors, and solid char [4, 5, 12]. Since biomass pyrolysis normally occurs in a non-oxidizing environment, the fluidization gas (carrier gas) is often pure nitrogen [12]. To maximize bio-oil yields, the reactor typically operates at temperatures near $500°C$ and must maintain particle residence times up to 10 seconds and gas residence times less than 2 seconds [5]. Deviations from these conditions can result in significant production and quality penalties, therefore optimal reactor design and control become crucial to achieving commercially viable bio-oil production.

To improve the economic possibilities of biomass fast pyrolysis systems, char can be burned for process heat while recycled pyrolysis gas can assist with fluidization [4, 10]. The major generated components of pyrolysis gas are CO, CO_2, CH_4, H_2, and other light hydrocarbons [1, 16]. Several experiments investigated the effects of these gases on reactor conditions and pyrolysis yields [10, 13, 16] but modeling the effects of the different gases was not discussed.

There are several models available that investigate the hydrodynamics and conversion of biomass at fast pyrolysis conditions in fluidized bed reactors [14, 11]. As is typical for biomass pyrolysis, these models assume the fluidization gas is pure nitrogen. The authors are not aware of any published models in the biomass pyrolysis literature that account for the effects of fluidization or carrier gas other than nitrogen.

This paper uses engineering correlations, reduced-order modeling techniques, and CFD simulations to investigate the effects of gas mixtures in a fluidized bed biomass pyrolysis reactor. The scope of this study is to evaluate different gas mixtures and there effects on the hydrodynamics and biomass conversion in fluidized bed reactors operating at fast pyrolysis conditions.

2   Experimental apparatus

The NREL 2FBR reactor system thermochemically converts biomass feedstock at fast pyrolysis conditions. The system is comprised of two bubbling fluidized bed (BFB) reactors where the first reactor is for biomass fast pyrolysis and the second reactor is for vapor phase upgrading. Modeling activities discussed in this paper refer to the BFB pyrolysis reactor.

An overview of the NREL 2FBR system is shown in Figure 1, components of the pyrolysis reactor are detailed in Figure 2, while dimensions and typical operating conditions of the pyrolysis unit are given in Figure 3. Sand is used as the dominant heat transfer medium in the pyrolyzer. Biomass particles are fed to the reactor via a screw auger and nitrogen is used as the fluidization/carrier gas. More information about the NREL 2FBR biomass pyrolysis system is available elsewhere [8, 15].
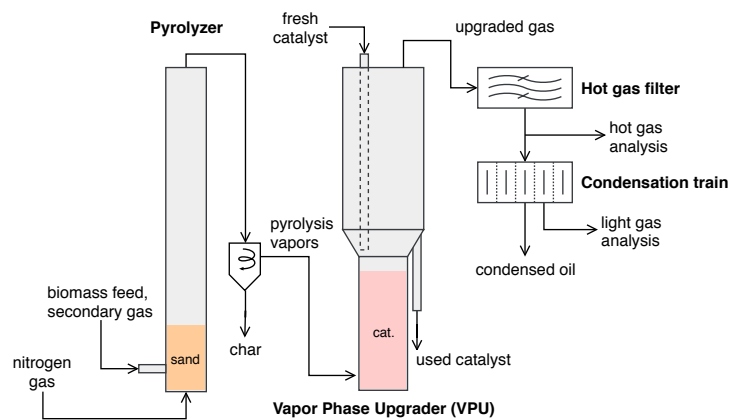
Figure 1: Overview of the NREL 2FBR system. Biomass fast pyrolysis occurs in the pyrolyzer (left) and gaseous products are catalytically upgraded in the vapor phase upgrader (right).
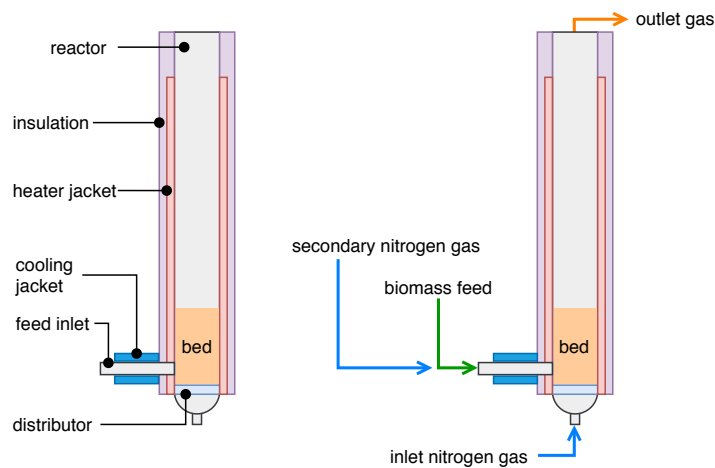

Figure 2: Components of the BFB biomass pyrolysis reactor referred to as the "pyrolyzer" in the NREL 2FBR system.

Figure 3: Dimensions and typical fast pyrolysis operating conditions for the BFB biomass pyrolysis reactor in the NREL 2FBR system.

3 Modeling approach

Engineering correlations, reduced-order models, and CFD modeling techniques were used to investigate the effects of recycled gas on the operation of a fluidized-bed biomass pyrolysis reactor. The following sections discuss approaches implemented in this work for calculating gas properties and the associated effects on fluidization conditions and pyrolysis yields.

3.1 Gas properties

Density (kg/m^3) of an individual gas is calculated from the ideal gas law

$$\rho_{gas} = \frac{P\,M}{R\,T} \tag{1}$$

where P is pressure (Pa), M is molecular weight (g/mol), R is the gas constant [(m^3 Pa) / (K mol)], and T is temperature (K). Gas viscosity (µP) is given as

$$\mu_{gas} = A + B\,T + C\,T^2 + D\,T^3 \tag{2}$$

where coefficients A, B, C, and D are obtained for a given gas from tables in Yaws' Handbook and T is gas temperature (K). Thermal conductivity (k) of the gas is given as

$$k_{gas} = A + B\,T + C\,T^2 + D\,T^3 \tag{3}$$

where coefficients A, B, C, and D are also from the Yaws' Handbook and T is again the gas temperature (K).

Several methods are available to calculate the viscosity of a gas mixture. Equation 4 calculates the mixture viscosity from the sum of the mole fraction

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and viscosity product of each gas component in the mixture [6] while Equation 5 accounts for the molecular weight of each gas component [7].

$$\mu_{mix} = \sum(x_i \cdot \mu_i) \tag{4}$$

$$\mu_{mix} = \frac{\sum(\mu_i \cdot x_i \cdot \sqrt{MW_i})}{\sum(x_i \cdot \sqrt{MW_i})} \tag{5}$$

3.2   Fluidization correlations

For a bed of particles, the minimum fluidization velocity U_{mf} is the gas velocity at which the drag force of the upward moving gas equals the weight of the particles. Kunii and Levenspiel [9] provide the following equation for calculating minimum fluidization velocity

$$U_{mf} = \frac{Re_{p,mf}\mu}{d_p\rho_g} \tag{6}$$

where μ is gas viscosity (kg/m s), d_p is particle diameter (m), ρ_g is gas density (kg/m^3), and $Re_{p,mf}$ is the particle Reynolds number (-) at minimum fluidization conditions.

The Reynolds number is calculated from the Archimedes number (Ar) and two dimensionless constants (a, b) which represent experimental coefficients.

$$Re_{p,mf} = \left(a^2 + bAr\right)^{1/2} - a \tag{7}$$

$$Ar = \frac{d_p^3\rho_g(\rho_s - \rho_g)g}{\mu^2} \qquad a = \frac{K_2}{2K_1} \qquad b = \frac{1}{K_1} \tag{8}$$

The constants K_1 and K_2 are determined from the following equations which are based on the Ergun pressure drop equation for a bed of particles

$$K_1 = \frac{1.75}{\epsilon_{mf}^3\phi} \qquad K_2 = \frac{150(1 - \epsilon_{mf})}{\epsilon_{mf}^3\phi^2} \tag{9}$$

where ϵ_{mf} is the bed void fraction (-) at minimum fluidization and ϕ is sphericity (-) of the bed particles. For this paper, three correlations based on the work of Ergun, Wen and Yu, and Grace were used to calculate U_{mf}. The Ergun approach applied the void fraction ϵ_{mf} and particle sphericity ϕ. The Wen and Yu approach utilized the experimental coefficients of $a = 33.7, b = 0.0408$ while the Grace approach used $a = 27.2, b = 0.0408$.

3.3   Pyrolysis kinetics

A pyrolysis kinetics scheme based on the work of Di Blasi was implemented to predict the conversion of biomass into gas, tar, and char products [2, 3]. Figure 4 gives an overview of the scheme and its reaction mechanisms. Reactions 1–3

represent the primary conversion of biomass while reactions 4–5 are secondary reactions that reduce tar yield at long residence times.
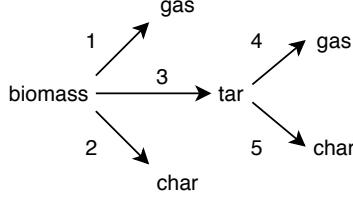

Figure 4: Diagram of the Di Blasi pyrolysis kinetics scheme for conversion of biomass to gas, tar, and char products.

The pyrolysis reactions were modeled as first-order Arrhenius type equations where the rate constant k for each reaction is given as

$$k = A\,e^{E/RT} \tag{10}$$

such that A is the pre-factor, E is the activation energy, R is the gas constant, and T is the reaction temperature. Kinetic parameters for each reaction are listed in Table 1.

Table 1: Kinetic parameters for the Di Blasi biomass pyrolysis scheme.

Reaction	A (1/s)	E (kJ/mol)	Reference
1	4.38×10^9	152.7	[3]
2	3.27×10^6	111.7	[3]
3	1.08×10^{10}	148.0	[3]
4	4.28×10^6	108.0	[2]
5	1.00×10^6	108.0	[2]

3.4 Parameters

Parameters for the reduced-order model and CFD simulations are provided in Table 2. Biomass particle characteristics and properties are representative of loblolly pine. Bed particle characteristics are for typical sand material. Operating conditions and reactor dimensions are based on the previously discussed NREL 2FBR fluidized bed pyrolysis unit.

Table 2: Biomass, bed, and reactor modeling parameters. Particle diameters represent the Sauter-mean diameter.

Parameter	Value	Units	Description
$d_{p,bed}$	235	µm	diameter of bed Particle
ϕ_{bed}	0.0		sphericity of bed particle
$d_{p,bio}$	135	µm	diameter of biomass particle
ϕ_{bio}	0.0		sphericity of biomass particle
ρ_{bio}	540	kg/m^3	density of biomass particle
$h_{reactor}$	43.18	cm	reactor height
h_{static}	10.16	cm	static bed height
T	773	K	reactor temperature

3.5   Simulation cases

Table 3 represents the CFD simulations conducted for this paper. Each row is for a different simulation case which is performed for a particular gas composition.

Table 3: Simulation cases for different gas mixtures where columns denote gas percentage.

Case	N_2	H_2	H_2O	CO	CO_2	CH_4
1	100	0	0	0	0	0
2	0	100	0	0	0	0
3	0	0	100	0	0	0
4	0	0	0	100	0	0
5	0	0	0	0	100	0
6	0	0	0	0	0	100
7	20	20	0	20	20	20
8	50	0	0	0	50	0
9	50	0	0	50	0	0
10	0	0	50	50	0	0
11	100	0	0	0	0	0
12	80	20	0	0	0	0
13	60	40	0	0	0	0
14	50	50	0	0	0	0
15	40	60	0	0	0	0
16	30	70	0	0	0	0
17	20	80	0	0	0	0
18	15	85	0	0	0	0
19	10	90	0	0	0	0
20	5	95	0	0	0	0
21	0	100	0	0	0	0

4 Results and discussion

This section provides results and related discussions for the effects of different fluidization gases on the operation and conversion of a bubbling fluidized bed reactor.

4.1 Comparison of gas properties

Molecular weight, viscosity, density, and thermal conductivity of the individual gases investigated in this paper are shown in Figure 5. The gas properties were calculated at a pressure of 101,325 Pa and a temperature of 773.15 K (500°C). The lightest gas in terms of molecular weight and density is hydrogen while the heaviest gas is carbon dioxide. Viscosity for all the gases except hydrogen and methane ranged from 300–350 μP. Thermal conductivity for all the gases is near 0.05 W/(m K) except for hydrogen which is approximately 0.35 W/(m K) and methane which is near 0.12 W/(m K).
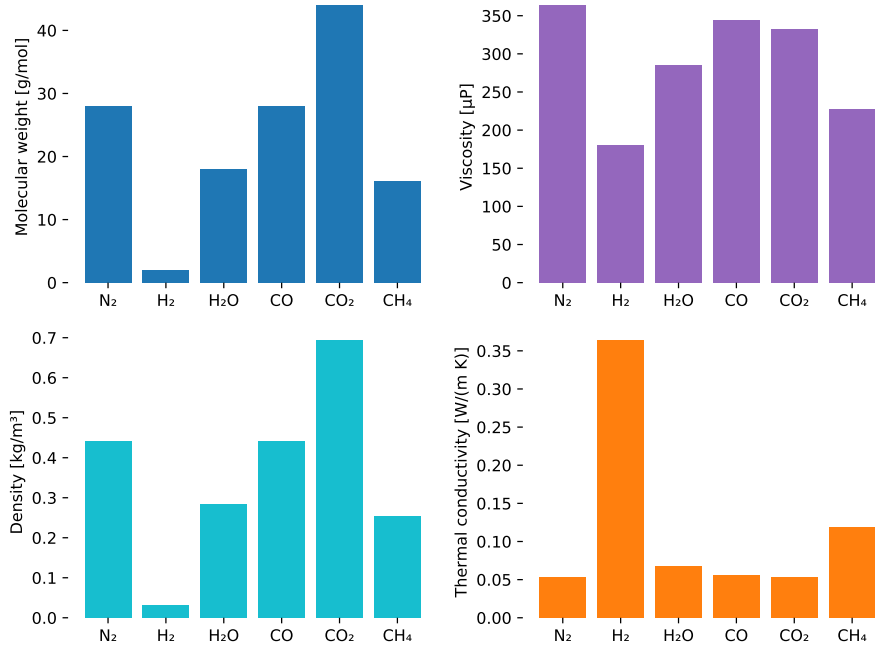

Figure 5: Comparison of molecular weight, viscosity, density, and thermal conductivity for individual gases at 101,325 Pa and 773.15 K.

Properties for molecular weight, viscosity, and density for the gas mixtures investigated in this paper are shown in Figure 6. Similar to the individual gas properties, the mixture properties were calculated at 101,325 Pa and 773.15 K

(500°C). The fraction of each gas in the mixture is given by the values shown at the top of each column in the figure. For example, the hydrogen and nitrogen mixture is comprised of 80% hydrogen and 20% nitrogen which is labeled as $0.8 + 0.2$. As expected, the carbon dioxide mixture is the heaviest in terms of molecular weight and density.
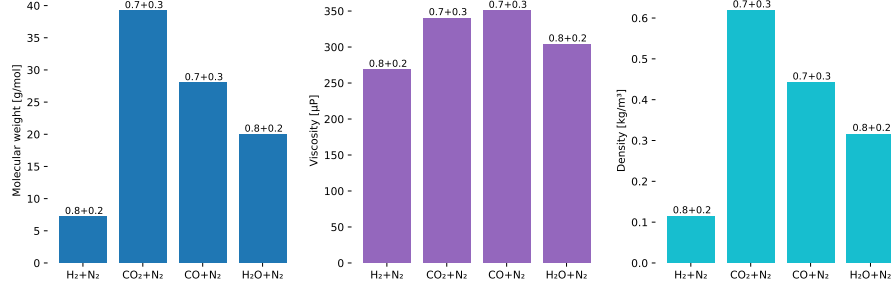

Figure 6: Comparison of gas mixture properties for molecular weight, viscosity, and density at 101,325 Pa and 773.15 K. Fraction of each gas component is shown at the top of each column.

4.2 Fluidization effects

Minimum fluidization velocity (Umf) of the bed material for the different fluidization gases is presented in Figure 7. The hydrogen gas requires about twice the gas velocity to fluidize the sand bed compared to the nitrogen gas.
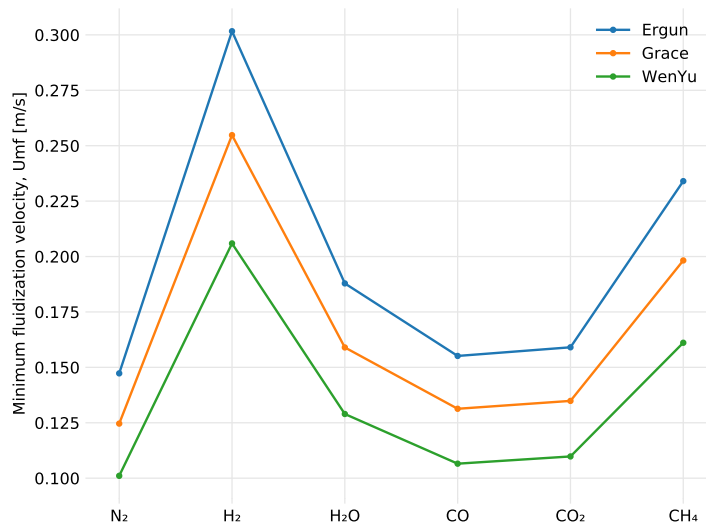
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Figure 7: Comparison of minimum fluidization velocity (Umf) for different fluidization gases. Values calculated with the Ergun, Grace, and Wen and Yu correlations.

5 Conclusion

Here.

6 Source code

Python models used to generate results for this article are available on the CCPC GitHub at `https://github.com/ccpcode` in the X repository. Functionality provided by the Chemics package was used for gas properties and various fluidization calculations. See the Chemics documentation at `https://chemics.github.io` for more information.

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