Thermal Decomposition Model of Biocrudes at High Heating Rates for Spray Combustion and Gasification

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ABSTRACT

Biocrudes are liquid products of the thermal processing of biomass, particularly fast pyrolysis and hydrothermal liquefaction. Biocrudes are being used as heating fuels, co-processed with fossil crudes in refineries, and are being considered for pressurized gasification to supply a Fischer-Tropsch catalytic reactor to produce renewable transportation fuels, particularly renewal diesel and sustainable aviation fuel.

These biocrudes are complex mixtures of organic compounds that can vaporize or polymerize when heated. With suitable nozzles, they can be atomized to minimize the internal heat transfer resistance. A reduced-order model (ROM) has been constructed to predict the yields of light gases, tar, and char produced from pressurized gasification of biocrude derived from corn stover. A sub-model for thermal decomposition of biocrude is proposed. Preliminary predictions obtained using this model are in reasonable agreement with literature data.

1 Introduction

Biocrudes are liquid products obtained from the thermal conversion of biomass using methods like fast pyrolysis (FP) and hydrothermal liquefaction (HTL) These biocrudes serve multiple purposes, including their utilization as heating fuels and co-processing alongside fossil crudes in refineries. Additionally, biocrudes hold potential as a valuable feedstock source for pressurized gasification. The resulting syngas can subsequently be supplied to a Fischer-Tropsch catalytic reactor, enabling the generation of renewable transportation fuels, specifically renewable diesel and sustainable aviation fuel.

In the current study, a reduced order model (ROM) is proposed for the pressurized gasification of biocrude derived from corn stover. This modelling study aims to improve understanding of the gasification process, thus enhancing process optimization and reliability. At CanmetENERGY, Natural Resources Canada, a steady-state ROM has been developed for pressurized gasification of solid fossil fuels in a short-residence time gasifier. [1,2,3] The model is able to provide good predictions of the product yields (i.e., syngas composition, char and tar yields), along with the temperature profile inside the gasifier. In the current work, this model is updated to capture the distinct behaviour of biocrudes during the gasification process. A sub-model describing the thermal decomposition of biocrudes is proposed. The reaction mechanism is also extended to account for additional reforming reactions. Using the updated ROM, a simulation for gasification of biocrude derived from corn stover is performed. Preliminary results obtained from this simulation are in good agreement with literature data.

The remainder of the article is as follows. First, important properties of biocrudes are reviewed. A sub-model for thermal decomposition of biocrudes is then proposed. Next, the updated ROM is described. Simulation results obtained using the updated ROM are shown and discussed, followed by suggestions for future work.

2 Biocrude Properties Relevant to Gasification

Biocrudes are noticeably different from fossil fuels like heavy fuel oil, petroleum coke, or coal that have been used in pressurized gasification. Table 1 provides the properties range of the biocrudes derived from woody biomass and agricultural residues.[4] Notably, the water content is particularly important, correlating with heat content and viscosity of the biocrude.

Table 1 – Properties of biocrudes on dry basis [4]

Carbon	36 - 62	(wt %)
Hydrogen	7 - 12	(wt %)
Oxygen	25 - 45	(wt %)
Nitrogen	0 - 1	(wt %)
Sulphur	< 0.5	(wt %)
Ash	0.1 - 3	(wt %)
Water	10 - 36	(wt %)
Higher Heating Value	14 - 26	(MJ/kg)

The standard approach to model the gasification of coal or petroleum coke is to divide the feedstock into water, volatiles, and solid char. The water is released during the initial drying step. This is followed by the thermal decomposition that releases the volatile species, including some representation of the tar compounds, while leaving behind the solid char. The char is in suspension and is then undergoes gasification. The division of elements C, H, O, N and S between the volatiles (including tar) and the char is the key feature of the model. This is generally a function of the heating rate and the size of the particles.

It becomes clear that the modeling scheme requires modifications to accommodate the unique properties of biocrude. Biocrude contains significant compounds with boiling points around and below that of water. Additionally, it includes compounds with high molar mass, some of which break down when heated, particularly sugars that undergo caramelization.

To address this, one approach is to replace the complex mixture of organic compounds with a much smaller number of characteristic compounds that cover the range of values for a property like molecular weight or boiling point. Examples of this approach are reported by Sallevelt *et al*.[5] and Fooladgar *et al*.,[6] where the biocrude is modelled as a mixture of seven compounds: water, methanol, acetic acid, acetol, phenol, eugenol and levoglucosan. A problem with this approach is that the formation of char from the biocrude is neglected.

In our approach, we aim to modify the traditional drying/devolatilization/char gasification scheme to account for the particular characteristics of biocrudes. The primary change is to include light organic species in the drying phase. Note that to calibrate the decomposition model for an individual biocrude, thermogravimetric analysis (TGA) tests are required.

3 Biocrude Decomposition

Entrained flow gasification operates at temperatures above 1000°C and typically at nearly atmospheric pressure but more likely at elevated pressures. The target operating conditions for the present work are set at 1350°C and 35 bar.

During the gasification process, the biocrude is injected into the gasifier together with oxygen and steam. The design of the burner promotes the mixing of the oxidant and biocrude resulting in a rapid reaction and a very high heating rate. The biocrude is atomized generating small droplets which are assumed to have a uniform size and spherical shape, specified by the droplet diameter.

The atomization and very high heating rate cause the biocrude to pass rapidly through the various stages. Biocrude generally has a high-water content. The first stage involves the evaporation of water and other light liquids that have a boiling point in the neighbourhood of water. The second stage entails the thermal decomposition of the organic compounds which then break down and polymerize leading to the formation of light gases, tars, and char. For the model developed in the present study, the vaporization and decomposition are assumed to be instantaneous.

Stage I: Vaporization

During the first stage of gasification, biocrude droplets, containing light organic compounds with boiling points below 125°C and water, undergo vaporization. This is different from a heavy oil that has negligible amounts of light hydrocarbons or a coal/water slurry that has only water to evaporate. The light organic compounds include formaldehyde, acetone, methanol, formic acid, and acetic acid.

Branca *et al*. examined the devolatilization of four different pyrolysis oil derived from wood. [7,8,9] From their study, an average water content of 21.9 wt% and an average fraction of 6.9 wt % of organic compounds with boiling point below 127 °C (i.e, 400 K) were computed for these pyrolysis oil. In the current study, these values are used as the default in Stage I, given the absence of data for biocrudes.

As water and light organic compounds evaporate, the biocrude droplets undergo some changes namely an increase in the density and a decrease in the mass of the individual droplet.

Stage II: Thermal Decomposition

Heavier organic compounds remaining after Stage I undergo thermal decomposition. This thermal decomposition, Stage II, involves a complex series of chemical reactions that breaks down large molecules as well as recombining them to make highly carbon-rich molecules. There are three categories of products in this stage: light gases, char, and tar.

Chhiti *et al*. studied the effects of temperature and heating rates on the thermal decomposition of biocrudes derived from softwood, focusing on the yields of gas and char. [10] Figure 1 shows the gas yields reported in experiments using heating rates ranging from 2 °C/s to 2000 °C/s, using a log scale, for final temperatures of 550 °C and 1000 °C, respectively. As shown in Figure 1, the gas yield increases with higher temperature, but is independent of heating rate. At 1000 °C, the gas release is equivalent to an average of 42 wt % of the initial biocrude mass for all heating rates. In the current study, we use this value as the gas fraction in Stage II.
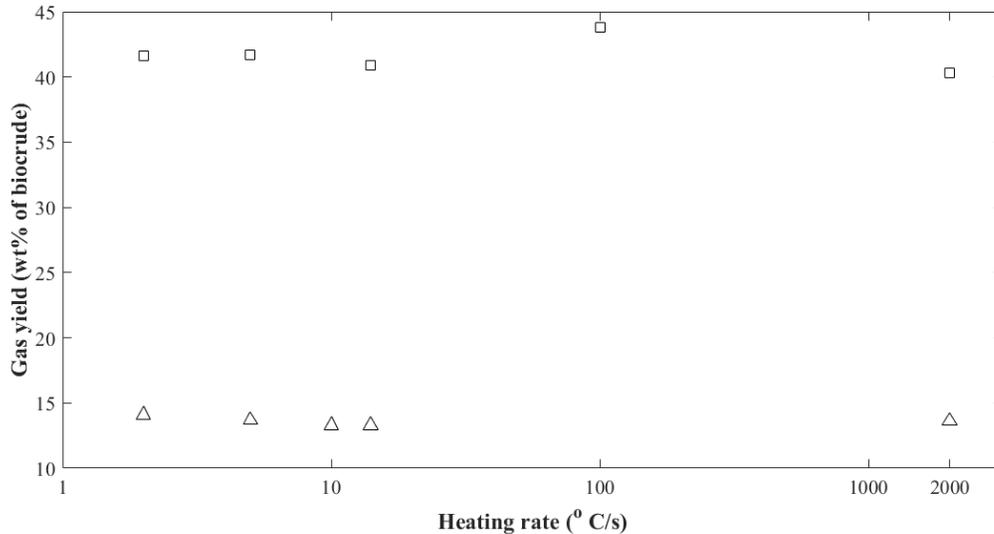

Figure 1 - Gas yield from thermal decomposition of biocrudes at different heating rates: △ final temperature of 550 °C and □ final temperature of 1000 °C. Data from Chhiti *et al*. [10]

The amount of char produced from biocrude is significantly less compared to coal, petroleum coke, or solid biomass like sawdust. However, unconverted char can still impact downstream operational issues. Chhiti *et al*. study shows that the char content remains during thermal decomposition of biocrudes is a strong function of the heating rate.[10] As heating rate increases, the char yield decreases, as depicted in Figure 2. Based on those data, the relationship between heating rate and char production during thermal decomposition of biocrudes at 1000 °C can be expressed using Equation 1:

$$f_{char} = 12.6 - 3.733 \log(\mathcal{H}) \qquad (1)$$

where f_{char} (in wt%) is the mass ratio of char compared to the initial biocrude mass (i.e., $f_{char} = 100 \left(\frac{m_{char}}{m_{biocrude}} \right)$), and $\mathcal{H}$ is the heating rate (in °C/s). Note that in their study, Chhiti *et al*. did not distinguish between primary, which is formed directly from the liquid phase of biocrude, and secondary char, which results from polymerization reactions of tar and the volatiles (also known as secondary reactions).

Xiong *et al*. investigated the effects of heating rate on thermal decomposition of biocrude derived from rice husk and reported the yields of primary and secondary char respectively. Table 2 presents their data for experiments conducted at a heating rate of 200 °C/s and final temperatures not exceeding 800 °C. Comparable to the char yield reported by Chhiti *et al*. [10,11], the total char yield of both primary and secondary char reported by Xiong et al. is comparable. Therefore, in our current study Equation 1 is used to compute a reference for the total char released in Stage II. The formation of secondary char is not a separate part of the model at this stage.
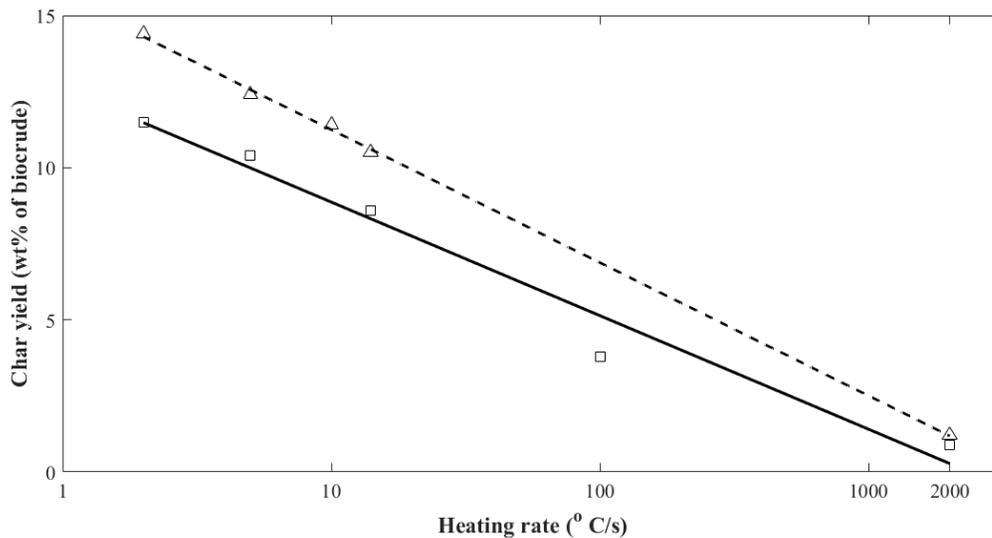

Figure 2 - Char yield from thermal decomposition of biocrudes at different heating rates: - -△ final temperature of 550 °C and −□ final temperature of 1000 °C. Data from Chhiti *et al*. [10]

Table 2 – Char yields from thermal decomposition of biocrude derived from rice husk at a heating rate of 200 °C/s. Data from Xiong *et al*. [11]

Temperature (°C)	Primary (wt %)	Secondary (wt %)	Total (wt %)
500	1	1.5	**2.5**
600	1	2	**3**
700	1.5	5	**6.5**
800	1.8	5.45	**7.25**

Unfortunately, Chhiti *et al*. did not measure the tar yield specifically in their study. Instead, they calculated a condensate yield, which was assumed to be a mixture of tar and water, as the complement to 100 wt.% of the yields in gas and char residue. In the current study, the same approach is applied at this stage of model. Tar is then assumed to undergo cracking reactions to produce light gases and char.

4 Modelling study

Previously, a reduced order model (ROM) has been developed for CanmetENERGY's pilot-scale gasifier. The gasifier is designed for entrained flow gasification and has a capacity of converting 1 tonne/day of different slurry/dry feedstocks to syngas. The ROM is capable of predicting important aspects of the gasification process, such as gas compositions, carbon conversions, and temperature profiles. Details of the ROM and the gasifier are described elsewhere. [1-3]

In the current work, the ROM is updated to provide predictions for entrained-flow gasification of pyrolysis oil derived from corn stover. A brief description of the updated ROM is presented in this section.

Reactor network

The current setup of the gasifier is designed for single-stage dry-fed gasification. It has a diameter of 0.21 m and a length of 1.9 m. More detailed information about CanmetENERGY's entrained-flow gasifier can be found elsewhere. [1]

As shown in Figure 3, the proposed ROM requires a reactor network consisting of plug flow reactors (PFRs) and continuous stirred tank reactors (CSTRs). This configuration is used to simulate different zones within the gasifier. The combustor is divided into three specific zones: the jet expansion zone, the external recirculation zone, and the downstream zone.

Fuel, oxygen, and steam enter at the gasifier the top. The oxygen nozzles are directed towards the fuel inlet to create a jet flow region, while steam is injected in close proximity to this jet flow field. At the gasifier inlet, the two phases (fuel and oxygen-steam mixture) undergo a sudden expansion, causing the flow to spread out. This expanded region is known as the jet expansion zone (JEZ). As the flow approaches the gasifier walls, it splits into two streams. One stream is recirculated back to the top of the gasifier through the external recirculation zone (ERZ), while the other continues its path towards the end of the gasifier, forming a one-dimensional flow jet region called the downstream zone (DSZ).

The positioning of the steam nozzles ensures that the steam is thoroughly mixed with the hot recirculated gases at the top of the gasifier before entering the JEZ. To account for this mixing zone's influence, the jet expansion and external recirculation zones are further divided into two sections: JEZ-1 and JEZ-2, and ERZ-1 and ER-Z2, respectively. ERZ-1 represents the zone where steam and recirculated gases mix at the top end of the gasifier and combine with the flow jet from JEZ-1. The extensive mixing in ERZ-1 and ERZ-2 is modeled using CSTRs, while JEZ-1, JEZ-2, and DSZ are modeled using PFRs. These regions are highly interconnected as they exchange materials, momentum, and energy with each other.

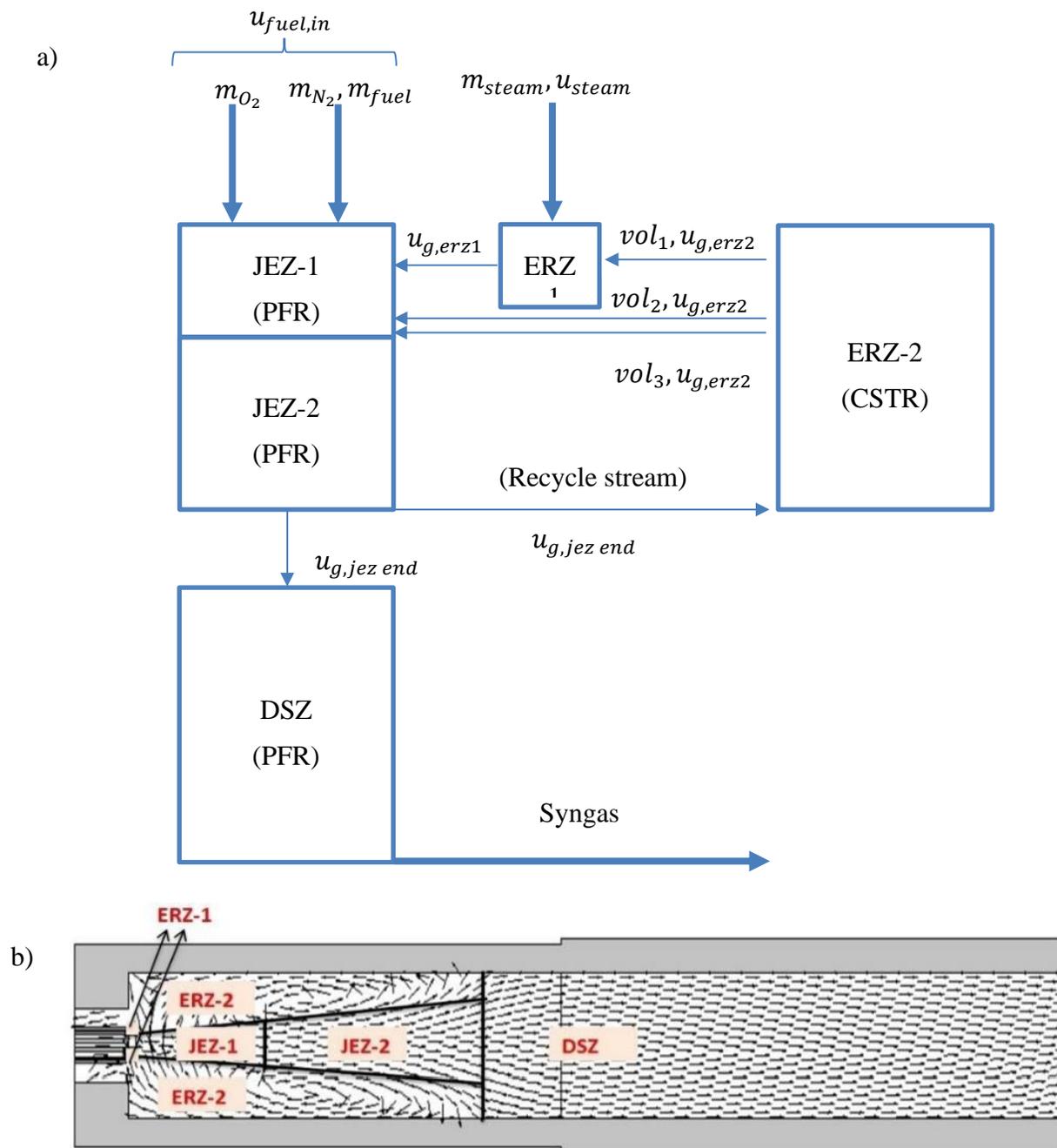More details of the reactor network can be found elsewhere. [1,2]

Figure 1: (a) Proposed reactor network of the gasifier; (b) Corresponding regions of the reactor network inside the gasifier.

Updated ROM

In the current work, the updated ROM is calibrated for gasification of pyrolysis biocrude derived from corn stover. Updates to the ROM include: *i*) spray pattern and droplet distribution which are described using a jet angle of 22 degrees and an average droplet size of 55 *μm*, respectively; *ii*) reaction mechanism that is extended to account for reforming reactions of tar, benzene, and ammonia; and *iii*) the model is solved as a boundary value problem (BVP).

Table 3 presents the additional reactions included in the updated mechanism. Compared to solid fuels, biocrudes release more tar in the decomposition stage. As we assume that tar undergoes reforming reactions to produce syngas, reactions involving benzene, which represents light tar, are accounted for in the updated mechanism. Also, reforming reactions of ammonia is accounted for to track the nitrogen content in the biocrude.

Originally, the ROM solves the conservation equations for momentum, heat, and mass transfer using the finite difference method (i.e., by discretizing the spatial derivatives on a one-dimensional grid with non-uniformly distributed nodes). The resulting algebraic equations are solved using a MATLAB® solver for non-linear equations (fsolve). As a result, obtaining accurate model results requires appropriate spacing of nodes in each zone. Increasing the number of nodes reduces errors in the model's outputs but prolongs the computational time. The computational time is also affected by the initial values provided to the solver.

In the current work, the method for solving the model equations is updated. The momentum, energy, and material balances in the model are addressed as ordinary differential equations (ODEs) and are solved using MATLAB® ODE solve ode15s. The new approach solves the model as a boundary value problem (BVP) rather than an initial value problem (IVP), ensuring the consistency of syngas conditions between the recirculation zone and the jet-expansion zone within the system. This approach enhances the efficiency and accuracy of gasifier simulations. Computational time is also substantially reduced. Details of these balances are provided elsewhere. [1,2]

Table 3: Additional reactions in the reaction scheme

$$C_6H_6 \; + \; 3\,O_2 \; \rightarrow \; 6\,CO \; + \; 3\,H_2 \qquad (3\text{-}1)$$

$$NH_3 \; + \; \frac{5}{4}\,O_2 \; \rightarrow \; NO \; + \; \frac{3}{2}\,H_2O \qquad (3\text{-}5)$$

$$C_6H_6 \; + \; 6\,H_2O \; \rightarrow \; 6\,CO \; + \; 9\,H_2 \qquad (3\text{-}2)$$

$$NH_3 \; + \; \frac{3}{4}\,O_2 \; \rightarrow \; N_2 \; + \; \frac{3}{2}\,H_2O \qquad (3\text{-}6)$$

$$C_6H_6 \; + \; 6\,CO_2 \; \rightarrow \; 12\,CO \; + \; 3H_2 \qquad (3\text{-}3)$$

$$NH_3 \; + \; NO \; + \; \frac{1}{4}\,O_2 \; \rightarrow \; N_2 \; + \; \frac{3}{2}\,H_2O \qquad (3\text{-}7)$$

$$Tar \; + \; 0.82\,H_2O \; \rightarrow \; CO + 1.22\,H_2 \; + 0.0015\,N_2 \qquad (3\text{-}4)$$

$$NH_3 \; \rightarrow \frac{1}{2}\,N_2 \; + \frac{3}{2}\,H_2 \qquad (3\text{-}8)$$

Simulation results

The revised ROM is applied to simulate the gasification of pyrolysis biocrude derived from corn stover. The operating condition of the simulation is presented in Table 4. An oxygen/fuel equivalent ratio (ER) of 0.53 was used in the simulation.

Table 4: Operating condition of the simulation

Fuel (kg/h)		41.2
Oxygen (kg/h)		21.65
Nitrogen(kg/h)		12.1
Steam (kg/h)		5.42
Pressure (bar)		35
Biocrude composition		**Mass fraction (wt%)**
Proximate analysis (as received)	Moisture	22.2
	Volatiles	74.3
	Char	3.5
Ultimate analysis (dry, ash free)	Carbon	45.7
	Hydrogen	7.2
	Oxygen	46.4
	Nitrogen	0.7

Figure 4 illustrates the gas composition variation along the gasifier. In Figure 4a, oxygen is rapidly consumed near the injection point due to combustion reactions, resulting in the predominant production of water and CO_2 in this initial region. Concurrently, CO and H_2 are also consumed in this region due to reactions with oxidizing species, as depicted in Figure 4b. As oxygen becomes depleted, the mole fractions of water and CO_2 reach their maximum values, while the mole fractions of CO and H_2 decline to their minimum values. Moving forward along the gasifier, gasification reactions continue to consume water and CO_2 and produce CO and H_2. As a result, the fractions of water and CO_2 gradually decrease, while the fractions of CO and H_2

progressively increase. At the outlet of the gasifier, the predicted wet syngas consists of 17.8 % H_2, 25.4 % CO, 12.8 % CO_2, 28.3 % H_2O, and 11.9 % N_2 in volume fraction. Additionally, a small amount of tar (i.e., ~ 1 %) and trace amounts (≤ 0.1 %) of char, benzene, H_2S and NO are predicted. The simulation predicts a 97.4 % conversion of the fuel. Table 5 presents the predicted syngas composition (dry, N_2 free).
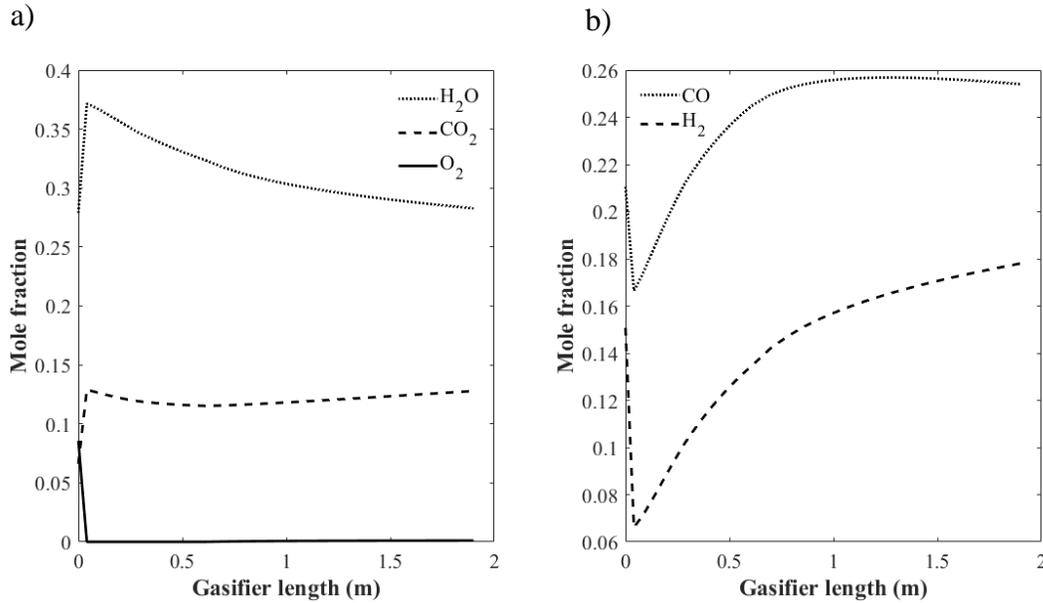
a)   b)

Figure 2: Syngas composition along the gasifier's length

Table 5: Predicted syngas composition (in mol %)

CO	45.3	C_6H_6	2×10^{-5}	Tar	1.8×10^{-4}
H_2	31.8	H_2S	3.7×10^{-5}		
CO_2	22.8	NO	1.25×10^{-5}		

The model also accurately captures the trend of gas temperature along the gasifier's length. As depicted in Figure 5, the gas temperature increases sharply in the region near the injection point where combustion reactions occur. The temperature reaches a peak as oxygen is depleted, then decreases gradually as the gasification reactions are endothermic. The updated ROM predicts

that the peak temperature of gas is ~ 2100 °C and the temperature of gas at the gasifier's outlet is ~ 1350 °C.
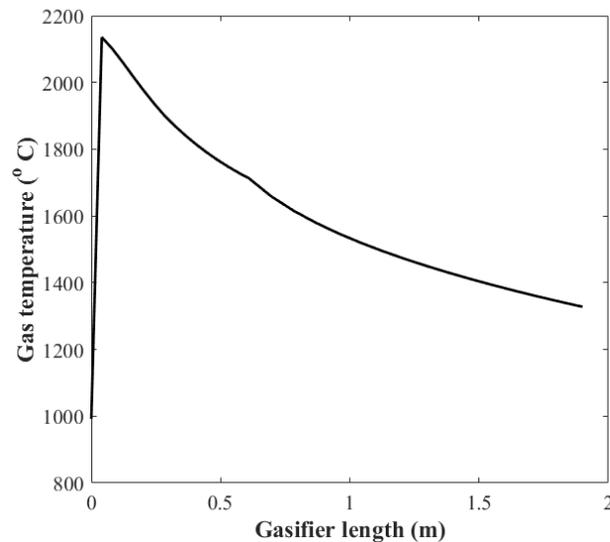

Figure 3: Temperature profile of gas along the gasifier's length

The updated ROM demonstrates reasonable predictions when compared with the literature data. At the Energy Technology Centre in Piteå, Sweden (ETC), tests have been conducted for pyrolysis oil derived from clean wood and wheat straw. The gasifier was operated under pressure of 4 bar, temperatures ranging from 1250 °C to 1300 °C, and an equivalent ratio (ER) of 0.4.[12] The resulting syngas consists of 46% CO, 30% H_2, and 23% CO_2 also in addition to ~ 2% CH_4 and trace amounts of H_2S, COS, and benzene. The Karlsruhe Institute of Technology (KIT) investigated gasification of a pyrolysis oil slurry comprising a mixture of pyrolysis oil and pyrolysis char derived from wood and wheat straw.[13] The gasification tests were operated at 26 bar and temperatures between 900 °C and 1600 °C for equivalence ratios between 0.36 and 0.65. The gasifier yields dry gas volume fractions varying between 52% and 23% for CO, 32% to 20% for H_2, and 31% to 13% for CO_2, with the higher value corresponding to higher equivalence ratio. The remaining gas consisted of N_2 and minor fractions of CH_4 (0% to 1%). For tests operated at temperatures above 1200 °C, carbon conversions are reported to be over 99%. In a more recent study, KIT also reported a data set for gasification of mono ethylene glycol (MEG) as a surrogate fuel for pyrolysis oil at atmospheric pressure.[14] The reported dry syngas consists of 34.7% CO, 30% H_2, and 35% CO_2. They also observed water gas shift equilibrium at 1222 °C (i.e.,1495 K) upstream of the gasifier outlet.

It should be noted that the reaction kinetics used in the current ROM are derived from literature or justified guesses, [1,2] which could lead to some discrepancies in the predictions. For future work, we plan to revisit and revise these kinetic parameters using a more appropriate methodology to enhance the accuracy of our predictions.

5 Conclusion

This work describes a model for the decomposition of biocrudes under a high heating rate to produce light gases, water, tar, and char. The model is based on bench-scale literature and can be adjusted for individual biocrudes through a series of TGA experiments conducted at different heating rates. Preliminary implementation of the model in a reduced order configuration of an entrained flow gasifier gives a reasonable match to the syngas composition when compared to pilot-scale data from the literature.

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