Modeling of the Chemical Looping Combustion of Hard Coal and Biomass Using Ilmenite as the Oxygen Carrier

Anna Zylka 1*, Jarosław Krzywanski 1, Tomasz Czakiert 2, Kamil Idziak 2, Marcin Sosnowski 1, Marcio L. de Souza-Santos 3, Karol Sztekler 4 and Wojciech Nowak 4

1 Faculty of Science and Technology, Jan Długosz University in Częstochowa, 42-200 Częstochowa, Poland; j.krzywanski@ujd.edu.pl (J.K.); m.sosnowski@ujd.edu.pl (M.S.)

2 Institute of Advanced Energy Technologies, University of Technology, 42-201 Częstochowa, Poland; tczakiert@is.pcz.czest.pl (T.C.); k.idziak@is.pcz.pl (K.I.)

3 Department of Energy, School of Mechanical Engineering, University of Campinas, Campinas, SP 13083-970, Brazil; dss@csfmb.com

4 Faculty of Energy and Fuels, AGH University of Science and Technology, 30-059 Cracow, Poland; sztekler@agh.edu.pl (K.S.); wnowak@agh.edu.pl (W.N.)

* Correspondence: a.zylka@ujd.edu.pl

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Abstract: This paper presents a 1.5D model of a fluidized bed chemical looping combustion (CLC) built with the use of a comprehensive simulator of fluidized and moving bed equipment (CeSFaMB) simulator. The model is capable of calculating the effect of gas velocity in the fuel reactor on the hydrodynamics of the fluidized bed and the kinetics of the CLC process. Mass of solids in reactors, solid circulating rates, particle residence time, and the number of particle cycles in the air and fuel reactor are considered within the study. Moreover, the presented model calculates essential emissions such as CO2, SOX, NOX, and O2. The model was successfully validated on experimental tests that were carried out on the Fluidized-Bed Chemical-Looping-Combustion of Solid-Fuels unit located at the Institute of Advanced Energy Technologies, Częstochowa University of Technology, Poland. The model’s validation showed that the maximum relative errors between simulations and experiment results do not exceed 10%. The CeSFaMB model is an optimum compromise among simulation accuracy, computational resources, and processing time.

Keywords: chemical looping combustion; CeSFaMB; ilmenite; oxygen carrier; hard coal; biomass

1. Introduction

Global climate change caused by the greenhouse effect is the main reason to look for new solutions for burning solid fuels. One of the most promising combustion methods with inherent CO2 separation is chemical looping combustion (CLC) technology, which uses oxygen carriers (OCs) in the fuel combustion process. This technology requires two separate fluidized bed reactors: air reactor (AR) and fuel reactor (FR) with circulating and bubbling fluidized bed, respectively. In the AR the OCs are oxidized. In contrast, the OCs are reduced in the FR’s reaction chamber, as shown in Figure 1 [1,2].
OCs are usually metals or metal oxides characterized with specific properties such as high mechanical resistance, high oxygen transfer capacity, adequate specific heat capacity, and low production costs. However, their most crucial advantage is their neutral impact on the environment [3–6].

In this work, ilmenite is selected as an OC. This natural mineral is characterized by good thermal properties and excellent mechanical resistance but reveals a tendency to agglomerate at high temperatures. In addition, ilmenite has a relatively low oxygen transfer capacity compared to, e.g., copper oxide [7–9].

This paper is a continuation and extension of previous work [1]. The novelty of the developed model is the use of a different oxygen carrier (ilmenite) and two different fuels: hard coal and biomass.

The two fuels used in this study differ mainly in their origin. Hard coal is a fossil and is considered a non-renewable energy source. Biomass grows above the ground, and during the photosynthesis process, it absorbs as much CO₂ as it releases during the combustion processes. Therefore, biomass is considered a carbon-neutral energy source and is much more environmentally friendly than hard coal. Thus, biomass combustion is one of the ways that helps to achieve greenhouse gas emission reduction targets. Biomass differs from lignite in many characteristics: carbon, sulfur, oxygen, ash, and volatile matter content, and the heating value [10,11]. Moreover, coal has a higher calorific value than biomass. In addition, there are also some differences in the content of the other components. Biofuels usually have a high sodium and potassium content, leading to lower ash softening points. This may cause operational problems during the combustion process, e.g., defluidization as the effect of the bed sintering, superheater fouling, and high-temperature corrosion [10–15].

2. Materials and Methods

The work aimed to develop a CLC model for biomass and coal as fuel and ilmenite as OC. The result is a 1.5-dimensional model where the simulation tool was the comprehensive simulator of fluidized and moving bed equipment (CeSFaMB) simulator.

In addition, the presented model permits a comparison of the simulation results of two different fuels (biomass and coal) combustion using the same OC. The comparison applies to both hydrodynamics of the fluidized bed as well as CO₂, SOₓ, and NOₓ emissions.

The ilmenite, imported from the Titania AS ilmenite ore mine on Norway’s southwest coast, was used as an OC in experimental and model studies. This natural mineral consists primarily of FeTiO₃ (FeO·TiO₂), but the active phase is an iron oxide that belongs to the iG-CLC process, meaning that it releases oxygen in the FR only after direct contact with the fuel [16–19].
The following properties of ilmenite were considered in the study:

1. density: 3879 kg/m³,
2. Sauter mean diameter of particles: 161 μm,
3. sphericity: 0.65.

A microscopic photograph of the OC is given in Figure 2, and its particle size distribution is shown in Figure 3.

![Microscopic photograph of ilmenite](image1.png)

**Figure 2.** The microscopic photograph of ilmenite.

![Particle size distribution](image2.png)

**Figure 3.** The particle size distribution of ilmenite.

Wood chips (biomass) and hard coal from the Polish coal mine “Sobieski” were used as solid fuels. Microscopic photographs of biomass and coal are shown in Figure 4, and particle size distribution of the fuels are given in Figures 5 and 6, respectively.
Figure 4. The microscopic photograph of fuel: (a) biomass (b) hard coal.

Figure 5. The particle size distribution of biomass.

Figure 6. The particle size distribution of hard coal.

The detailed analysis of hard coal and biomass composition is presented in Table 1.
Table 1. Proximate and ultimate analysis of hard coal and biomass.

| Proximate Analysis/ wt. %          | Hard Coal | Biomass |
|-----------------------------------|-----------|---------|
| Net calorific value [kJ/kg]       | 23,429    | 17,253  |
| Moisture, % (wet)                 | 13.30     | 6.20    |
| Ash, % (wet)                      | 8.20      | 1.40    |
| Volatile, % (wet)                 | 29.49     | 77.00   |
| Fixed carbon                      | 49.01     | 15.40   |

| Ultimate Analysis/ wt. %          |           |         |
|-----------------------------------|-----------|---------|
| Carbon, % (wet)                   | 61.90     | 47.70   |
| Hydrogen, % (wet)                 | 3.66      | 5.47    |
| Nitrogen, % (wet)                 | 0.99      | 0.27    |
| Total sulfur, % (wet)             | 1.39      | 0.11    |
| Oxygen, %                         | 10.56     | 38.95   |

The FB-CLC-SF Unit

Experimental studies were carried out on the Fluidized Bed—Chemical Looping Combustion of Solid Fuel (FB-CLC-SF) unit. The research unit’s schematic diagram is given in Figure 7. This unit is located at the Institute of Advanced Energy Technologies, Czestochowa University of Technology, Poland.

![Diagram of the FB-CLC-SF unit](image-url)
The comprehensive CeSFaMB simulator was applied in the study, as the software is dedicated to fluidized bed analysis. This simulator provides information at each point throughout the unit. The results obtained are dimensional simulations and consider differential mass and energy balances for all phases throughout the bed and the freeboard [20–23].

CeSFaMB was successfully used as a modeling tool in many scientific papers for various objects such as furnaces, boilers, dryers, and gasifiers [23–25], including applications of the CLC processes [1,3,26–28].

Validation of the developed model concerning hydrodynamics, including the mass of solids in reactors, solids circulating rate, particle residence time, and the number of particle cycles in the reactors, was successfully performed in [1,3]. The maximum relative error between experimental and numerical results does not exceed 10%. The developed model was also used to determine emissions, i.e., CO₂, SOₓ, (SO₂ + SO₃), and NOₓ (NO + NO₂ + N₂O).

The CeSFaMB simulator allows for the performance of numerical simulations only after defining the boundary and initial conditions. These primary operational data necessary to perform the simulation process are listed in Table 2.

| Operational Parameters | Value | Test with Biomass | Test with Hard Coal |
|------------------------|-------|-------------------|---------------------|
| Average bed temperature in AR, [K] | 1078  | 1152 |
| Average bed temperature in FR, [K] | 1079  | 1156 |
| Absolute pressure below the gas distributor in AR, [Pa] | 103,935  | 104,148 |
| Absolute pressure below the gas distributor in FR, [Pa] | 104,659  | 105,360 |
| Total mass of solids in the AR, [kg] | 1.61  | 1.42 |
| Total mass of solids in the FR, [kg] | 2.91  | 2.36 |
| Gas mass flow rate in AR, [×600⁻¹ kg s⁻¹] | 4.21  | 4.21 |
| Gas mass flow rate in FR, [×600⁻¹ kg s⁻¹] | 6.52  | 6.52 |
| Fuel mass flow rate, [kg s⁻¹] | 8 × 10⁻⁶  | 8 × 10⁻⁶ |

The models prepared by CeSFaMB are classified into the 1.5D models. This is because, despite the overall 1D (axial) approach, the model also computes some essential variables based on the 2D approach. These include the point-by-point circulation rates of particles in the bed. Then, the radial variations are integrated to provide the average in the axial direction. The basic equations are fundamental differential mass and energy balances using the classic Eulerian approach. The CeSFaMB simulator also uses auxiliary semi-empirical relations to evaluate bed dynamic, heat, and mass transfer parameters. The Eulerian approach is also applied to evaluate the circulation rates of particles inside the bed. However, when it comes to relations to compute reactions within solid particles, the model uses the Lagrangian approach.

The results obtained with the CeSFaMB software are in good agreement with the experimental ones. The maximum relative error does not exceed 10%. The calculations carried out by the CeSFaMB simulator are not time-consuming compared to other methods, including the CFD approach. A detailed description of the CeSFaMB simulator can also be found elsewhere [1].

Since the active phase in ilmenite is iron oxide, the CLC model presented in this work takes into account the set of the following chemical equations [1,3]:

\[
2\text{Fe} + \text{O}_2 = 2\text{FeO} \quad (1)
\]

\[
3\text{Fe} + \text{O}_2 = \text{Fe}_3\text{O}_4 \quad (2)
\]

\[
4\text{Fe} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 \quad (3)
\]
Fe₂O₃ + 3H₂ = 2Fe + 3H₂O  
Fe₃O₄ + 4H₂ = 3Fe + 4H₂O  
FeO + H₂ = Fe + H₂O  
Fe₂O₃ + 3CO = 2Fe + 3CO₂  
Fe₃O₄ + 4CO = 3Fe + 4CO₂  
FeO + CO = Fe + CO₂  
FeO + CO₂ = FeCO₃  
4Fe₂O₃ + 3CH₄ = 8Fe + 3CO₂ + 6H₂O  
Fe₂O₃ + 3H₂ = 2Fe + 3H₂O  
Fe₂O₃ + 3CO = 2Fe + 3CO₂  

The kinetics of chemical reactions, as well as the dynamics of the fluidized bed, have been presented in the literature [29].

3. Results and Discussion

3.1. CLC Model Validation

The first attempts to validate the CLC model for ilmenite using the CeSFaMB simulator were presented in other studies [3,27]. This paper shows numerical simulations with the latest version of the CeSFaMB 4th generation for biomass and coal CLC combustion with ilmenite oxygen carrier. The CLC model’s validation includes such parameters as the average temperature in the reactors, pressure drop in the fluidized bed, void fractions, gas mass flow rate, superficial gas velocity, and primary emissions: CO₂, O₂, NOx, SOx.

3.1.1. The Average Temperature in the Reactors

The AR’s average temperature in both experiments with hard coal and wood chips was similar and amounted to 1152 K and 1156 K, respectively. In the FR, the average temperature in both experimental tests was similar and equal to 1078 K and 1079 K, respectively.

The comparison of the experimental results with numerical simulations for the average temperature in reactors is depicted in Figure 8. The maximum relative error for this parameter is equal to 1.39%.
3.1.2. Pressure Losses in the Fluidized Bed

The pressure decreases with the height of the fluidized bed. This phenomenon is referred to as a pressure drop in the fluidized bed; the greater the height of the dense fluidized bed, the greater the pressure drop in the bed [30].

The highest dense fluidized bed in the FR, i.e., 0.39 m, was observed during ilmenite experiments with biomass. Therefore, in this case, the pressure drop was the highest and amounted to 2822 Pa. The second highest dense fluidized bed in the FR, equal to 0.38 m, was noticed for ilmenite with hard coal CLC combustion. The pressure drop was 2755 Pa, in this case.

The lowest pressure drops were recorded in the AR for the ilmenite-hard coal test. The 0.30 m height of the dense fluidized bed corresponded to a pressure drop of 1879 Pa. Similar to previous observations, higher pressure drops in the AR were obtained for ilmenite with biomass test. In this case, the height of the dense fluidized bed was 0.32 m and, the pressure drop was 2303 Pa.

The maximum relative error between the experiment results and the numerical simulation results for the bed pressure drop was about 3%, as shown in Figure 9.

3.1.3. Void Fractions

A fluidized bed consists of dense and lean regions located in the lower and the upper parts of the reaction chamber, respectively. A high concentration of solid material characterizes the dense
part of the fluidized bed. Moreover, as mentioned before, the most significant pressure drop occurs in this part of the reactor.

The experimental value for void fractions ($v_f$) is determined in the following steps:

1: Pressure sensors are located along with the reactor chamber every few centimeters. The pressure measurements along the reactor’s length determine the lean and dense part of the fluidized bed. Then, using the classic formula for the pressure loss:

$$\Delta p = q_{fb} \cdot g \cdot h$$

where $\Delta p$ = pressure difference between sensors [Pa]; $q_{fb}$ = bulk density of fluidized bed at a specific height of the reactor [kg/m$^3$]; $g$ = 9.81 m/s$^2$ acceleration of gravity; $h$ = height between sensors [m].

2: From the formula above, the bulk density is determined as:

$$q_{fb} = \frac{\Delta p}{g \cdot h}$$

3: Then, knowing the particle true density ($q_p$) the formula below is used to determine void fractions:

$$v_f = 1 - \frac{q_{fb}}{q_p}$$

Figures 10 and 11 show the comparison between experiment and simulation results for void fractions of the fluidized bed in the AR and FR.

Figure 10. Experiment and simulation results for the dense region: (a) AR (b) FR.
As indicated in the above Figures 10 and 11, the maximum relative errors between simulation and experimental results are 0.88% for the dense region and 1.41% for the lean part of the fluidized bed, respectively.

3.1.4. Gas Mass Flow Rate

Figure 12 shows the comparison between measured and calculated results for the gas mass flow rates in both AR and FR. The CO₂ was fed to the FR while the AR was supplied by air.

The above comparison showed that the maximum relative error for the gas mass flow rate is 3.8% in the FR and 1.02% in the AR.

3.1.5. Superficial Gas Velocity in the Bed

The comparison between measured and calculated results for superficial gas velocity in the AR and FR is shown in Figure 13.
3.1.6. Emissions

The emissions for hard coal and biomass are shown in Table 3.

| Fuel     | Emission | Experiment | Simulation | Err [%] |
|----------|----------|------------|------------|---------|
| Biomass  | CO₂ [%]  | 98.27      | 97.80      | 0.49    |
| Hard coal| CO₂ [%]  | 98.09      | 97.40      | 0.70    |
| Biomass  | O₂ [ppm] | 0.00       | 0.00       | 0.00    |
| Hard coal| O₂ [ppm] | 0.00       | 0.00       | 0.00    |
| Biomass  | SOₓ [ppm]| 9.24       | 10.15      | 9.85    |
| Hard coal| SOₓ [ppm]| 85.55      | 78.60      | 8.12    |
| Biomass  | NOₓ [ppm]| 124.93     | 113.10     | 9.47    |
| Hard coal| NOₓ [ppm]| 56.22      | 61.40      | 9.21    |
| Biomass  | O₂ [%]   | 20.27      | 20.19      | 0.39    |
| Hard coal| O₂ [%]   | 18.09      | 19.47      | 7.87    |

As can be seen, there is no oxygen in emissions. Since the ilmenite is an OC that belongs to the iG-CLC OCs group, oxygen is released in direct contact with the fuel and is consumed immediately. Therefore, no oxygen was recorded in the flue gas.

Model validation taking into account essential emissions for hard coal and biomass as fuels showed that the maximum relative error between the experiment and simulation results does not exceed 10%.

3.2. A CLC Model

The developed CLC model also allows taking into account the effects of the superficial gas velocity in the FR on fluidization hydrodynamics and emissions during CLC combustion in the FB-CLC-SF unit.
3.2.1. Solid Circulating Rate

The effect of superficial gas velocity in a FR on a solid circulating rate is shown in Figure 14.

\[
G_s (\text{ilmenite+biomass}) = 0.0023e^{0.31U}
\]

(14)

\[
G_s (\text{ilmenite+hard coal}) = 0.0022e^{0.35U}
\]

(15)

3.2.2. Mass of the Solid Fraction in Reactors

Figure 15 shows the total mass of solids in the reactors versus superficial gas velocity in the FR.

The increase in superficial gas velocity in the combustion chamber causes the increase of the solids circulating rate in both cases. The following equations describe these correlations:

\[
m_{(\text{ilmenite+biomass})} = 1.26U + 1.01
\]

(16)
m_{(ilmenite+hard coal)}^{AR} = 0.84U + 0.93 \tag{17} \\
m_{(ilmenite+biomass)}^{FR} = -1.26U + 3.50 \tag{18} \\
m_{(ilmenite+hard coal)}^{FR} = -0.84U + 2.72 \tag{19}

3.2.3. Particles’ Residence Time

The superficial gas velocity in both reactors affects many of the analyzed parameters, including the mass of material in the reactors, which in turn affects the residence time of the particles in the reactors. Figure 16 shows the particles’ residence time in the reactors versus superficial gas velocity in the FR.

Figure 16. The particles’ residence time in the reactors versus superficial gas velocity in the FR (a) AR; (b) FR.

The increase of superficial gas velocity in an FR causes an increase in the particles’ residence time in the AR and a decrease in the particles’ residence time in the FR. This behavior can be described by formulas Equations (20)–(23):

\[ t_{R}^{AR \text{ (ilmenite+biomass)}} = 719.05U^{0.20} \tag{20} \]
\[ t_{R}^{AR \text{ (ilmenite+hard coal)}} = 566.45U^{-0.10} \tag{21} \]
\[ t_{R}^{FR \text{ (ilmenite+biomass)}} = 753.74U^{0.48} \tag{22} \]
\[ t_{R}^{FR \text{ (ilmenite+hard coal)}} = 633.17U^{-0.46} \tag{23} \]

3.2.4. The Number of Oxygen Carrier Cycles

The number of OC cycles indicates how many times the particle will flow through the reactor in one hour. The number of OC cycles in reactors versus superficial gas velocity in the FR is shown in Figure 17.
The number of ilmenite cycles in reactors versus superficial gas velocity in the FR (a) AR; (b) FR.

The decrease in the number of OC cycles in the AR and increase of OC cycles in the FR is resulting from an increase in the superficial gas velocity in FR, as described by Equations (24)–(27):

\[
\begin{align*}
n^{\text{AR}}_{\text{C( ilmenite+biomass)}} &= -1.88U + 6.78 \\
n^{\text{AR}}_{\text{C( ilmenite+hard coal)}} &= -1.16U + 7.45 \\
n^{\text{FR}}_{\text{C( ilmenite+biomass)}} &= 3.12U + 1.78 \\
n^{\text{FR}}_{\text{C( ilmenite+hard coal)}} &= 3.61U + 2.25
\end{align*}
\]

3.2.5. Emissions from the Fuel Reactor

The primary gas emissions versus the superficial gas velocity in the FR are shown in Figure 18. The effect of superficial gas velocity in FR on CO\textsubscript{2}, SO\textsubscript{X}, and NO\textsubscript{X} emissions can be described by the following Equations (28)–(33):

\[
\begin{align*}
\text{CO}_2^{\text{dry ( ilmenite+biomass)}} &= 0.92 \ln(U) + 98.47 \\
\text{CO}_2^{\text{dry ( ilmenite+hard coal)}} &= 0.89 \ln(U) + 98.73 \\
\text{SO}_X^{\text{dry ( ilmenite+biomass)}} &= -0.58 \ln(U) + 9.56 \\
\text{SO}_X^{\text{dry ( ilmenite+hard coal)}} &= -3.38 \ln(U) + 58.43 \\
\text{NO}_X^{\text{dry ( ilmenite+biomass)}} &= -10.98 \ln(U) + 102.7 \\
\text{NO}_X^{\text{dry ( ilmenite+hard coal)}} &= -3.65 \ln(U) + 75.18
\end{align*}
\]

The increase of superficial gas velocity in the FR causes a significant increase in CO\textsubscript{2} emissions, shown in Figure 18a. Since CO\textsubscript{2} constitutes the FR’s fluidizing gas, it dilutes other flue gas components, leading to the decrease in SO\textsubscript{X} and NO\textsubscript{X} emissions, shown in Figure 18.
Figure 18. The emissions from hard coal and biomass combustion versus the superficial gas velocity in the FR: (a) CO₂, (b) SOₓ, (c) NOₓ.

The high concentration of CO₂ in the exhaust gas (97–99%) confirms that the end product is practically pure CO₂ that can be stored. Thus, energy is saved for the capture of CO₂ from the flue gas, which proves the thermoeconomic benefits [31–35].

4. Conclusions

The CLC model developed and presented in this work concerns ilmenite as an OC and two different solid fuels, i.e., wood chips and hard coal. The model was successfully validated against measured data. The relative error calculated during the validation of the developed model does not exceed 10%.

The increase in superficial gas velocity leads to an increase in the number of OC cycles and the decrease in the mass of materials and residence time of the particles in the FR. Moreover, the increase in gas superficial velocity in the FR causes the increase of CO₂ emissions and a simultaneous decrease in NOₓ and SOₓ concentrations in the flue gas. The increase in CO₂ concentrations is because the fuel reactor is fluidized by CO₂, hence the dilution of the other flue gas components concentrations.

The obtained high concentration of CO₂ in the exhaust gas means that there is no need to clean the exhaust gas of CO₂, which is favorable from the thermoeconomic point of view.

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Nomenclature

| Symbol | Definition |
|--------|------------|
| CeSFaMB | Comprehensive Simulator of Fluidized and Moving Bed equipment |
| FB-CLC-SF | The Fluidized-Bed Chemical-Looping-Combustion of Solid-Fuels |
| CLC | Chemical Looping Combustion |
| AR | Air reactor |
| FR | Fuel reactor |
| OC | Oxygen carrier |
| iG-CLC | in-situ Gasification Chemical Looping Combustion |
| U | Superficial gas velocity [m s⁻¹] |
| mf | Gas mass flow rate [kg s⁻¹] |
| GS | Solid circulating rate [kg (m² s)⁻¹] |
| nc | Number of oxygen carrier cycles [cycles h⁻¹] |
| tr | Particles residence time [s] |
| m | Mass of solid in reactors [kg] |

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