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Synthesis Gas Composition Prediction for Underground Coal Gasification Using a Thermochemical Equilibrium Modeling Approach

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Abstract: Underground coal gasification (UCG) is an in situ conversion technique that enables the production of high-calorific synthesis gas from resources that are economically not minable by conventional methods. A broad range of end-use options is available for the synthesis gas, including fuels and chemical feedstock production. Furthermore, UCG also offers a high potential for integration with Carbon Capture and Storage (CCS) to mitigate greenhouse gas emissions. In the present study, a stoichiometric equilibrium model, based on minimization of the Gibbs function has been used to estimate the equilibrium composition of the synthesis gas. Thereto, we further developed and applied a proven thermodynamic equilibrium model to simulate the relevant thermochemical coal conversion processes (pyrolysis and gasification). Our modeling approach has been validated against thermodynamic models, laboratory gasification experiments and UCG field trial data reported in the literature. The synthesis gas compositions have been found to be in good agreement under a wide range of different operating conditions. Consequently, the presented modeling approach enables an efficient quantification of synthesis gas quality resulting from UCG, considering varying coal and oxidizer compositions at deposit-specific pressures and temperatures.

Keywords: underground coal gasification; Cantera; thermodynamic equilibrium composition; synthesis gas; oxidizer

1. Introduction

UCG technology aims at the in situ conversion of coal deposits for the production of a high-calorific synthesis gas, which is applicable to fuel, hydrogen, fertilizer, chemical feedstock production and optionally natural gas substitution [1–4]. UCG allows for utilization of deep-seated coal deposits that are not economically extractable by conventional coal mining, and therefore has the potential to increase worldwide coal reserves. This re-emerging technology could provide a relevant contribution to the development of Clean Coal Technologies, whereby CO_2 may be used (Carbon Capture and Utilization: CCU) as raw material for fuel production (e.g., methanol), while excess CO_2 can be stored in exhausted UCG reactors in the subsurface (Carbon Capture and Storage: CCS) [5,6]. Aiming at a preferably CO_2 emission-neutral synthesis gas production, the integrated process can substantially reduce the carbon emissions resulting from coal utilization [7].

The complexity of the simultaneously occurring physical and chemical processes during UCG, such as chemical reactions, heat and mass transport phenomena, dynamic flow in the reactor and water inflow from the surrounding rock mass is remarkably high [8–10]. Therefore, various simplifying physical and chemical assumptions are required to isolate and understand the processes driving coal conversion, while improving numerical model convergence, and thus reducing the required computational times [11]. Efficient synthesis gas production in an UCG reactor depends on a number of tightly coupled chemical reactions, including pyrolysis, partial oxidation of pyrolysis products, gasification of the resulting char and conversion of tar and lower hydrocarbons [11,12]. Hereby, gasification is the thermochemical conversion of carbonaceous materials (coal and/or biomass) into a high-calorific synthesis gas in the presence of an oxidizer, which may consist of air, oxygen-enriched air and/or water vapor. In the past decade, it has received increasing attention due to the growing demand for fuels and chemical feedstocks [13–18]. The chemical mechanisms of gasification are well documented and have been studied extensively, i.e., by [12,17,19–21]. Different types of gasification models have been developed so far, including simplified zero-dimensional to complex 3D models. These models have been published using different classifications, designations and categories [13]. Gasification simulation models can be generally classified into the following three groups: thermodynamic equilibrium [14,15,17,18,22–26], kinetic [27–30] and artificial neural network (ANN) models [31,32]. Guo et al. [31] have shown that ANNs, which have been extensively used in the fields of pattern recognition, signal processing, function approximation and process simulation can also be applied to predict product yield and synthesis gas compositions of a gasification process. In their study, a hybrid neural network has been developed to simulate the gasification of biomass in a fluidized-bed gasifier. This modeling approach usually combines a partial first principles model, which incorporates the available prior knowledge about the process being simulated with a multi-layer feed-forward neural network and serves as an estimator of unmeasured process parameters that are difficult to model from first principles [32]. It has the ability to approximate any continuous function to an arbitrary precision, even without a priori knowledge on the structure of the function to be approximated. Therefore, these characteristics provide an efficient approach, especially in cases where the form of the function is unknown or too complex to simulate and explore gasification processes [31]. In this context, kinetic models allow in some instances for a better accuracy of the estimation of the synthesis gas composition [16], but require knowledge on kinetic parameters, which are usually obtained experimentally [14]. The synthesis gas yield and composition are provided by a kinetic model for a finite time period. This involves parameters such as reaction rates and residence times of the involved chemical species as well as reactor hydrodynamics and their integration with the kinetics of the gasification reactions [20]. Kinetic modeling is therefore more suitable and accurate at relatively low operating temperatures, where reaction rates are slow compared to those at high temperatures [20,33].

The equilibrium model proposed in the present study offers a general application with predictive capabilities without requiring an extended set of data to fit or train the model itself [16]. In this context, an equilibrium model allows for the investigation of the thermodynamic process limits and can be applied for process analysis and optimization [24]. Consequently, this modeling approach enables the estimation of the impacts of coal composition, reactor temperature and pressure as well as the oxidizer composition and formation water inflow on the synthesis gas quality. Although chemical or thermodynamic equilibrium may not be reached in a gasification reactor, equilibrium models provide the modeler with reasonable predictions on the bandwidth of the achievable yield of a desired gaseous product, especially at higher temperatures where the reaction rate is high and unstable species exist in the gas phase [17]. However, equilibrium models cannot predict the influence of hydrodynamic or geometric parameters such as fluidizing velocities or design variables, e.g., the reactor width and height [20]. Notwithstanding that this modeling approach has some inherent limitations, it can be used to predict the theoretical performance of an UCG process. Furthermore, research findings have highlighted the operational similarity between UCG

and surface fixed-bed gasifiers with regard to synthesis gas composition [34–36]. Numerous previous studies focussing on UCG operation and optimization have used the equilibrium modeling approach [26,37–41].

In the present study, the focus is on modeling the thermochemical processes taking place during UCG by applying the open-source thermodynamic software package Cantera with the Open Source GRI-Mech 3.0 mechanism [42] to determine the gaseous products. Our model implementation has been validated by comparison against a published pyrolysis test, experimental data recorded during ex situ gasification experiments and field trials, using air, pure oxygen and steam as oxidizer. Further, it is suitable for integration with numerical flow and transport simulators.

2. Materials and Methods

During UCG, temperatures of more than to 1,500 °C can be reached in the UCG reactor and its close vicinity [43]. Thereby, pyrolysis reactions occur at a specific temperature range (350-900 °C) [4], followed by a number of competing intermediate reactions including both, heterogeneous reactions between gas and char and homogeneous gas phase reactions [25]. Char, ash, tar and a synthesis gas are produced during the gasification process (Table 1).

Table 1. The most relevant heterogeneous (gas–char) and homogeneous (gas phase) chemical reactions that occur in underground coal gasification [19].

Reaction Name	Stoichiometry	Standard Heat of Reaction, ΔH^0_{298} (kJ/mol)
Pyrolysis	$Coal \longrightarrow Char, ash, tar, CO, CO_2,$ H_2, H_2O, CH_4	~ 0
Oxidation	$C + O_2 \longrightarrow CO_2$	-393.0
Boudouard	$C + CO_2 \longleftrightarrow 2CO$	$+172.5$
Methanation	$C + 2H_2 \longrightarrow CH_4$	-75.0
Steam Gasification	$C + H_2O \longrightarrow H_2 + CO$	$+131.0$
Water-Gas Shift	$CO + H_2O \longleftrightarrow CO_2 + H_2$	-41.0
Carbon Monoxide Oxidation	$CO + \frac{1}{2}O_2 \longrightarrow CO_2$	-283.0
Methane-Steam Reforming	$CH_4 + H_2O \longleftrightarrow CO + 3H_2$	$+206.0$

A Python code has been developed using the Cantera software package to simulate the coal gasification process by means of the thermodynamic equilibrium approach. Cantera is an open-source suite of object-oriented software tools for simulation of chemical kinetics, thermodynamics and transport processes [44]. The GRI-Mech 3.0 [42] database has been used to determine the thermodynamic properties (e.g., enthalpy, entropy and specific heat capacity as function of temperature) of the chemical species considered in the model. The equilibrium method used in the present study is based on minimizing the Gibbs function. The three independent equilibrium reactions used for the equilibrium calculations are the water-gas shift, methanation and Boudouard reactions (see Figure 1).
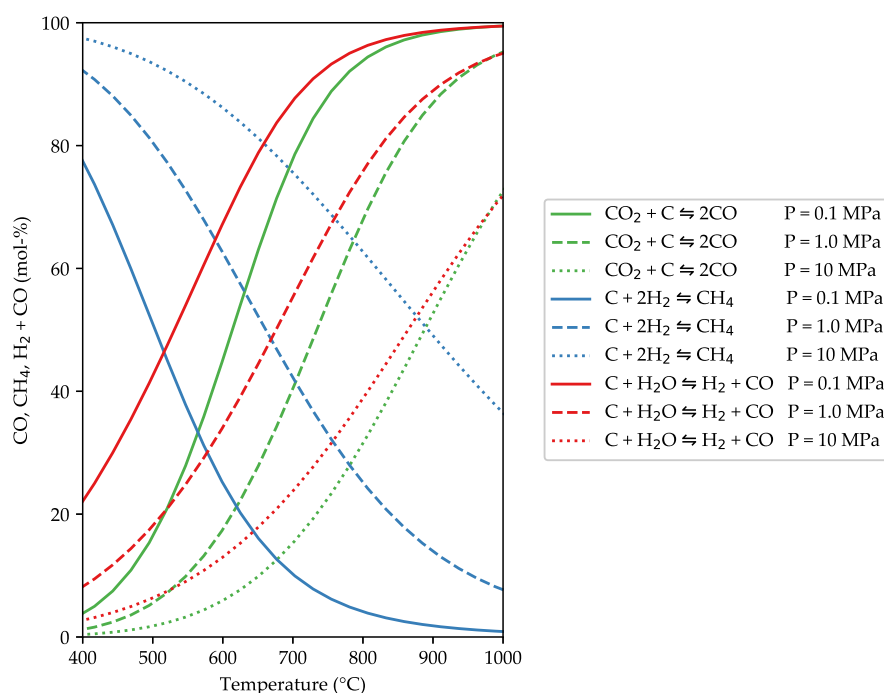
Figure 1. Equilibrium states of the Boudouard (green), methanation (blue) and water-gas reactions (red) at varying temperatures and pressures simulated with the Cantera software package [44].

This set of competitive reactions plays an important role in determining the hydrogen-to-carbon monoxide ratio in the synthesis gas. To sustain the process, the conversion reactions must generate sufficient heat to provide the required activation energy as well as to overcome the heat losses due to water evaporation and the endothermic gasification reactions at appreciable rates [45].

One of the main advantages of the applied method is that it does not require a selection of specific chemical reactions allowing for the formation of reaction products. However, it is necessary to provide a database of chemical species including those expected in the reaction product [16]. The main equilibrium models discussed in the literature consider following simplifying assumptions, resumed by La Villetta et al. [46] and Ferreira et al. [13]:

- reactions are considered not to vary in time and space (steady-state batch reactions),
- reactions are fast enough to reach an equilibrium state (infinite residence time),
- homogeneous mixing with uniform pressure and temperature are assumed, although different hydrodynamics are observed in practice,
- kinetic and potential energies are neglected,
- ideal gas behavior of the gas phase,
- pyrolysis is considered as a single step reaction producing gas,
- the reactor is considered adiabatic,
- the produced gas does not contain any oxygen, and
- solely major species compose the produced synthesis gas (e.g., CO, CO_2, H_2, CH_4, N_2 and H_2O).

Tar has been generally neglected in simulation studies based on equilibrium models. However, Klebingat et al. [37,47] presented an innovative and flexible modeling approach for coupled synthesis gas quality and tar production quantification. For the equilibrium model applied in the present study, some general assumptions have been made to simulate the gasification process [12]:

- temperature of the products is equal to the gasification temperature,
- oxygen is completely consumed,
- the final synthesis gas mixture is in equilibrium and homogeneous,
- all involved chemical reactions can reach an equilibrium state,
- coal is composed of C, H, O, N and S,
- solid gasification products include only char, which is entirely composed of carbon, and,
- ash and tars are not considered in the simulations.

The model comprises one solid species C(s) and 60 chemical species for the gas phase. The chemical species considered in the model are shown in Table 2.

Table 2. Chemical species considered in the applied equilibrium model (modified after Baratieri et al. [16]).

Phase	Group	Compounds
Solid	Carbon	$C(s)$
Gas	Inorganic carbon compounds	$C(g)$, CO, CO_2
	Hydrogen compounds	H, H_2, O, O_2, OH, H_2O, HO_2, H_2O_2, HCO
	Nitrogen compounds	N, N_2, NH, NH_2, NH_3, NNH, NO, NO_2, N_2O, HNO, CN, HCN, H_2CN, $HCNN$, $HCNO$, $HOCN$, $HNCO$, NCO
	Sulfur compounds	S, SO_2, SO_3, H_2S, COS, CS_2
	Hydrocarbons	CH, CH_2, CH_3, CH_4, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_3H_7, C_3H_8, C_6H_6, $C_{10}H_8$, $C_{12}H_{10}$
	Other organic compounds	CH_2O, CH_2OH, CH_3O, CH_3OH, $HCCO$, CH_2CO, $HCCOH$, CH_2CHO, CH_3CHO

Minimisation Problem of the Thermodynamic Equilibrium

The following description of the minimisation problem of the thermodynamic equilibrium is borrowing the terminology from Smith and Missen [48], Wong [49] and Meyer [50]. Here, only a summary of the concept is given, while its comprehensive representation is discussed in the references given above.

Chemical equilibrium analyses are done in general for a system with a number of constraints, which can be classified in mandatory constraints (conservation of mass and non-negativity) and specific constraints (temperature and pressure). In a closed thermodynamic system, chemical stoichiometry is a constraint on the compositional changes, requiring that elemental abundances are conserved during physiochemical changes within a system. In such a system, the chemical equilibrium state will be reached including thermodynamic and phase equilibrium. Constant temperature and pressure as specific constraints have to be determined as defining parameters of the system, whereby the thermodynamic properties are provided by suitable equations of state. A system in a stable equilibrium state contains a total number of chemical species N and a number of elements M without mass exchange with its surroundings. The conservation of mass constraint can be expressed by a set of atom-balance equations as formulated by the following relation between the fixed number of moles b_k of the element k, and the number of moles of the ith species n_i [50]:

$$\sum_{i=1}^{N} a_{ki} n_i = b_k \quad \text{with} \quad k \in \{1, 2, ..., M\}, \tag{1}$$

whereby, a_{ki} is defined as the index of the element k in the molecular formula of the ith species. The species considered in the system must either be present or absent at chemical equilibrium, therefore the mathematical form

$$n_i \geq 0, \quad \text{where} \quad i \in \{1, 2, ..., N\} \tag{2}$$

expresses the non-negativity constraint. A change in the element abundance δn_i is not feasible in a closed system; therefore, the number of moles of the ith species between two compositional states of the system must satisfy

$$\sum_{i=1}^{N} a_{ki} \delta n_i = 0 \quad \text{with} \quad k \in \{1, 2, ..., M\}. \tag{3}$$

The second law of thermodynamics provides a statement for conditions that allow to connect chemical equilibrium conditions to the Gibbs potential function G, where $G = H - TS$ with H as the total enthalpy and S as total entropy of the system [49]. In a closed adiabatic system with fixed temperature and pressure, the Gibbs function G can not increase and the entropy can not decrease. The Gibbs function G has its global minimum when the system is in equilibrium. Thereby, the total differential of the Gibbs function is depending on the number of moles of the ith species n_i, the corresponding chemical potential μ_i, and is expressed as

$$dG = \sum_{i=1}^{N} \mu_i dn_i. \tag{4}$$

The standard chemical potential μ_i characterizes the tendency of a species to pursue a change of composition and aggregate state. It is a function of the moles of the different compounds n_i and defined by

$$\mu_i = \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}. \tag{5}$$

The closed-system constraint is treated by means of the linearly independent stoichiometric Equation (6) to result in an unconstrained minimization problem, where n_i^0 is any solution (e.g., an initial composition of the chemical system), ν_{ij} represents the stoichiometric coefficient vector of the ith species in the jth stoichiometric vector, ξ_j the reaction extents variable and R denotes the maximum number of linearly independent solutions

$$n = n_i^0 + \sum_{j=1}^{R} \nu_{ij} \xi_j \quad \text{with} \quad i \in \{1, 2, ..., N\}. \tag{6}$$

If n_i^0 is fixed, the stoichiometric coefficient vector ν_{ij} can be written as

$$\left(\frac{\partial n_i}{\partial \xi_j} \right)_{\xi_{k \neq j}} = \nu_{ij} \quad \text{with} \quad i \in \{1, 2, ..., N\} \text{ and, } j \text{ and } k \in \{1, 2, ..., R\}. \tag{7}$$

The minimization procedure applied to the Gibbs function G implies the computation of its partial derivatives with respect to ξ_j given in Equation (8) and provides the equilibrium condition for the chemical potential μ_i (Equation (5)), which is a function of the number of moles n_i of the different compounds (Equation (7)).

$$\left(\frac{\partial G}{\partial \xi_j} \right)_{T,P,\xi_{i \neq j}} = \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} \left(\frac{\partial n_i}{\partial \xi_j} \right)_{\xi_{k \neq j}} = 0 \quad \text{with} \quad j \in \{1, 2, ..., R\}. \tag{8}$$

This is, in consistence with Equations (5) and (7) equal to

$$\sum_{i}^{N} \nu_{ij} \mu_i = 0 \quad \text{with} \quad j \in \{1, 2, ..., R\}, \tag{9}$$

and states the equilibrium conditions.

Mathematically, chemical equilibrium problems can be classified on the basis of the algorithm used for Gibbs function minimization of the gasification system into stoichiometric and non-stoichiometric formulations. Non-stoichiometric formulations do not use chemical stoichiometry and treat the conservation of mass separately, while stoichiometric formulations use chemical stoichiometry for mass conservation, so that the result is essentially an unconstrained problem [51]. The nonlinear equations resulting from the first-order conditions required for a minimum G at fixed T and P as a function of ξ can be rewritten alternatively to Equations (7) and (9) as

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0. \tag{10}$$

This equation can be solved by modifying the reaction extent variable ξ by first- and second-order optimization methods. Further improvement has been done by Smith and Missen [48], who developed the Villars-Cruise-Smith (VCS) algorithm, which represents an optimized stoichiometric formulation.

Cantera currently offers non-stoichiometric and stoichiometric formulations to apply the Gibbs function minimization technique for a given chemical system [44]. In the present study, the stoichiometric formulation incorporated in Cantera is applied. The stoichiometric solver uses the VCS algorithm [48], which is more efficient if there are only a few independent stoichiometric equations. The VCS algorithm has been developed for systems with constant temperature and pressure constraints and is applied in Cantera iteratively until the difference of the chemical potential between two computational steps is less than a pre-defined convergence criterion [16]. Using the previously introduced approach, the present equilibrium model allows calculating an equilibrium state with a large number of phases and chemical species [14]. A database of expected species in the solid and gaseous products must be established a priori (Table 2). Thus, a large solution space has to be used, comprising even rarely occurring species, such as single-atom species at high temperatures.

3. Results and Discussion

The present model has been validated against published thermodynamic equilibrium and kinetic modeling results as well as experimental and field trial data on gasification processes. Table 3 shows the characterization of the considered fuel properties and oxidizers used.

As a test case for the present equilibrium model, the thermochemical conversion of pine sawdust has been simulated and the results compared to those of Baratieri et al. [16]. The latter support the interpretation of the achieved results on the synthesis gas composition, since their models include pyrolysis simulations and show the limits of the thermochemical process in absence of any oxidizer. Another equilibrium model implemented by Li et al. [17] has been chosen to analyze the impact of the oxidizer on the synthesis gas composition. Thereby, the stoichiometric ratio (SR) is defined as the ratio between the oxygen fed into the gasification system and the stoichiometric quantity of oxygen required for complete oxidation of the reacting chemical species. Further, different laboratory gasification results have been chosen for model validation, since these combine detailed information on feedstock, product composition and its lower heating value (LHV) under typical operating conditions and distinct gasifier configurations [52]. In addition, two experiments from the large block experiments (Centralia, USA) have been chosen for comparison of our modeling results against UCG trial data, which is also discussed and compared with a kinetic model introduced by Perkins and Sahajwalla [53]. Finally, our modeling results are also compared against the field-scale experiments from the Hanna I pilot site (Wyoming, USA) and the equilibrium model published by Klebingat et al. [37].

Table 3. Characterization of fuels considered for model validation.

Type	Case	Ultimate Analysis (% by mass, af *)							Oxidizer	SR **	References
		C	H	O	N	S	Moisture	Chemical formula (mol/mol C)			
Pine sawdust	Pyrolysis test	45.20	5.40	39.00	0.10	0.00	9.40	$CH_{1.466}N_{0.002}S_{0.000}O_{0.662}$	-	-	[16]
Subbituminous coal	Highvale, CA	66.05	3.81	18.70	0.80	0.20	10.39	$CH_{0.692}N_{0.010}S_{0.001}O_{0.212}$	Air	0.4	[17]
Ortho-lignite	Oltenia, ROU	57.67	4.59	19.95	1.56	2.83	13.39	$CH_{0.955}N_{0.023}S_{0.018}O_{0.259}$	Oxygen	0.35	[52]
Subbituminous coal	LBK-4, Centralia, USA	76.00	4.70	18.70	0.10	0.40	0.00	$CH_{0.742}N_{0.001}S_{0.002}O_{0.185}$	Steam	0.3	[53]
Subbituminous coal	LBK-5, Centralia, USA	76.00	4.70	18.70	0.10	0.40	0.00	$CH_{0.742}N_{0.001}S_{0.002}O_{0.185}$	Air	0.3	[53]
Subbituminous coal	Hanna I, Hanna, USA	74.33	6.03	16.68	1.94	1.02	0.00	$CH_{0.973}N_{0.022}S_{0.005}O_{0.168}$	Air	0.12	[37]

* af = ash free; ** SR = stoichiometric ratio, defined as ratio between the oxygen fed into the gasification system and the stoichiometric quantity of oxygen required for the complete oxidation of the reacting chemical species.

3.1. Model Validation against Other Equilibrium Models

Baratieri et al. [16] developed an equilibrium model (gas–solid), based on the minimization of Gibbs energy to estimate the theoretical yield and equilibrium composition of the reaction products (synthesis gas and char) of thermochemical biomass conversion processes. In their model, only five major species are present at significant amounts in the synthesis gas produced during the pyrolysis of a pine sawdust. The synthesis gas equilibrium composition is plotted as a function of temperature and compared to literature data in Figure 2. Comparing these results against those produced by the model developed in the present study shows that the predicted molar fractions of the synthesis gas components match very well. Analyzing the results of the thermodynamic equilibrium composition of the synthesis gas demonstrates that the formation of CH_4 and CO_2 is favored at lower temperatures, whereas CO and H_2 are the dominant equilibrium products at higher temperatures. Considering the equilibrium reactions, this effect mainly results from the increasing influence of the endothermic water-gas shift reaction that induces a corresponding decrease in the synthesis gas steam content generated by the drying of the feedstock. The CO_2 trend goes through a maximum according to its exothermic formation and endothermic conversion at about 500 °C [16]. Furthermore, the results emphasize the fundamental role of the process temperature which directly influences the calorific value of the synthesis gas, and therefore the overall gasification efficiency.
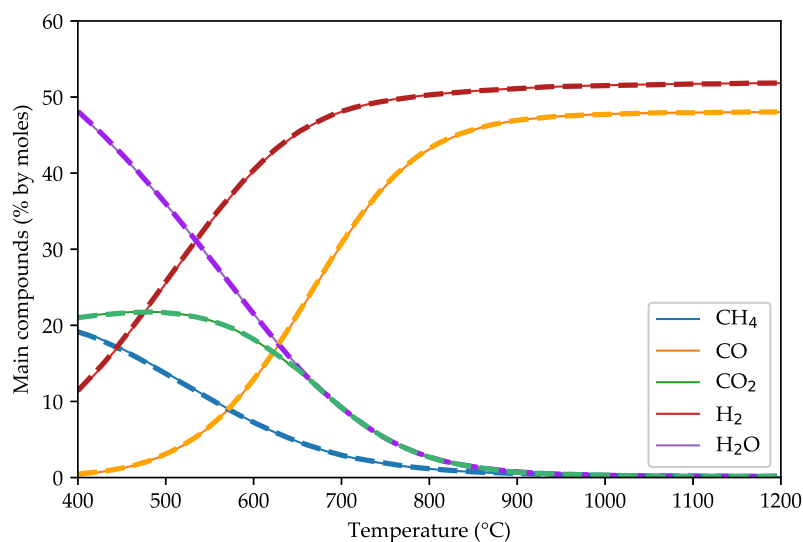

Figure 2. Simulation results for the synthesis gas equilibrium composition plotted as function of process temperature for the pine sawdust pyrolysis test at 0.1 MPa (dashed lines) compared to literature data [16] (solid lines).

Three general approaches of fixed-bed gasification are currently focused in ongoing research activities, whereby gasification using air as oxidizer besides pure oxygen and steam is the most widely applied method to produce synthesis gas [15]. Using different feedstock at varying operating conditions and oxidizer compositions, a significant variation in the synthesis gas composition can be achieved in view of its envisaged end-use. Therefore, we further compared our model with that of Li et al. [17], who used a non-stoichiometric equilibrium model based on Gibbs free energy minimization to predict the performance of an air-blown pressurized circulating fluidized-bed coal gasifier. Figure 3 shows their results on the variation of the molar contents of the six main species in the synthesis gas with temperature for a

subbituminous coal, plotted against our simulation results. The synthesis gas composition predicted by our model agrees very well with that calculated by Li et al. [17].
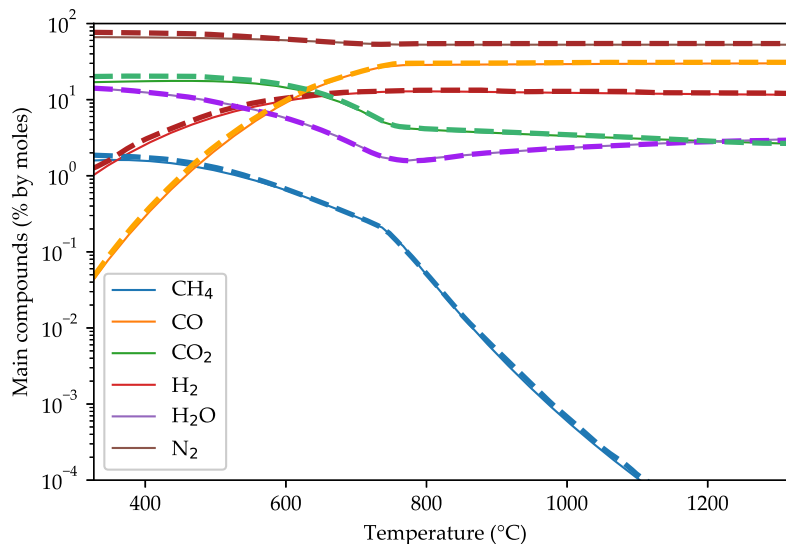

Figure 3. Comparison of the simulated (dashed line) variation of the equilibrium synthesis gas composition with temperature for Highvale coal against the modeling results produced by Li et al. [17] (solid lines) ($p = 0.155$ MPa, stoichiometric ratio = 0.4).

The simulated species fraction in the synthesis gas corresponds with that in the previously discussed pyrolysis test introduced by Baratieri et al. [16], except for N_2 which is present in the synthesis gas when air is used as oxidizer. The concentrations of CO and H_2 increase with temperature, while the number of moles of CO_2, H_2O and CH_4 decrease. A sudden upturn of H_2O content with a simultaneous decrease in methane occurs at about 750 °C, where water production first exceeds water consumption [17]. Especially in the context of UCG, this transition shows the far-reaching importance of the role of water. The presence of water plays a vital role in the UCG process, providing a source of hydrogen for the steam gasification and methanation reactions, which contribute significantly to the calorific value of the synthesis gas [54]. Water also favors the water–gas shift reaction, which trades carbon monoxide for hydrogen and produces water by oxidation of CH_4 and H_2. Accompanying this transition, CO_2 becomes the dominant product of carbon combustion, limiting the sharp decrease occurring at higher temperatures [17].

3.2. Model Validation against UCG Experimental Data

The UCG process is difficult to control in the subsurface. Hence, much effort has been invested into feasibility assessments and technology development by high-pressure experimental testing to increase its efficiency and stability (e.g., [52,55–57]). Wiatowski et al. [52] conducted experimental simulations of UCG, using large bulk samples of two lignites in an ex situ laboratory installation. Their study aimed at assessing the feasibility of synthesis gas production from low-grade high-moisture lignites by gasification [52]. Amongst other things, the changes in the composition of the synthesis gas, its production rates, oxidizer compositions, supply rates and temperatures were measured during the experiments. For the ortho-lignite gasification test (see ultimate characteristics of coal in Table 3), pure oxygen has been applied as oxidizer at a pressure of 1 MPa. During the 72-hour lasting experiment, the gasification has been separated into particular stages with different oxidizer compositions. The average synthesis gas compositions obtained

from the gasification of the ortho-lignite are compared against our modeling results in Figure 4. In general, the gasification period was characterized by a very high concentration of CO_2 and a low overall LHV ($\leq$ 4 MJ/Nm^3). Our modeling results show a good agreement with the gas compositions and LHV achieved during the experiments. However, the simulated CO amount is slightly higher than that in the experimental findings. During the final stage (Stage III) of the experiment, combustion reactions start to dominate, gradually increasing CO_2 concentrations in the synthesis gas [52].
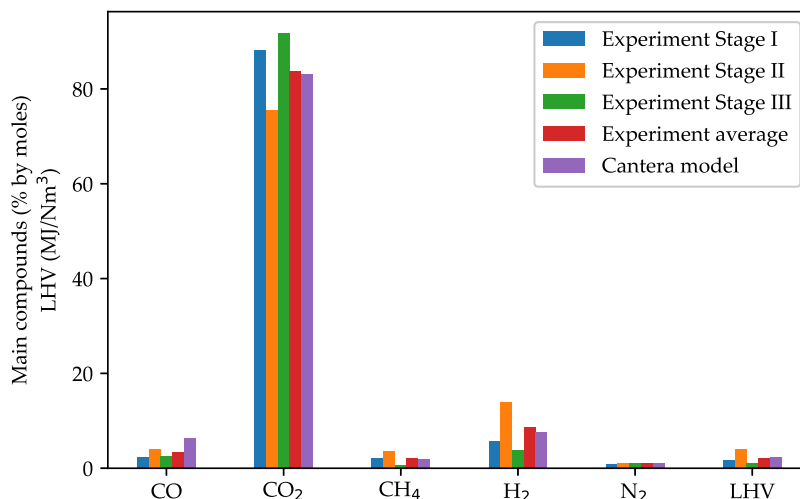
Figure 4. Comparison of average gas compositions for the three gasification stages and the average total gas composition of the Oltenia ortho-lignite experiment [52] against the results of our Cantera model (T = 580 $^\circ$C, *p* = 1 MPa, stoichiometric ratio = 0.35).

3.3. Model Validation against UCG Field Trials

UCG field trials have been performed in different coal seams worldwide under a variety of operating conditions, using different techniques to evaluate the effects of various factors on its overall performance [11]. During the early 1980s, the Lawrence Livermore National Laboratory conducted a series of small-scale UCG field trials at shallow depths in Centralia (WA, USA) to determine the general feasibility of in situ coal gasification [58]. Five trials, named LBK-1 to LBK-5, have been originally designed to study reactor growth in isolated coal blocks and to improve the understanding on the impacts of operating conditions on synthesis gas production and reactor development [53,58]. Perkins and Sahajwalla [53] developed a pseudo one-dimensional gasification channel model to estimate gas production from UCG and compared the resulting synthesis gas compositions with those from the Centralia field trials for model validation. Their kinetic modeling approach incorporates a zero-dimensional steady-state reactor growth submodel for the reaction of solid coal with the gas phase, which has been validated independently via a comparison against laboratory experiments.

A comparison of the data observed at the LBK-4 and LBK-5 UCG field tests, model simulation results of Perkins and Sahajwalla [53] and those produced by our model is presented in Figures 5 and 6, respectively. The LBK-4 field trial has been conducted with a steam-to-oxygen ratio of 1:1. At the LBK-5 field trial, a variety of injected oxidizer compositions has been tested during the experiment [58]. However, Perkins and Sahajwalla [53] only discuss the synthesis gas compositions achieved by air-blown UCG operation.
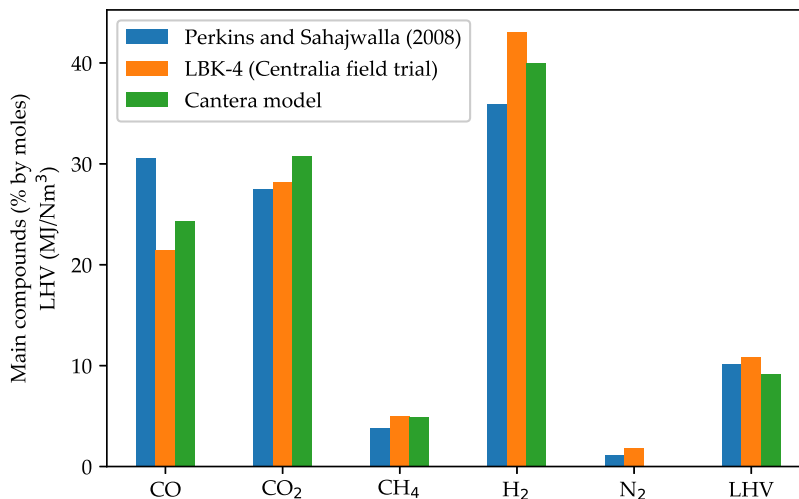
Figure 5. Comparison of our simulation results on the Centralia Large Block experiment LBK-4 (T = 630 °C, *p* = 0.125 MPa, stoichiometric ratio = 0.3) against field data [58] and the kinetic modeling results of Perkins and Sahajwalla [53].

Figures 5 and 6 demonstrate that our model also exhibits a good agreement with the synthesis gas composition achieved during small-scale field trials under different operating conditions, including operation with air and steam-oxygen mixtures.
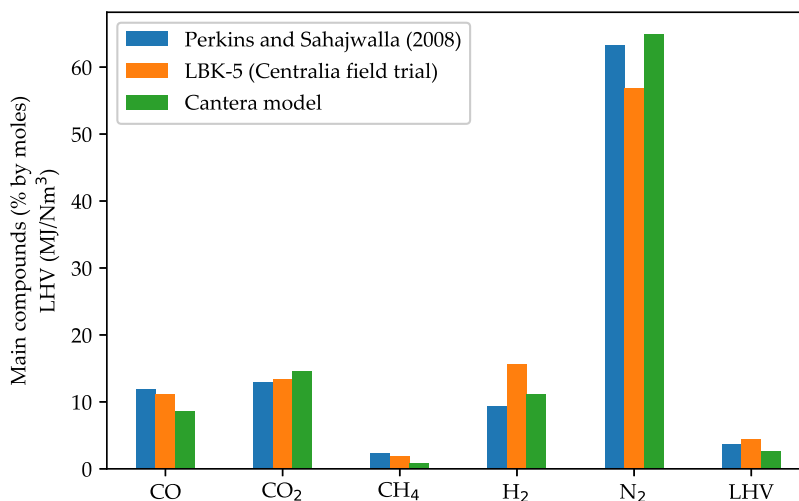

Figure 6. Comparison of our simulation results on the Centralia Large Block experiment LBK-5 (T = 585 °C, *p* = 0.125 MPa, stoichiometric ratio = 0.3) against field data [58] and the kinetic modeling results of Perkins and Sahajwalla [53].

The results are comparable with those achieved by the kinetic modeling approach of Perkins and Sahajwalla [53]. However, there is a notable underprediction of the H_2 content and overprediction of the CO_2 content in the synthesis gas, although it is lower in our modeling results than in those produced by Perkins and Sahajwalla [53] model. This also leads to a slight underestimation of the synthesis gas LHV. In addition, the applied gasification temperature of 630 °C has been much higher than that of the synthesis gas temperature measured in the field at the production well head (200 °C). Perkins and Sahajwalla [53] expect that these differences are mainly due to the injection of water into the production well for cooling purposes as reported by Hill et al. [58].

During the mid to late 1970s, the Laramie Energy Technology Center conducted five pilot tests at the Hanna site (Wyoming, USA). In the context of the Hanna I large-scale experiment, a thick subbituminous coal seam at a depth of 120 m has been assessed for its suitability to be developed by UCG [59].

In order to obtain the composition of the produced tar pollutant products and synthesis gas, Klebingat et al. [37] considered the experimental data of the Hanna I site for validation of their model. It is based on chemical and phase equilibrium balances under minimization of the Gibbs function and allows to simulate tar production to optimize operating conditions in view of synthesis gas quality and tar products [37]. Thereby, their thermodynamic tar production model considers the main chemical in situ gasification sub-processes of drying, pyrolysis, partial oxidation, gas mixing, water influx, optional gas losses, and a selected model tar set including the typical pollutants [37]. The simulated main tar product and synthesis gas compounds are close to the data reported for the Hanna I site [37]. A comparison of our modeling results with the synthesis gas composition determined by Klebingat et al. [37] and that obtained during the Hanna I trial (Figure 7) shows a reasonably good agreement for the H_2 and CH_4 contents. However, the simulated CO and CO_2 amounts are slightly lower than those reported in the experimental findings, whereas the N_2 amount is slightly overestimated by both simulations. The synthesis gas LHV shows only a slight deviation with lower values determined by our model.
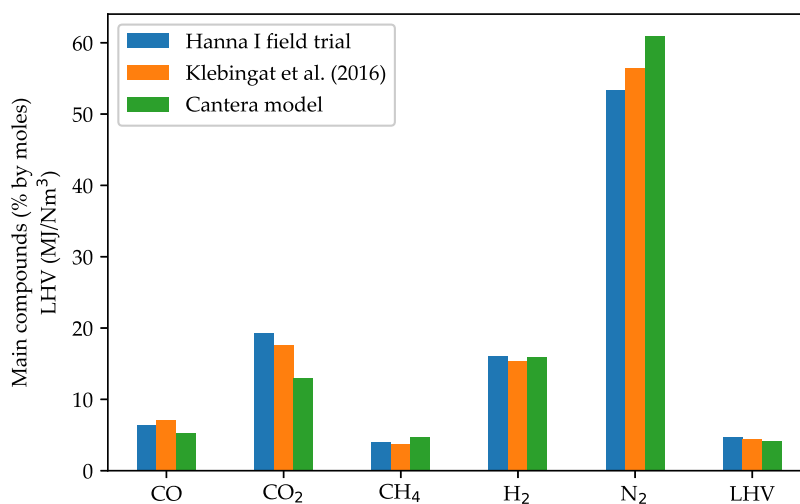

Figure 7. Comparison of our simulation results (T = 600 °C, *p* = 0.48 MPa, stoichiometric ratio = 0.12) against the Hanna I experiment field data [60] and the thermodynamic modeling results of Klebingat et al. [37].

We conclude from the presented results that our modeling approach is capable of reflecting the most important processes, required to predict the UCG synthesis gas composition. Nevertheless, it has to be noted that the reported average gas composition combines those of the different stages of the gasification experiments, e.g., heating by increasing the oxygen content in the oxidizer, injection of steam to trigger H_2 production, etc. This is expected to be the main reason for deviations in the gas composition between the field trials and numerical simulations, in addition to the aforementioned simplifications introduced by zero-dimensional steady-state equilibrium models. Further, the field-trial simulation models discussed above are more complex than our implementation. The model approach from Perkins and Sahajwalla [53] is considering steady-state reactor growth and simulates mass transfer from the synthesis gas to the reactor wall using a correlation for natural convection. Klebingat et al. [37] used a system with various subunits, required for the simulation of tar pollutant production.

4. Summary and Conclusions

In the present study, we introduced a zero-dimensional coal gasification model to quantify and predict UCG synthesis gas compositions and LHV. The simulation results have been successfully validated against different numerical equilibrium and kinetic models from literature as well as UCG experimental and field data. Consequently, our modeling approach allows to assess the UCG process in order to find the optimum composition and calorific value of the synthesis gas under site-specific operating conditions, considering pressure, temperature, coal properties and oxidizer composition.

The synthesis gas composition resulting from coal gasification can be determined by applying different methods, such as artificial hybrid neural networks as well as kinetic or thermodynamic equilibrium approaches. Although kinetic models can provide essential information on reaction mechanisms and rates, equilibrium models are valuable because they can be applied to determine the thermodynamic limits to support process design, evaluation and improvement [17]. Equilibrium models require a reduced amount of information and are only valid under the assumption of chemical equilibrium [14]. Ferreira et al. [13] reported that thermodynamic equilibrium models are often applied as guideline, especially at high temperatures above 800 °C, supporting the prediction of the maximum feasible conversion rates at specific operating conditions. However, equilibrium conditions may not be reached in practice at relatively low temperatures. Underestimation of CH_4 and CO_2 and overestimation of CO and H_2 in the synthesis gas are frequently reported [12,61] and have been also observed in our simulations. We presume that the thermodynamic results deviate from experimental data due to the fact that a thermodynamic equilibrium may not have been achieved in the respective laboratory-scale and in situ reactors. Nevertheless, equilibrium models are suitable to estimate the influence of operating parameters on the synthesis gas composition of a thermochemical conversion process, especially at high temperatures of up to 1500 °C as observed during UCG operations [12].

Despite some simplifications, our modeling approach enables a computationally efficient thermodynamic and remarkably good prediction of synthesis gas compositions and calorific values at different scales of underground coal gasification. Therefore, the presented equilibrium model will substantially contribute to a better understanding of the underlying thermodynamic principles, governing the process of underground coal gasification.

In summary, we have developed and validated a fast thermodynamic equilibrium model that can be applied to assess synthesis gas compositions in UCG. In future work, the presented model will serve as basis for coupled thermo-hydro-chemical-mechanical transport models and process-unit level simulations employed in techno-economical models.

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