Thermodynamic modeling of solid fuel gasification in mixtures of oxygen and carbon dioxide

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Abstract. One of the main problems in the use of solid fuels is inevitable formation of significant amounts of carbon dioxide. The prospects for reducing CO$_2$ emissions (carbon capture and storage, CCS) are opening up with the use of new coal technologies, such as thermal power plants with integrated gasification (IGCC) and transition to oxygen-enriched combustion (oxyfuel). In order to study the efficiency of solid fuel conversion processes using carbon dioxide, thermodynamic modeling was carried out. Results show that difference between efficiency of fuel conversion in O$_2$/N$_2$ and O$_2$/CO$_2$ mixtures increases with an increase in the volatile content and a decrease in the carbon content. The effect of using CO$_2$ as a gasification agent depends on the oxygen concentration: at low oxygen concentrations, the process temperature turns out to be low due to dilution; at high oxygen concentrations, the CO$_2$ concentration is not high enough for efficient carbon conversion.

1. Introduction
Oxyfuel combustion (i.e. combustion using mixtures of oxygen with combustion products instead of air) is a promising way to increase efficiency of post-combustion carbon capture units [1]. Oxyfuel technologies for coal power plant are considered as the most efficient yet the most expensive for CCS systems [2]. Gasification allows capturing carbon dioxide using pre-combustion carbon capture method by means of water shift reactors [3]. There are some interesting projects on oxyfuel and high-temperature gasification processes of solid fuels [4-6]. The question arises: how much the characteristics of the gasification process change when using O$_2$/CO$_2$ mixtures instead of the commonly used O$_2$/N$_2$/H$_2$O mixtures?

Thermodynamic analysis is traditionally used to assess the limit values of physicochemical systems, so we use the thermodynamic model [7]. In [8, 9] equilibrium thermodynamic models and their combinations with models of heterogeneous kinetics were used to simplify the submodels of thermochemical transformations of solid fuels. In [10], one of the variants of kinetic-thermodynamic models was used to study the efficiency of high-temperature gasification of pulverized coal in O$_2$/CO$_2$ mixtures: calculations showed that a high concentration of CO$_2$ allows more efficient use of the combustion heat in spite of a decrease in the reaction temperature (due to the high heat capacity of CO$_2$). In this paper, the gasification process is considered without heating, but with various oxygen concentration.

2. Thermodynamic model
To study the limits of the thermochemical efficiency of solid fuel conversion in carbon dioxide, thermodynamic modeling was carried out. A similar model was applied in [11] to assess the effect of
excess water vapor on the efficiency of the coal gasification process. The problem of calculating the chemical state of the gas-fuel system is written as follows [12]:

\[ \mathbf{n}^{eq} = \arg \max S(\mathbf{n}), \]

\[ S(\mathbf{n}, T) = \sum_{j=1}^{N_g} n_j^{eq} \left( s_j^g(T) + R \ln \frac{n_j^n}{\sigma^g} \right) + \sum_{k=1}^{N_c} n_j^c s_j^c(T), \]

\[ A(\mathbf{n} - \mathbf{n}^{in}) = 0, \]

\[ \sum_{j=1}^{N_g + N_c} h_j(T) n_j = \sum_{j} h_j(T^{in}) n_j^{in}, \]

\[ n \geq 0. \]

Here \( S \) is entropy of system, J K\(^{-1}\); \( \mathbf{n} \) is composition in moles (\( \mathbf{n}^{in} \) is initial composition, \( \mathbf{n}^{eq} \) is equilibrium composition); indexes \( g \) and \( c \) refer to gaseous and condensed phases respectively; \( s_j \) is specific molar entropy of the \( j^{th} \) component, J mol\(^{-1}\) K\(^{-1}\); \( h_j \) is specific molar enthalpy of the \( j^{th} \) component, J mol\(^{-1}\); \( R \) is universal gas constant; \( \sigma^g \) is molar sum of gaseous components; \( A \) is atomic balance matrix. Thermochemical properties of individual substances are taken from handbook [13]. Solid fuel enthalpy is determined by higher heating value and enthalpy of combustion products. Coke properties are approximated by properties of pure graphite. Solution of the problem is not sensitive to the values of specific entropy of raw fuel, if these characteristics are arbitrary small.

The gasification efficiency indicators are the adiabatic temperature of the process, the yield of the char-coke residue and the cold gas efficiency, equal to the ratio of the produced gas combustion and the solid fuel heat value:

\[ \eta = \frac{q_{co} n_{co} + q_{H_2} n_{H_2} + q_{CH_4} n_{CH_4}}{Q_f} \times 100\% \]

Here \( Q_f \) is specific heating value of solid fuel, \( q_j \) is heating value of the \( j^{th} \) gaseous product, \( n_j \) is equilibrium yield of the \( j^{th} \) gaseous product (referred to 1 kg of raw fuel). Equilibrium cold gas efficiency is determined by stoichiometric and temperature factors [14]. In present calculations, the influence of fuel grade and fuel-oxidizer ratio on gasification efficiency is investigated. Initial temperature of gasification agent is 300 K, and working pressure is 1 atm.

Four different fuels were chosen for calculations. Coke is an example of "ideal" fuel with high carbon content; biomass is a typical low-grade fuel; also, two coals were studied, Kuznetsk coal and Berezovsk brown coal [15]. Compositions of fuels are presented in Table 1.

| Fuel       | \( W_r \), % | \( A_d \), % | \( V_{daf} \), % | \( C_{daf} \), % | \( H_{daf} \), % | \( O_{daf} \), % | \( N_{daf} \), % | \( S_{daf} \), % |
|------------|--------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Coke       | 5            | 10           | 9             | 92             | 2.5            | 5              | 0.01           | 0.5            |
| Kuznetsk coal | 9            | 20           | 30            | 81             | 3.5            | 13.2           | 2.0            | 0.3            |
| Berezovsk coal | 12           | 9            | 48            | 69.4           | 4.9            | 24.3           | 0.9            | 0.5            |
| Biomass    | 10           | 1            | 85            | 49.5           | 6.3            | 44.15          | 0.05           | 0              |
In addition to the fuel composition, variable parameters in the calculations are the oxidizer consumption $\alpha$ (calculated in relation to the stoichiometric oxygen consumption) and the oxygen concentration in the gasification agent (from 21 to 90 vol. %). Two diluents are considered: nitrogen and carbon dioxide. Due to the facts that the specific molar heat capacity of CO$_2$ is higher than that of N$_2$, and the gasification reaction with CO$_2$ has an endothermic effect, the adiabatic temperature of coke gasification in O$_2$/CO$_2$ mixtures turns out to be much lower than the temperature of gasification in O$_2$/N$_2$ mixtures. With an increase in oxygen concentration, the effect of the diluent decreases; therefore, the difference between two diluents decrease.

**Figure 1.** Equilibrium cold gas efficiency of solid fuels gasification (%): coke (a, e), Kuznetsk coal (b, f), Berezovsk coal (c, g) and biomass (d, h); gasification agents are O$_2$/N$_2$ (a-d) and O$_2$/CO$_2$ (e-h).

The equilibrium characteristics of coke gasification in O$_2$/N$_2$ mixtures depend weakly on the oxygen concentration at $\alpha$ values lower than 0.5 (Figs. 1 and 2). At high temperatures, the course of isolines changes, which is associated with thermal dissociation of combustion products. Thermochemical data for temperatures above 3000 K were determined by extrapolating the data [13]; however, this range is almost unrealizable due to the requirements for materials. Maximum cold gas efficiency in O$_2$/N$_2$ mixtures is equal to 72% and is almost independent of the oxygen concentration. In O$_2$/CO$_2$ mixtures, the maximum cold gas efficiency rises sharply to 89% due to the use of oxidation heat in endothermic gasification reactions with CO$_2$.

Similar dependences are observed for coal gasification, however, due to the lower carbon content in the composition, the maximum cold gas efficiency in O$_2$/N$_2$ mixtures is about 83%. Due to the lower heating value as compared to coke, the gasification temperature is lower. The maximum cold
gas efficiency in O$_2$/CO$_2$ mixtures is 88% (almost at the same level as for coke gasification). The maximum cold gas efficiencies of lignite in O$_2$/N$_2$ and O$_2$/CO$_2$ mixtures are close: about 88% for both diluents.

Figure 2. Equilibrium gas temperature (K): coke (a, e), Kuznetsk coal (b, f), Berezovsk coal (c, g) and biomass (d, h); gasification agents are O$_2$/N$_2$ (a-d) and O$_2$/CO$_2$ (e-h).

The maximum values of the equilibrium cold gas efficiency for different concentrations of the oxygen are shown in Fig. 3. With an increase in the volatile content and a decrease in the carbon content, the differences between the dependences of the cold gas efficiency in O$_2$/N$_2$ and O$_2$/CO$_2$ mixtures are becoming less and less noticeable (although they do not disappear). The higher the carbon content in the fuel, the greater the positive effect of using CO$_2$ as a diluent: oxidation of volatile substances of lignite and biomass produces enough gaseous oxidants to generate the heat released during oxidation. Thus, high-carbon content fuels such as coal and coke are the most suitable fuels for gasification in O$_2$/CO$_2$ mixtures.
Figure 3. Maximum cold gas efficiency: coke (a), Kuznetsk coal (b), Berezovsk coal (c), biomass (d).

Conclusion
The equilibrium model was used to estimate the efficiency of gasification process of different fuels in mixtures of oxygen with carbon dioxide. In contrast to gasification processes in O₂/N₂ mixtures, stoichiometric restrictions on carbon conversion are weakened when using O₂/CO₂ mixtures. Carbon dioxide reacts with carbon, increasing the yield of combustible gases, but significantly lowering the temperature (by 100-200 K). The use of O₂/CO₂ mixtures as a gasifying agent is beneficial only for high-carbon fuels. Optimal oxygen concentration is about 50-60 vol. %.

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