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Study of the equilibrium of air-blown gasification of biomass to coal evolution fuels

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ABSTRACT

A non-stoichiometric equilibrium model based on the minimization of the Gibbs free energy was used to study the isothermal and adiabatic air-blown gasification of solid fuels on a carbonization curve from fossil (hard/brown coals, peat) to renewable (green biomasses and cellulose) fuels, including torrefied biofuels. The maps of syngas composition, heating value and process efficiency were provided as functions of equivalent ratio (oxygen-to-fuel ratio) in the range 0–0.6, temperature in 500–2000 K, and a fuel parameter, which allowed different cases to be quantitatively compared. The effect of fuel moisture, unconverted carbon and conditions to limit the tar formation was also studied. Cold gas efficiency >0.75 can be achieved for coals at high temperature, using entrained beds (which give low unconverted carbon), and improved by moisture/added steam. The bigger efficiency of green biomasses is only potential, as the practical limits (high temperature required to limit tar formation, moisture content and unconverted carbon in small gasifiers) strongly reduce the gasification performance. Torrefied biomasses (and plastics having an intermediate fuel parameter between coals and green biomasses) can attain high efficiency also in real conditions. The results shown in this work can be useful to evaluate the most promising feedstock (depending on its composition and possible pre-treatment/upgrading), define the operating conditions for maximizing the syngas heating value or the global efficiency, assess the techno-economic-environmental feasibility of a gasification-based system.

1. Introduction

The use of unconventional fuels (such as battle coals, peats, tar sands) and renewable biofuels (forest-agro-food residues, energy crops, algae) has found current applications and studies on most promising options and energy efficient solutions increased significantly in the last two decades. Furthermore, the emergence of 'pre-treated' fuels (torrefied, steam exploded, and hydrotreated biomasses, biochar, see for instance [14,35,48,36,17,4]) and mixtures of them with fossil derived (co-combustion, waste-to-energy) have extended the range of compositions available for energy fuels. The use of these solid fuels can be seen as a valuable option to face the near depletion of traditional fossil resources, extend/enhance the availability of local energy sources, reduce the global warming/climate change.

Due to the different properties of these fuels, the energy conversion options are numerous. Among them, the gasification showed high efficiency and versatility in feedstock selection, technology choice and product opportunity. The gasification was applied to coals, biomasses and industrial/municipal/agricultural wastes to give a combustible/synthetic gas with a greater efficiency than the direct combustion (see reviews of [34,22,2,51,6]). The plant size ranged from small gasifiers for dislocated applications (50–500 kW) to large IGCC plants (100–1000 MW). The gasifier configuration can be based on fixed (downdraft, countercurrent), fluidized (bubbling, circulating), or entrained beds. The use of different feedstocks and operating conditions (temperature, pressure, residence time, gasifying agent, catalyst) can give a wide range of gasification products/byproducts: heat, electricity, biochar, syngas for further conversion, e.g. production of methane, hydrogen, ammonia, Fischer-Tropsch fuels [29,15]. The most common gasifying agents are air, pure oxygen, steam and CO_2, also in mixtures.

The gasification is an ensemble of homogeneous and heterogeneous reactions, starting from the pyrolysis of the solid fuels and involving the gasifying species and pyrolysis products. The entire process can be autothermal, in which the reactor temperature is achieved by the balance of exothermic and endothermic reactions, as in a partial oxidation, or allothermal, in which an external energy source provides the heat necessary for the reactor to achieving the desired temperature, for instance the hot sand in cir-

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Nomenclature

a, b	correlation parameters	mod	abbreviation for model
CB	subscript for Carbon Boundary	n	molar amount
CGE	Cold Gas Efficiency	N	number of gaseous species
EBP	Evolution Biomass Parameter (EBP = H/C $*$ O/C)	O/C	oxygen to carbon mass ratio
ER	Equivalent Ratio	PKS	Palm Kernel Shells
exp	abbreviation for experimental	Q_{ext}	external heat flow rate needs [MW]
F	abbreviation for fuel when followed by index j	R	ideal gas constant
G	Gibbs function	SFDB	Solid Fuel DataBase
gas	superscript for gaseous state	SGP	Specific Gas Productivity [kg syngas/kg fuel]
G_f^0	free energy of formation on a molar basis	sol	superscript for solid state
H/C	hydrogen to carbon mass ratio	T	absolute temperature [K]
i	generic index for gaseous product	T_0	initial temperature of the feed [K]
IFRF	International Flame Research Foundation	TG	Thermo-Gravimetry
IGCC	Integrated Gasification Combined Cycle	tot	subscript for total amount of gas
j	generic index for fuel F	UC	unconverted carbon (mass basis)
LHV	Lower Heating Value (dry) [MJ/kg for solids, MJ/m^3 for gas]	w	flow rate [kg/s or kg/h for solids, m^3/s or m^3/h for gas]
M	moisture content of the fuel (mass basis)		

culating fluidized beds. In the choice of the most profitable option for the gasification configuration, the following are general points:

- the presence of oxygen gives an exothermic contribution, so that the higher the oxygen content in the feeding stream, the higher the achieved temperature, but the lower the heating value of the produced syngas;
- the presence of H_2O gives an endothermic contribution, so that the higher the water in the feed (as fuel moisture as well as added steam), the lower the temperature in the reactor, but the higher the potential heating value of the produced syngas;
- the presence of nitrogen from air reduces the achievable temperature inside the reactor, dilutes the syngas and reduces its heating value.

The composition and properties of the syngas can be related to the feedstock characteristics, gasifying agent and gasifier conditions, for estimating the process parameters and optimizing the efficiency. Innumerable models exist to simulate the gasification and predict the composition of the syngas. Their classification can be based on the accuracy, complexity, and specificity (see for instance the reviews by [20,40,37]). The starting point of all models is the equilibrium approach, which assures a general applicability. It consists in calculating the composition of gasification products at the thermodynamic equilibrium, so it is based on the feedstock composition, in terms of ultimate analysis, and process conditions (temperature, pressure, gasifying agent-to-fuel ratio), but it is independent of the feedstock structure and gasifier design/operation. The calculation may follow two approaches: stoichiometric, which defines the equilibrium constants of constituent gasification reactions, and non-stoichiometric, which minimizes the Gibbs free energy of the gasification products. The results of the two approaches were proved to be equivalent (see [40] and references therein). Therefore, the non-stoichiometric approach is more advantageous as it only requires the definition of the list of chemical species expected in the product mixture [5].

The equilibrium model is simple, is based on non-specific process parameters, requires a small calculation effort and allows a wide range of conditions (process parameters and fuel compositions) to be studied. These are the reasons for its widespread use as a general tool or starting point for modified versions and comparison with more detailed models. Its predictability has been validated only for specific fuels and single reactor configurations. In those cases, the limited reliability and accuracy of the equilibrium model results have been imputed to the fact that real plants operate under conditions, which may be far from equilibrium. The equilibrium approach is indeed useful for predicting what is thermodynamically attainable, indicates the maximum efficiency of gasification [39] and can be a guide for process design, evaluation and optimization [28].

The aim of this work is to validate an equilibrium non-stoichiometric model for fuels ranging from coals to biomasses and quantify its accuracy. Hence the equilibrium model is used to study the gasification process and evaluate the effect of fuel composition, temperature and oxygen-to-fuel ratio on syngas composition, heating value and process efficiency. A fuel parameter is defined to verify a comprehensive connection of different fuels, involving also brown coals, torrefied biomasses and plastics. The maps of the results obtained in isothermal and adiabatic conditions may represent useful tools for producers and operators of small and medium gasifiers to evaluate the most promising feedstock (depending on its composition and possible pretreatments), predict syngas composition and heating value, and determine the most efficient conditions (temperature, oxygen-to-fuel ratio) of gasification. They are also useful for process and system analysis, as preliminary study and application to techno-economic and environmental assessments (see for instance [47]).

2. Model description

Every fuel was treated as an exclusively C—H—O system, since carbon, hydrogen and oxygen are by far the most abundant elements in coal and biomass gasification (see similar assumptions in [16,28,39,3]). Each fuel was characterized by the H/C and O/C mass ratios from the ultimate analysis normalized on a C—H—O basis. The fuel parameter EBP (Evolution Biomass Parameter) was defined as the product of H/C and O/C. The values of H, C and EBP are listed in Table 1. The smallest values of EBP are specific of hard coals, the greatest ones are specific of green biomasses. Intermediate values of EBP may denote brown coals, peats and torrefied biomasses. 18 fuels were selected to run the simulations described in this work. The fuel F1 is a low volatile coal (Tower coal, from [11]), for which EBP = 0.0040, F2–F6 are different rank