

## GAS COMPOSITION AND EXERGY EFFICIENCY DETERMINATION AT CARBON BOUNDARY POINT IN THE DOWNDRAFT BIOMASS GASIFICATION PROCESS

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**Abstract:** Biomass as a renewable energy resource has a great energetic potential. There are a lot of incentives all over the world, such as for example CDM program, for implementation of waste biomass. This paper focuses on the wood chips gasification in an idealized downdraft equilibrium gasifier. The model for determination of carbon boundary temperature and other important parameters at carbon boundary temperature such as gas composition, exergy efficiency of the process was developed. The purpose of this paper is to determine upper limit for exergy efficiency that should be expected from the downdraft gasification process in dependance of moisture content in wood chips. In addition to this, to diagnose if and what kind of measures should be taken with wood chips' moisture prior to the gasification process. In the model idealized gasifier is used in which chemical equilibrium is achieved, ashes are not taken into consideration and heat losses are ignored. The gasification efficiencies are calculated at carbon boundary temperature, where exactly enough air is added to achieve complete gasification and avoid carbon in the solid residual. It is shown that the exergy efficiencies are lower than the energy efficiencies, and also, that exergy efficiencies decrease with the increase of moisture content in the biomass. Also it is shown that overall exergy efficiency of the process decrease with slower rate than exergy efficiency based only on chemical exergy. For wood chips with high moisture content exergy efficiency could be improved by drying the biomass prior to gasification process.

**Keywords:** Biomass, wood chips, gasification, chemical equilibrium, carbon boundary point, exergy efficiency, energy efficiency.

### 1. INTRODUCTION

According to [1] Serbia has relatively large biomass energy potential. The total excess biomass energy potential is estimated at 115 000 Tera Joules per year (TJ/year) of which 50 000 TJ/year accounts for the local wood waste, while the remaining amount of 65 000 TJ/year accounts for agriculture waste. This work is focused to wood chips that are nowadays piled and wasted. Huge amounts of wood chips are deposited especially during summer period of year into rivers, and cause great environmental problems in the area of Kraljevo. Also, from huge piles of wood chips there are methane emissions that are caused from the anaerobic biomass decay. This methane emissions and wind dispersion are the main reason why wood chips are not allowed to pile just for the heating season.

Biomass gasification is an interesting energy conversion technology where this biomass could be used. Gasification is the process of gaseous fuel production by partial oxidation of a solid fuel. This means in common terms to burn with oxygen deficit. The gasification of coal is well known, and has a history back to year 1800. The oil-shortage of World War II imposed an introduction of almost a million gasifiers to fuel cars, trucks and busses especially in Scandinavian countries [2].

The main differences concern how reactants and products are moved around in the reactor, and the

The Kyoto protocol emphasizing the need to combat carbon dioxide emission has also been an impetus for the interest in biomass gasification. Carbon dioxide emissions from using biomass as a fuel are perceived as neutral because this carbon dioxide is fixed by photosynthesis in a relatively short period.

Gasification belongs to thermochemical conversion processes together with combustion, pyrolysis, and liquefaction.

As a medium for gasification air, pure oxygen, water vapor, carbon dioxide and hydrogen can be used. In practice and in commercial applications air and water vapor are the most common, but also there are cases where pure oxygen is used as a gasifying medium.

The product of gasification is synthesis gas that consists mainly from carbon monoxide, carbon dioxide, methane, nitrogen, hydrogen and water vapor. The heating value depends on the gasification medium, solid fuel characteristics, gasification process and the temperature in the gasifier. The gas is used for electricity, heat and fuel production.

The types of gasifiers are various, but may be divided into three main groups [3]: entrained flow gasifiers, fluidized bed gasifiers (bubbling/circulating) and fixed bed gasifiers, where the last is subdivided into: counter-current (updraft), co-current (downdraft) and cross-current moving bed.

resulting reaction conditions. The reactors may be operated at atmospheric pressure or at higher pressures,

but the latter is only available to bubbling or circulating fluidized bed reactors, but at considerable higher cost. The higher cost may be earned downstream due to smaller equipment size and higher reactivity.

## 2. GASIFIER MODEL

The gasification process considered in this paper is schematically presented in Fig.1. Biomass, in this case wood chips enter the gasifier from the top. Biomass, and air which is used as a gasification medium, are at the standard reference state ( $p = 0.1 \text{ MPa}$ ,  $t = 25^\circ\text{C}$ ).

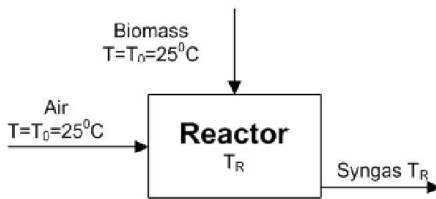


Fig. 1. Schematic diagram of the downdraft gasifier

A chemical equilibrium model is applied to predict carbon boundary temperature, product gas composition, gas amount and carbon conversion in the gasifier. There are a lot of equilibrium models in the literature [4] – [7]. In [7] there are a lot of references on gasification equilibrium models in literature, and on characteristics of these models.

Equilibrium models are valuable because they predict the thermodynamic limits of the gasification reaction system. However, equilibrium models are based on the following assumptions:

- The gasifier is regarded as a perfectly insulated device. It means that heat losses are neglected. In practice, gasifiers have heat losses to the environment, but this term can be incorporated in the enthalpy balance of the equilibrium model. In this model of the gasifier heat losses are included in energy balance equation as a parameter.
- Perfect mixing and uniform temperature are assumed for the gasifier. This can lead to large errors in some types of gasifier where residence time is too short and where uniform temperature could not be assumed. But, for downdraft gasifiers according to [7], the equilibrium model has good predictive potential. The reason is that in the downdraft gasification process devolatilization takes place in the upper part of the gasifier, and devolatilization products are forced to pass through a narrow cross-section, the so-called throat, in which the temperature is high. The syngas leaves the gasifier at the bottom with the temperature equal to the temperature in the reduction zone, which is placed under the hot oxidation zone.

- The model assumes that gasification reaction rates are fast enough and residence time is sufficiently long to reach equilibrium state.
- No information about reaction pathways/formation of intermediates.
- Tar is not modeled.

Under gasification conditions (with temperature between 600 and 1500K) the only species present at concentrations greater than  $10^{-4} \text{ mol\%}$  are  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$  and solid C. Carbon monoxide, hydrogen and methane contribute to the heating value of the product gas, other gases are not desired in the synthesis gas. The following reactions are relevant for carbon conversion into gaseous components [7]:



In steam and air gasification, all these reactions occur so that the endothermic water-gas (2) and Boudouard (3) reactions are coupled to the exothermic methane formation (1) reaction. Coupling of endothermic and exothermic reactions is very attractive in order to achieve a high thermodynamic efficiency.

Another very important characteristic of the gasification process that should be defined prior to the introduction of the model is the equivalence ratio ER. It is defined as the ratio of the oxygen (air) that is introduced into the gasifier to the amount of oxygen (air) which is needed for complete combustion of the given fuel, in this case wood chips.

The model calculates also the carbon boundary temperature. The temperature obtained when exactly enough oxygen is added to achieve complete gasification (no solid carbon present). It is important to say that the gasification process has its optimum at the carbon boundary temperature, because exactly enough oxygen is added to achieve complete gasification. If more oxygen is used the produced gas loses its heating value, until complete combustion is achieved.

The unknowns in the model are:

- gas amount,
- gasification temperature (carbon boundary temperature),
- molar fractions of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,
- equivalence ratio ER.

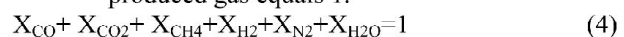
In total there are nine unknowns, and two parameters:

- amount of ungasified carbon and
- gasification pressure.

In the model as gasifying medium combustion air is used with molar fractions of 21% and 79% for oxygen and nitrogen respectively.

The following reactions are used in the model:

- the sum of unknown molar fractions in the produced gas equals 1.



- equilibrium equations for the three reactions (1)-(3)

for methane formation reaction (1)

$$K_e = \frac{X_{CH_4}}{X_{H_2}^2} \cdot \left( \frac{p_o}{p} \right), \quad (5)$$

for Boudouard reaction (3)

$$K_e = \frac{X_{CO}^2}{X_{CO_2}} \cdot \left( \frac{p_o}{p} \right), \quad (6)$$

for water gas reaction (2)

$$K_e = \frac{X_{CO} + X_{H_2}}{X_{H_2O}} \cdot \left( \frac{p_o}{p} \right). \quad (7)$$

For determination of the left hand sides of reactions (5)-(7) theoretical expressions are used. For determination of heat capacities for gases expressions were taken from [8], page 813. These heat capacities are used for determination of enthalpies, entropies and gibbs functions of all gases. In these calculations all gases are considered to be ideal, and expressions for ideal gases are used. For determination of solid carbon heat capacity that is used in energy balance equation the polynomial expression is taken from [9] (page 277).

The other reactions that are used in the model are:

- $H_2/C$  balance,
- $O_2/C$  balance,
- $O_2/N_2$  balance,
- Mass balance equation, and
- Energy balance equation.

Biomass composition that is used in the model was taken from [10] (page 210).

The model was made in Modelica language. It is object orientated language for modeling of large scale physical systems. As a tool that supports the language was used Dymola.

### 3. EXERGY EFFICIENCY

Exergy is defined in thermodynamics as a measure of the actual potential of a system to do work. In processes, such as combustion, gasification, hydrogenation and steam reforming, fossil and renewable fuels are converted into a different fuel and/or heat and/or electricity. For example, gasification of a fuel involves converting the chemical energy contained in the fuel into chemical energy contained in the gaseous products and sensible heat of the produced gas. According to the first law of thermodynamics, energy can never be lost. Therefore it is justified to state that energy conversion processes do not have energy losses, except for losses from the process system into the environment. However, the second law of thermodynamics should also be considered. Energy conversion processes are accompanied by an irreversible increase in entropy, which leads to a decrease in exergy (available energy). Thus, even though the energy is conserved, the quality of energy decreases because energy is converted into a different form of energy, from which less work can be obtained.

The exergy balance of the biomass conversion process is presented in the following form:

$$\sum_{in} E_J = \sum_{out} E_K + I \quad (8)$$

In this equation first and second term represents exergy flows of all entering and leaving stream, respectively.

In equation (8) the term  $I$  represents irreversibilities. It is the difference between all entering exergy streams and that of leaving streams. Exergy is not conserved but subjected to dissipation. It means that the exergy leaving any process step will always be less than the exergy in.

The exergy of stream of matter  $E$  depends on its composition (chemical exergy  $E_{ch}$ ) and its temperature and pressure (physical exergy  $E_{ph}$ )

$$E = E_{CH} + E_{PH} \quad (9)$$

In the above formula all terms are in kJ.

The standard chemical exergy of a pure chemical compound  $\epsilon_{ch}$  is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterized by the environmental temperature  $T_o$  and environmental pressure  $p_o$ , to the dead state, characterized by the same environmental conditions of temperature and pressure, but also by the concentration of reference substances in standard environment. The chemical exergy of the mixture  $\epsilon_{ch,M}$  is determined by the composition and concentration of components in the mixture:

$$\epsilon_{ch} = \sum_i x_i \cdot \epsilon_{oi} + R \cdot T_o \sum_i x_i \cdot \ln x_i \quad (10)$$

In this formula  $X_i$  are molar fractions of gases in the mixture,  $R = 8.314$  kJ/kgmole universal gas constant, and  $T_o = 298$  K environment temperature.

The physical exergy of a mixture can be calculated using enthalpies and entropies of all gases that are presented in the mixture:

$$\epsilon_{ph} = (h - h_o) - T_o \cdot (s - s_o) \quad (11)$$

where  $h$  (kJ/kgmole) and  $s$  (kJ/kgmoleK) are enthalpy and entropy of a system at given temperature and pressure, and  $h_o$  (kJ/kgmole) and  $s_o$  (kJ/kgmoleK) are the values of these functions at the environmental temperature and pressure.

The exergy of the biomass is obtained by using the following formula [11]:

$$\beta = \frac{\epsilon_{ch}}{LHV_{biomass}} \quad (12)$$

Where  $\epsilon_{ch}$  is the chemical exergy of biomass (kJ/kg), and LHV (kJ/kg) is the lower heating value of the biomass. The ratio  $\beta$  was statistically determined by Szargut and Styrylska (1964) and is taken from [11].

$$\beta = \frac{1.044 + 0.0160 \cdot (H/C) - 0.3493 \cdot (O/C) \cdot [1 + 0.0531 \cdot (H/C)] + 0.0493 \cdot (N/C)}{1 - 0.4124 \cdot (O/C)} \quad (13)$$

(13) – for solid biofuels.

Biomass' lower heating value is obtained by a formula taken from [10], page 214.

$$LHV = 340 \cdot C + 1190 \cdot \left( H - \frac{O}{8} \right) + 93 \cdot S - 25 \cdot W \quad (14)$$

## D.4

Where in equations (13) and (14) C, H, O, S, W are mass fractions of carbon, hydrogen, oxygen, sulphur and water in the biomass.

Having defined all previous quantities all three efficiencies can be calculated. Chemical efficiency represents chemical energy that is conserved in the produced gas and is calculated by:

$$\eta_{ch} = \frac{LHV_{gas}}{LHV_{biomass}} \quad (15)$$

This efficiency is also known as the cold-gas efficiency. The chemical exergy efficiency is defined as the ratio between chemical exergy of product gas and biomass:

$$\eta_{ex-ch} = \frac{\mathcal{E}_{ch,gas}}{\mathcal{E}_{ch,biomass}} \quad (16)$$

The definitions (15) and (16) have drawbacks [11] they ignore sensible heat contained in the synthesis gas. This gas at elevated temperature is preferred over environmental temperature and therefore the calculated efficiency should be higher. However, if the sensible heat were to be added to the energetic efficiency, this efficiency would always be 100% because the gasifier operates adiabatically. This problem can be overcome by using exergetic efficiency based on chemical as well as physical exergy:

$$\eta_{ex} = \frac{\mathcal{E}_{ch,gas} + \mathcal{E}_{ph,gas}}{\mathcal{E}_{ch,biomass}} \quad (17)$$

In all three equations (15)-(17) all terms are previously defined.

## 4. MODEL RESULTS

Table 1 shows the results of the model calculations. For large moisture content in the wood chips, larger than 25% (mass fraction), carbon boundary temperature is less than 600 °C. Since, under this temperature equilibrium is very difficult to be achieved and formation of high hydrocarbons take place, for moisture contents above 25 % (mass fraction) the amount of air that is introduced in the gasifier is larger than the amount needed to achieve carbon boundary temperature. And for wood chips with the moisture content larger than 25% in the gasifier are introduced larger amounts of air in order to achieve gasification temperature of 600°C.

The efficiencies: chemical efficiency, chemical exergy efficiency and exergy efficiency of the gasification process are presented in Fig. 2.

W	0	5	7.5	10	12.5	15	17.5	20	22.5	25	27.5	30	32.5	35	37.5
C	50.57	48.04	46.78	45.51	44.25	42.99	41.72	40.46	39.19	37.93	36.66	35.40	34.14	32.87	31.61
H	6.00	5.70	5.55	5.40	5.25	5.10	4.95	4.80	4.65	4.50	4.35	4.20	4.05	3.90	3.75
O	41.86	39.76	38.72	37.67	36.63	35.58	34.53	33.49	32.44	31.39	30.35	29.30	28.25	27.21	26.16
N	0.57	0.54	0.53	0.51	0.50	0.49	0.47	0.46	0.44	0.43	0.41	0.40	0.39	0.37	0.36
A	1.00	0.95	0.93	0.90	0.88	0.85	0.83	0.80	0.78	0.75	0.73	0.70	0.68	0.65	0.63
Sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
LHVbiomass	19056	17981	17444	16905	16369	15831	15294	14756	14219	13681	13144	12606	12069	11531	10994
Exergy - biomass	21887	20652	20036	19417	18800	18183	17566	16948	16331	15714	15096	14479	13862	13244	12627
Equivalence ratio	0.3057	0.2579	0.281	0.3	0.3152	0.329	0.336	0.339	0.347	0.3536	0.422	0.432	0.442	0.453	0.466
Omin (m <sup>3</sup> /kg)	0.987	0.938	0.913	0.888	0.864	0.839	0.814	0.790	0.765	0.740	0.716	0.691	0.666	0.642	0.617
Air flow (m <sup>3</sup> /kg)	1.437	1.152	1.220	1.269	1.296	1.313	1.303	1.276	1.265	1.247	1.438	1.422	1.402	1.384	1.369
Carbon boundary T (K)	986	998	973	953	937	922	910	900	887	874	873	873	873	873	873
Carbon boundary T (°C)	713	725	700	680	664	649	637	627	614	601	600	600	600	600	600
CO	0.274	0.295	0.26	0.229	0.204	0.181	0.163	0.147	0.129	0.112	0.104	0.097	0.091	0.085	0.079
CO <sub>2</sub>	0.067	0.061	0.08	0.096	0.11	0.123	0.133	0.142	0.152	0.161	0.142	0.124	0.109	0.095	0.082
CH <sub>4</sub>	0.007	0.009	0.01	0.011	0.013	0.015	0.016	0.018	0.021	0.023	0.022	0.021	0.02	0.019	0.018
H <sub>2</sub>	0.202	0.235	0.225	0.217	0.211	0.206	0.204	0.203	0.199	0.194	0.189	0.184	0.18	0.175	0.17
N <sub>2</sub>	0.42	0.37	0.386	0.398	0.406	0.412	0.413	0.411	0.412	0.412	0.453	0.491	0.526	0.558	0.59
H <sub>2</sub> O	0.03	0.031	0.039	0.048	0.055	0.063	0.071	0.079	0.088	0.098	0.09	0.082	0.074	0.068	0.061
ngas(kgmole/kg)	0.1236	0.1062	0.111	0.114	0.1168	0.119	0.119	0.118	0.118	0.1173	0.117	0.1168	0.116	0.1151	0.1143
ngas(m <sup>3</sup> /kg)	2.770	2.380	2.481	2.561	2.617	2.660	2.660	2.635	2.635	2.629	2.629	2.617	2.600	2.579	2.561
LHVsyngas	5897	6563	6063	5651	5321	5034	4843	4706	4513	4338	4143	3969	3803	3639	3467
Physical exergy	1341	1178	1186	1193	1193	1190	1173	1148	1130	1109	1088	1065	1041	1018	996
Chemical exergy	15921	15248	14647	14061	13499	12950	12440	11955	11449	10956	10461	9974	9491	9009	8524
Eff.(LHV)	0.857	0.868	0.862	0.856	0.851	0.846	0.842	0.84	0.837	0.833	0.829	0.824	0.819	0.814	0.808
Eff.(chem.exergy)	0.727	0.738	0.731	0.724	0.718	0.712	0.708	0.705	0.701	0.697	0.693	0.689	0.685	0.68	0.675
Eff.(exergy)	0.789	0.795	0.79	0.786	0.781	0.778	0.775	0.773	0.77	0.768	0.765	0.762	0.76	0.757	0.754

Table 1. Results of equilibrium model



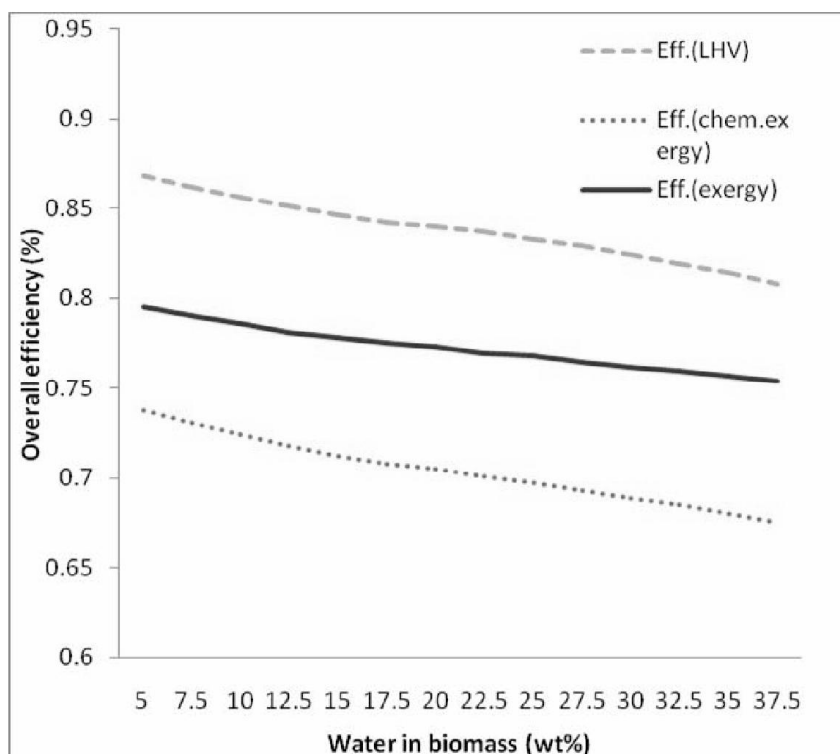


Fig. 2. Efficiencies of the gasification of wood chips with different moisture content at the carbon boundary temperature

## 5. CONCLUSION

Water content in wood chips can present huge problem for the gasification. Also, the product gas composition and the gasification temperature depend of the moisture content in the wood chips. The results of the model presented in the Table 1. give clear picture of the problem. Also, these data could be used to diagnose gasification of wood chips.

From Table 1. it is obvious, as it was expected, that with increase of moisture content in the wood chips the carbon boundary temperature decreases. Also, as it is known, the lower heating value and the biomass exergy decrease with an increase of the moisture content in the biomass. From Table 1. is obvious that the biomass exergy is larger than the biomass heating value. This is explained in [11] by the fact that polymers such as cellulose and hemi-cellulose are highly ordered structures, and work can be delivered if these are decomposed.

With change of the moisture content in wood chips product gas composition also changes. With the increase of moisture in wood chips the amounts of carbon dioxide, hydrogen, methane and water vapour increase and the amount of carbon monoxide decreases.

From Fig. 2 is apparent that energy efficiency is larger than both exergy efficiencies. In addition, chemical energy efficiency and chemical exergy efficiency decrease faster than overall exergy efficiency with the increase of moisture in the biomass.

From the data presented in Table 1. it is apparent that wood chips with the moisture content above 22.5 % must be dried prior to the gasification process.

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