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Energy Conversion and Management 47 (2006) 1723–1737

ENERGY CONVERSION & MANAGEMENT

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Solid waste plasma gasification: Equilibrium model development and exergy analysis

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Received 14 April 2005; accepted 15 October 2005
Available online 7 December 2005

Abstract

Plasma gasification technology has been demonstrated in recent studies as one of the most effective and environmentally friendly methods for solid waste treatment and energy utilization. This study focuses on the thermodynamic analysis of plasma gasification technology, which includes prediction of the produced synthesis gas, energy and exergy calculations. To that purpose, an equilibrium plasma gasification model, called GasifEq, is developed here by using recent thermodynamic data, which also considers the possibility for soot formation, as a solid carbon by-product. The GasifEq model also has the capability of energy and exergy calculations that are required for the optimization of such processes. This is demonstrated by the presentation of the effect of the most important process parameters on the energetic performance of the process.
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Keywords: Equilibrium; Modeling; Plasma gasification; Exergy

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1. Introduction

A factor common to all developed countries is the generation of excessive amounts of waste per capita. As societies developed, the amount of waste material generated has increased to a level that is becoming unmanageable. This, together with the increasing awareness of the general public for the damage caused to the environment, explains the need to plan for and implement sustainable and integrated strategies for handling and treating wastes.

Plasma gasification is a technologically advanced and environmentally friendly process of disposing of waste and converting them to usable by-products. It is a non-incineration thermal process that uses extremely high temperatures in an oxygen starved environment to decompose completely the input waste material into very simple molecules [1]. The products of the process are a combustible gas, known as synthesis gas, and an

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0196-8904/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.enconman.2005.10.015

inert vitreous material, known as slag. Furthermore, it consistently exhibits much lower environmental levels for both air emissions and slag leachate toxicity [2] than competing technologies, e.g. incineration.

Standard gasification technologies operate the reactor in the 400–850 °C range. They do not use any external heat source and rely on the process itself to sustain the reaction. Normal gasifiers are really "partial combustors", and a substantial portion of the carbon is combusted just to support the reaction [3]. Their gasification process produces a fuel gas similar to the gas produced by the plasma process, although it is much dirtier and contains char, tars and soot. The lower temperatures cannot break down all the materials. With standard gasification, many materials must be sorted out of the waste stream before reaching the reactor and landfilled or processed in other ways. Because of the low temperature used, the gas that is produced by a standard gasifier has tars that are difficult to remove and other contaminants that must be further cleaned. The char residue is up to 15% of the weight of the incoming material and must still be landfilled. In addition to these drawbacks, most standard gasification systems cannot feed heterogeneous waste, e.g. municipal solid waste, directly from the truck.

Plasma gasification uses an external heat source to gasify the waste, resulting in very little combustion. Almost all of the carbon is converted to fuel gas. Plasma gasification is the closest technology available to pure gasification. Because of the temperatures involved, all the tars, char and dioxins are broken down. The exit gas from the reactor is cleaner, and there is no ash at the bottom of the reactor.

In this work, the equilibrium model work focuses on plasma gasification of the organic fraction of the solid waste due to the fact that this fraction is linked to a greater extent to the energy terms of analysis. On the other hand, the plasma treatment of the inorganic fraction of the solid waste results in its vitrification that is of great importance, mainly for its environmental performance and not for its energetic characteristics. More specifically, the objective of this work is the development of an equilibrium gasification model that can describe the plasma gasification process and incorporate recent thermodynamic data as well as energy and exergy terms, which are proven to be very useful for process studies.

2. Process description

The block diagram presented in Fig. 1 includes the main sections of a plasma waste treatment plant. The waste feed sub-system is used for treatment of each type of waste in order to meet the inlet requirements of the plasma furnace. For example, for a waste material with high moisture content, a drier will be required. However, a typical feed system consists of a shredder for solid waste size reduction prior to entering the plasma furnace.

The plasma furnace is the central component of the system where gasification/vitrification are taking place. Two graphite electrodes, as a part of two transferred arc torches, extend into the plasma furnace. An electric current is passed through the electrodes, and an electric arc is generated between the tip of the electrodes and

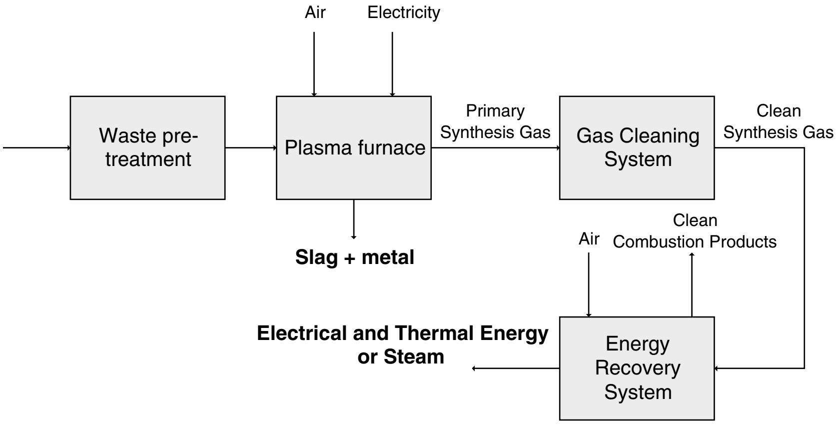

Fig. 1. Block diagram of waste plasma gasification process.

the conducting receiver, i.e. the slag in the furnace bottom. The gas introduced between the electrode and the slag that becomes plasma can be oxygen, helium or some other, but the use of air is very common due to its low cost.

The gas cleaning sub-system has to achieve the elimination of acid gases (HCl, SO_x), suspended particulates, heavy metals and moisture from the synthesis gas prior to entering the energy recovery system. The energy recovery system can be based on a steam cycle, gas turbine cycle or a gas engine. Depending on the quality of the produced synthesis gas, the best option can be one of the above energy recovery scenarios. In addition, alternatively, the energy recovery system can be a chemical fuel production unit, such as for hydrogen or methanol.

3. Model development

3.1. Equilibrium modeling of gasification process

The central part of the plasma gasification process is the plasma furnace. The thermal chemical conversion process that takes place inside the plasma furnace can be described well by the term "gasification", and the model development will be based on the chemical reactions that describe better the gasification process. During the plasma gasification process, various chemical reactions take place that are difficult to be reproduced by a simple equilibrium model. Nevertheless, models based on thermodynamic equilibrium have been used widely, and they are convenient enough for process studies on the influence of the most important waste and process parameters [4,5].

The following simplified chemical conversion formulas describe the basic gasification process [5,6]:

$$\begin{array}{ll} C(s) + H_2O = CO + H_2 & \text{(Heterogeneous water gas shift reaction—endothermic)} \\ C(s) + CO_2 = 2CO & \text{(Boudouard equilibrium—endothermic)} \\ C(s) + 2H_2 = CH_4 & \text{(Hydrogenating gasification—exothermic)} \\ CH_4 + H_2O = CO + 3H_2 & \text{(Methane decomposition—endothermic)} \\ CO + H_2O = CO_2 + H_2 & \text{(Water gas shift reaction—exothermic)} \end{array}$$

For the development of an equilibrium model approach, the number of independent reactions has to be determined by applying the phase rule, as described by Tassios [7]. In the case where no solid carbon remains in the equilibrium state, only two independent reactions need to be considered for the equilibrium equations. In the case of some remaining solid carbon, i.e. soot, in the gasification products, three independent reactions have to be considered in the equilibrium calculations.

Two examples from the literature relevant to the gasification process are presented below. Zainal et al. [4] have selected one reaction resulting from the combination of the Boudouard equilibrium and heterogeneous water gas shift reaction and the hydrogenating gasification as the main gasification reactions, while Schuster et al. [5] have selected the gas shift reaction along with the methane decomposition reaction. According to the thermodynamic theory of independent reaction selection, there is no significant difference between the above reported modeling efforts [7]. The only point that differentiates the equilibrium reactions is that the methane decomposition reaction is favored in the case of steam gasification (high feed moisture content) and not in the case of the conventional gasification process.

An important point in the modeling procedure is whether equilibrium is reached in the plasma gasification process, i.e. whether the operating conditions allow the chemical reactions to reach an equilibrium state. As far as the gasification temperature is concerned, it is stated that equilibrium is not achieved when the gasification temperature is sufficiently below 800 °C (common gasifiers), while it is reached for higher temperatures like those of plasma gasification [8,9].

Regarding the other crucial factor relevant to an equilibrium state, i.e. residence time, Prins et al. [10] reported that for air gasification, the residence time is sufficiently long and equilibrium is well verified, while for steam gasification, equilibrium may not reached due to the lower operating temperatures, which is not the fact in plasma gasification. In addition, Calaminus and Stahlberg [11], based on experimental facts, stated that during gasification in the Thermoselect plant, which is a similar process to plasma gasification, the residence times for the gas phase and also for the molten phases are sufficient for equilibrium to be attained, i.e. for the solids it is about 1–2 h and for the gas phase 2–4 s at about 1200 °C. In addition, Chen et al. [12] presented that in such processes, a significant increase of gas yield is noted between 2 and 3 s (as a result of a tar cracking reaction), and after that time period, equilibrium is assumed to be attained.

Consequently, plasma gasification is studied in this work based on equilibrium terms in order to describe the process and to present its energetic performance in relevance to the main operational parameters, e.g. moisture, oxygen and temperature.

3.2. The GasifEq equilibrium model

The GasifEq equilibrium model that is developed in this work describes the plasma gasification of solid waste. It includes the energy supplied to the main section of the plasma gasification process, i.e. electricity, the formation of the basic gasification gaseous products and the possibility of some remaining solid carbon, i.e. soot particles.

3.2.1. Thermodynamic database

The thermodynamic data that are required for development of the equilibrium gasification model are the Gibbs energies of formation at 298 K, the enthalpies of formation at 298 K and the temperature dependent heat capacities c_p, which are required to evaluate the change of the equilibrium constants with temperature.

The thermodynamic databases that were used in this work are: the database of the National Institute of Standards and Technology–NIST [13], the Chemical Properties Handbook by Professor Carl L. Yaws of Lamar University, Texas, [14] and the DIPPR database [Design Institute for Physical Properties] [15].

The first criterion for the choice of database is the temperature range in which the heat capacities can be calculated. In Table 1, the temperature range for the gaseous compounds that are taking part in the gasification equilibrium is presented. Although the greater temperature range is offered by the NIST database [13], there is an important drawback because it breaks the whole range into two or three compartments in which the constants for calculation of the heat capacities have different values. This fact causes difficulties and abnormalities in the calculation of the thermodynamic values at temperatures of special interest in this work, such as 1000 K, 1200 K or 1300 K. Moreover, the NIST database [13] does not propose a specific equation for calculation of the heat capacity of solid carbon.

From the remaining two databases, that of the Chemical Properties Handbook [14] has been selected for the thermodynamic calculations due to the fact that it is the most recent one (last updated on 10th of March 2003) and that it can be applied in a greater temperature range than that of the DIPPR [15] (this is valid for the edition of DIPPR's database that is available for this work). All the pertinent data are presented in Table 1.

It must also be mentioned that the values reported in the above databases for the Gibbs energy of formation and the enthalpy of formation (at the reference temperature of 298 K) do not differ in a great extent. Additionally, the small difference noted in the values of the heat capacities have a minor effect on the calculated equilibrium constant values, and as a consequence, they result in similar equilibrium gasification calculations. This is demonstrated in Table 2, where the equilibrium constants were calculated for two of the most important gasification reactions by using the Chemical Properties Handbook [14] and DIPPR's databases [15].

Table 1
Applicability temperature range for calculation of gas and solid heat capacities, enthalpy changes and equilibrium constants

Substance	National Institute of Standards and Technology—NIST	Chemical Properties Handbook	DIPPR
H_2 (g)	298–1000/1000–2500/2500–6000 K	250–1500 K	250–1500 K
CO_2 (g)	298–1200/1200–6000 K	50–5000 K	250–1500 K
H_2O (g)	500–1700/1700–6000 K	100–1500 K	250–1500 K
N_2, O_2 (g)	298–6000 K	50–1500 K	250–1500 K
CO (g)	298–1300/1300–6000 K	60–1500 K	250–1500 K
CH_4 (g)	298–1300/1300–6000 K	50–1500 K	250–1500 K
C (s)	–	200–1100 K	–

Table 2
Equilibrium constants calculation by using different databases

Temperature (K)	$CH_4 + H_2O = CO + 3H_2$		$CO + H_2O = CO_2 + H_2$	
	Chemical Properties Handbook	DIPPR	Chemical Properties Handbook	DIPPR
298.15	1.240E−25	1.195E−25	98,460	104,602
500	8.503E−11	8.260E−11	130.1	138.1
700	2.622E−04	2.537E−04	8.885	9.457
900	1.280	1.236	2.152	2.307
1100	305	295	0.916	0.989
1273.15	8857	8585	0.557	0.607
1500	226,018	220,998	0.355	0.394

Table 3
Equilibrium constants calculation by three models at 1273 K

Reactions	GasifEq	GasEq	ChemEq
$CO + H_2O = CO_2 + H_2$	0.558	0.607	0.568
$CH_4 + H_2O = CO + 3H_2$	8835	8861	8624
$C + H_2O = CO + H_2$	94.71	82.71	82.55

Furthermore, Table 3 presents the equilibrium constant values at 1273 K for the three reactions selected in this work, as presented in the next paragragh, that are obtained with the database used here and two well known equilibrium models that calculate the equilibrium constant: the GasEq model developed by Chris Morley [16] (GasEq Version 0.79, 2005) and the ChemEq model developed by Stanley Sandler [17].

It appears that the model proposed by this work gives comparable results to that of the other two models, GasEq and ChemEq. The GasifEq model proposed here uses the most recent thermodynamic data that are valid for the temperature range that is of special interest for high temperature thermal methods, such as the plasma gasification studied here.

3.2.2. Equilibrium reactions—calculation of equilibrium constants

Waste material is described by its ultimate analysis ($C_XH_YO_Z$), and the global gasification reaction is written as follows:

$$CH_xO_y + wH_2O + mO_2 + 3.76mN_2 = n_1H_2 + n_2CO + n_3CO_2 + n_4H_2O + n_5CH_4 + n_6N_2 + n_7C \qquad (1)$$

where w is the amount of water per kmol of waste material, m is the amount of oxygen per kmol of waste, n_1, n_2, n_3, n_4, n_5, n_6 and n_7 are the coefficients of the gaseous products and soot (all stoichiometric coefficients in kmoles).

The equilibrium is, thus, calculated considering the components CH_4, CO, CO_2, H_2, H_2O and C (soot). System analysis shows that the simultaneous equilibrium is described by three independent reactions, three partial mass balances (for C, H and O) and one heat balance. The specific heat and enthalpy changes of the gas products are expressed as a function of the gasification temperature as well as the equilibrium constants of the chemical reactions.

The three main independent equilibrium reactions that are selected for the equilibrium calculations are shown below:

1. $CH_4 + H_2O = CO + 3H_2$ (Methane decomposition—endothermic) (2)
2. $CO + H_2O = CO_2 + H_2$ (Water gas shift—exothermic) (3)
3. $C + H_2O = CO + H_2$ (Primary water gas shift—endothermic) (4)

The equilibrium constants are: for the methane decomposition

$$K_1 = \frac{[\mathrm{CO}] \cdot [\mathrm{H_2}]^3}{[\mathrm{CH_4}] \cdot [\mathrm{H_2O}]}, \tag{5}$$

for the water gas shift reaction $K_2 = \dfrac{[\mathrm{CO_2}] \cdot [\mathrm{H_2}]}{[\mathrm{CO}] \cdot [\mathrm{H_2O}]}$ (6)

and for the primary water gas shift reaction $K_3 = \dfrac{[\mathrm{CO}][\mathrm{H_2}]}{[\mathrm{H_2O}]}$. (7)

The equilibrium constant is a function of temperature T and is written as follows: $\ln K = \frac{-\Delta G^0}{RT^2}$ and, after considering the dependence of ΔG^0 on temperature T, can be written as $\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^0}{RT^2} \Rightarrow \left[\Delta H^0 = A \cdot T + B \cdot \frac{T^2}{2} + C \cdot \frac{T^3}{3} + D \cdot \frac{T^4}{4}\right]$. Thus,

$$\ln K = \ln K^0 + \frac{\Delta A}{R} \ln \frac{T}{T_0} + \frac{\Delta B}{2R}(T - T_0) + \frac{\Delta C}{6R}(T^2 - T_0^2) + \frac{\Delta D}{12R}(T^3 - T_0^3) \tag{8}$$

where $\ln K_0 = \frac{-\Delta G^0}{RT_0} = \frac{-\sum v_i \Delta G_{f_i(T_0)}}{RT_0}$ and ΔA, ΔB, ΔC and ΔD are calculated for each equilibrium reaction, e.g. $\Delta A_1 = A_{\mathrm{CH_4}} + A_{\mathrm{H_2O}} - 3A_{\mathrm{H_2}} - A_{\mathrm{CO}}$, by using the values reported in the thermodynamic data tables—Chemical Properties Handbook—for the reported temperature range [14].

3.2.3. Mass and energy balances

From the global gasification reaction, there are seven unknowns n_1, n_2, n_3, n_4, n_5, n_7 and m, representing the six unknown stoichiometric coefficients of the products and the oxygen content for the reaction. Therefore, seven equations are required, which are formulated based on the following:

Carbon balance: $1 = n_2 + n_3 + n_5 + n_7$, (9)

Hydrogen balance: $2w + 1.44 = 2n_1 + 2n_4 + 4n_5$, (10)

Oxygen balance: $w + 0.66 + 2m = n_2 + 2n_3 + n_4$, (11)

Equilibrium constant for methane decomposition: $K_1 = \dfrac{x_1^3 \cdot x_2}{x_4 \cdot x_5}$, (12)

Equilibrium constant for water gas shift reaction: $K_2 = \dfrac{x_1 \cdot x_3}{x_2 \cdot x_4}$, (13)

Equilibrium constant for soot formation reaction: $K_3 = \dfrac{x_1 \cdot x_2}{x_4}$, (14)

where x_i is the mole fraction of the compound i in the gas mixture, $x_i = \frac{n_i}{\sum_1^6 n_i}$.

The enthalpy balance equation includes the amount of electricity used in the plasma furnace:

$$\begin{aligned} &H^0_{\mathrm{f,waste}} + wH^0_{\mathrm{f,H_2O}(l)} + mH^0_{\mathrm{f,O_2}} + 3.76mH^0_{\mathrm{f,N_2}} + E_{\mathrm{Electricity}} \\ &\quad = n_1 H^0_{\mathrm{f,H_2}} + n_2 H^0_{\mathrm{f,CO}} + n_3 H^0_{\mathrm{f,CO_2}} + n_4 H^0_{\mathrm{f,H_2O}(g)} + n_5 H^0_{\mathrm{f,CH_4}} + n_6 H^0_{\mathrm{f,N_2}} + n_7 H^0_{\mathrm{f,C}} \\ &\qquad + \int_{T_1}^{T_2} (n_1 c_{p,\mathrm{H_2}} + n_2 c_{p,\mathrm{CO}} + n_3 c_{p,\mathrm{CO_2}} + n_4 c_{p,\mathrm{H_2O}} + n_5 c_{p,\mathrm{CH_4}} + n_6 c_{p,\mathrm{N_2}} + n_7 c_{p,\mathrm{C}})\,\mathrm{d}T, \end{aligned} \tag{15}$$

where $H^0_{\mathrm{f,waste}}$ is the heat of formation of the waste material, $H_{\mathrm{f,H_2O}(l)}$ is the heat of formation of liquid water, $H^0_{\mathrm{f,H_2O}(g)}$ is the heat of formation of water vapor, $H^0_{\mathrm{f,H_2}}, H^0_{\mathrm{f,CO}}, H^0_{\mathrm{f,CO_2}}$ and $H^0_{\mathrm{f,CH_4}}$ are the heats of formation of the gaseous products, $H^0_{\mathrm{f,C}}$ is the heat of formation of solid carbon, $c_{p,\mathrm{H_2}}$, $c_{p,\mathrm{CO}}$, $c_{p,\mathrm{CO_2}}, c_{p,\mathrm{H_2O}}, c_{p,\mathrm{CH_4}}, c_{p,\mathrm{N_2}}$ are the specific heats of the gaseous products and $c_{p,\mathrm{C}}$ is the specific heat of the solid carbon—soot ($=f(T)$), T_2 is the gasification temperature (1273 K) and T_1 is the ambient temperature (298 K). It is also mentioned that the $E_{\mathrm{Electricity}}$ value accounts for the energy required for the gasification reaction only and not for the vitrification of the inorganic fraction of the solid waste.

Concerning the calculation of specific heat for solid carbon, the equation below is used

$$c_p = A + B \cdot T + C \cdot T^2 \quad (T = 200 - 1100\ \mathrm{K}),$$

where the constants A, B and C are reported in the Chemical Properties Handbook [14].

3.2.4. Soot formation

Soot, an unwelcome by-product in many practical combustion systems, may be formed when carbonaceous fuels are burned under reducing conditions. In fact, at the temperature range over 800 °C, soot formation competes with its oxidation. With solid fuels, e.g. coal, soot is formed by the pyrolysis of tarry materials ejected by particles undergoing devolatilisation. The droplets dehydrogenate and/or partially oxidize into chains of soot spherules. Most are burned before exiting the flame region, but a significant residual can be found in the fly ash of some combustors [18].

In the present work, the term "soot" is used to indicate the presence of solid carbon as a by-product of the waste plasma treatment process that is in equilibrium with the gas phase. The chemical reaction that is selected to describe the formation of soot is the primary water gas reaction ($C + H_2O = CO + H_2$) due to the fact that the high feed moisture content reported in the majority of gasification studies seems to play a more important role in the chemistry of gasification than the low amounts of carbon dioxide ($C + CO_2 = 2CO$) produced. As presented above, the consideration of soot formation results in a system of seven equations: three mass balances, i.e. for carbon, hydrogen and oxygen, one enthalpy balance and three equations for the three chemical equilibrium constants.

Owing to the complexity of the resultant system of equations, an advanced software program (MathCad) is used for development of the GasifEq model in order to solve this non-linear system of seven equations with seven unknown values. The GasifEq model can be used for prediction of the amount of solid carbon that is not converted to gaseous components. Moreover, GasifEq can be used for the representation of the C–H–O equilibrium for a variety of organic waste materials and different gasification conditions (oxygen and moisture amount, gasification temperature) in the form of a ternary diagram. In the case where no soot particles remain in the produced gas, the model is simplified to a system consisted of six equations that can be relatively easily transformed to a linear-like one, and it can be solved with the help of conventional spreadsheet software packages.

4. Model validation

4.1. Synthesis gas prediction results

In order to validate the equilibrium gasification model (GasifEq), experimental data taken from the literature were used and compared to the results predicted by GasifEq. The results are shown in Table 4 for two different gasification scenarios with common waste material treated, i.e. wood waste.

It appears that the equilibrium gasification model results are satisfactorily close to the experimental values. The observed difference with the experimental values may be due to the fact that equilibrium is not attained in the experiments. This fact is indicated by the increased amount of methane in both experimental data sets, which would not be expected in the equilibrium state for the reported gasification temperature of the experiments.

Considering the results reported by other models in the literature, they agree closely with the GasifEq results. However, it is mentioned that in these models, presented also in Table 4, the enthalpy formation of wood was set to be equal to 118,050 kJ/kmol, as reported by Zainal et al. [4], while the enthalpy of formation of wood calculated by GasifEq model, according to its elemental composition, is equal to 149,752 kJ/kmol. This difference in the calculation process of the higher heating value (HHV) is due to the erroneous use by the above authors of the enthalpy of formation of gaseous water, while the enthalpy of formation of liquid water has been used here, according to the HHV definition.

Finally, the differences observed between the GasifEq results and the ones reported by Zainal et al. [4] may be due to the oxygen amount used by Zainal et al. [4], which is not reported.

4.2. Soot formation—ternary diagram

In order to investigate the possibility of the formation of solid carbon, i.e. soot, as a by-product of the plasma gasification process, the molar ternary diagram was drawn in Fig. 2, and the points for each gasification scenario are plotted.

Table 4
Prediction results and comparison with experimental values

Gaseous products % v/v dry basis	GasifEq model	Predicted Zainal et al. [4]	Experimental, Zainal et al. [4]
Panel a: 20% moisture, 1073 K, no electricity, wood waste described by Zainal et al. [4]			
H_2	18.44	21.06	15.23
CO	17.46	19.61	23.04
CO_2	13.13	12.01	16.42
CH_4	0.00	0.64	1.58
N_2	50.96	46.68	42.31
Sum	100.00	100.00	98.58

Gaseous products % v/v dry basis	GasifEq model	SynGas model Altafini et al. [8]	Cycle-Tempo model Altafini et al. [8]	Experimental, Altafini et al. [8]
Panel b: 10% moisture, 1073 K, no electricity, wood waste described by Altafini et al. [8]				
H_2	19.80	20.06	21.40	14.00
CO	23.45	19.70	23.00	20.14
CO_2	9.16	10.15	9.74	12.06
CH_4	0.01	0.00	0.01	2.31
N_2	47.57	50.10	45.31	50.79
Sum	100.00	100.01	99.56	99.20
Air/waste ratio	2.01	1.96	1.96	1.83

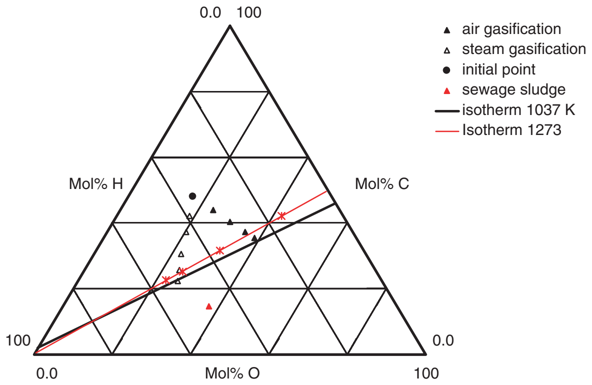

Fig. 2. Molar ternary diagram showing carbon formation boundaries for C–H–O system at pressure of 1 atm.

An indicative gasification scenario is the case of sewage sludge as a solid waste material (C: 54.8, H: 8, O: 33.4, N: 3.8) with moisture content of 30% w/w and with oxygen amount added in the process to be equal to 0.661 mol/mol dry ash free sludge. The rhomboid point in the diagram corresponds to this scenario of sewage sludge gasification. It is shown clearly that this point is below the carbon deposition boundary for the temperatures of 1073 K and 1273 K, which means that no solid carbon exists in equilibrium with the gaseous components.

The so-called carbon deposition boundaries are the lines that are drawn for the group of points where marginally no solid carbon is present in heterogeneous equilibrium with the gaseous products. In order to draw the isothermal carbon boundary lines, an initial point in the diagram is selected for which equilibrium calculations are performed. For example, a solid organic material (C: 90, H: 4, O: 5) that is gasified with a specified amount of oxygen (0.1 mol/mol waste material) and a specified amount of moisture content (0.1 mol/mol waste material) corresponds to a molar mixture of C–H–O that is considered as the initial point in the ternary diagram of Fig. 2. By adding oxygen in two forms, i.e. air or steam, the points for the case of air gasification (addition of air–oxygen) and steam gasification (increase of moisture content) are predicted by the GasifEq model and are drawn in the ternary diagram. In this way, two points are found where no solid carbon is formed in equilibrium. In such a way, more points are predicted for a specific temperature where no solid carbon is present in the gasification products. This group of points is the carbon deposition boundary for a specific temperature.

It is mentioned that the isothermal carbon boundary for the temperature of 1037 K, shown in Fig. 2, was extracted from the literature [10], while the isotherm of 1273 K was predicted with the help of the GasifEq model. It is also shown in Fig. 2 that the points predicted by GasifEq model for the temperature of 1037 K and for the marginally zero production of soot agree closely with the isothermal carbon boundary reported in the literature.

5. Energy and exergy calculations

Exergy analysis (availability analysis, second law thermodynamic concept) is applied to the plasma gasification system by calculating the exergy input and output rates for the main section of the process, i.e. the plasma treatment sub-system. The idea that something can be destroyed is useful in the design and analysis of thermal systems. This idea does not apply to energy (energy cannot be destroyed according to the first law of thermodynamics) but to exergy (useful, available energy), a concept that gauges the quality (usefulness) of each form of energy. The exergetic efficiency, a parameter that is introduced by exergy analysis, provides a true measure of the performance of the plasma system from the thermodynamic viewpoint.

The chemical exergy of the produced gas mixture is determined by the composition and concentration of the components in the mixture [19]:

$$\varepsilon_{0,m} = \sum_i x_i \varepsilon_{0,i} + RT_0 \sum_i x_i \ln x_i, \tag{16}$$

where x_i are the molar fractions of each component, $\varepsilon_{0,i}$ is the standard chemical exergy (kJ/kmol) of each component (Table 5), e.g. $\varepsilon_{H_2} = 236,100$ kJ/kmol and $\varepsilon_{CO} = 275{,}100$ kJ/kmol, and $\varepsilon_{0,m}$ is the chemical exergy of the mixture (kJ/kmol).

Regarding the physical exergy calculation, the equation $E = Q \cdot \left(1 - \frac{T_0}{T}\right)$ [7] is applied as shown below:

$$\begin{aligned} E &= Q \cdot \left(1 - \frac{T_0}{T}\right) \Rightarrow \mathrm{d}E = \mathrm{d}Q \cdot \left(1 - \frac{T_0}{T}\right) \Rightarrow \mathrm{d}E = c_p \cdot \left(1 - \frac{T_0}{T}\right) \mathrm{d}T \Rightarrow E \\ &= \int_T^{T_0} c_p \, \mathrm{d}T - T_0 \cdot \int_T^{T_0} \frac{c_p}{T} \, \mathrm{d}T \Rightarrow E = \int_T^{T_0} \left(\sum x_i c_{p,i}\right) \mathrm{d}T - T_0 \cdot \int_T^{T_0} \frac{\left(\sum x_i c_{p,i}\right)}{T} \mathrm{d}T, \end{aligned} \tag{17}$$

where $c_{p,i} = A + B \cdot T + C \cdot T^2 + D \cdot T^3$ and A, B, C and D are the coefficients for each gas component as presented in the previous paragraph.

5.1. Chemical exergy of the waste material

In principle, the standard chemical exergy of a substance not present in the environment can be evaluated by considering an idealized reaction of the substance with other substances (usually reference substances) for which the chemical exergies are known.

Table 5

Standard molar chemical exergy of various substances at 298.15 K and 1 atm [19]

Substance	ε (kJ/kmol)
Nitrogen (g)	720
Carbon dioxide (g)	19,870
Water (g)	9,500
Hydrogen (g)	236,100
Carbon monoxide (g)	275,100
Methane (g)	831,650

For the case of organic solid waste material, it is assumed that dry and ash free material (daf) enters the control volume at T_0, p_0 and reacts completely with the oxygen entering separately at T_0, p_0 to form CO_2 and $H_2O(l)$, which exits separately at T_0, p_0. The nitrogen contained in the material also exits separately at T_0, p_0 as N_2. All heat transfer occurs at temperature T_0.

On the basis of 1 kg of daf waste material entering the control volume, the combustion reaction is described by

$$(c\mathrm{C} + h\mathrm{H} + o\mathrm{O} + n\mathrm{N}) + \nu_{\mathrm{O_2}}\mathrm{O_2} \to \nu_{\mathrm{CO_2}}\mathrm{CO_2} + \nu_{\mathrm{H_2O}}\mathrm{H_2O}_{(l)} + \nu_{\mathrm{N_2}}\mathrm{N_2}$$

where c, h, o and n are expressed in kmol/kg daf waste material.

Balancing the reaction equation, we have

$$\nu_{\mathrm{CO_2}} = c, \quad \nu_{\mathrm{H_2O}} = \frac{1}{2}h, \quad \nu_{\mathrm{N_2}} = \frac{1}{2}n, \quad \nu_{\mathrm{O_2}} = c + \frac{1}{4}h - \frac{1}{2}o.$$

Assuming no irreversibilities, the chemical exergy of the waste material according to the exergy balance reads:

$$\varepsilon_{\mathrm{waste}} = \left(\frac{W_{\mathrm{c}}}{n_{\mathrm{waste}}}\right) + \nu_{\mathrm{CO_2}} \cdot \varepsilon_{\mathrm{CO_2}} + \nu_{\mathrm{H_2O}} \cdot \varepsilon_{\mathrm{H_2O}(l)} - \nu_{\mathrm{O_2}} \cdot \varepsilon_{\mathrm{O_2}}, \tag{18}$$

where $(\frac{W_{\mathrm{c}}}{n_{\mathrm{waste}}})$ is obtained by eliminating the heat transfer term from the expressions of the energy and entropy balances as shown below:

$$\text{Energy balance:} \quad \left(\frac{W_{\mathrm{c}}}{n_{\mathrm{waste}}}\right) = \frac{Q_{\mathrm{cv}}}{n_{\mathrm{waste}}} + (h_{\mathrm{waste}} + \nu_{\mathrm{O_2}} \cdot h_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}} \cdot h_{\mathrm{CO_2}} - \nu_{\mathrm{H_2O}} \cdot h_{\mathrm{H_2O}}), \tag{19}$$

$$\text{Entropy balance:} \quad 0 = \frac{Q_{\mathrm{cv}}/n_{\mathrm{waste}}}{T_0} + s_{\mathrm{waste}} + \nu_{\mathrm{O_2}} \cdot s_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}} \cdot s_{\mathrm{CO_2}} - \nu_{\mathrm{H_2O}} \cdot s_{\mathrm{H_2O}}. \tag{20}$$

Adding Eqs. (19) and (20)

$$\begin{aligned}\left(\frac{W_{\mathrm{c}}}{n_{\mathrm{waste}}}\right) &= (h_{\mathrm{waste}} + \nu_{\mathrm{O_2}} \cdot h_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}} \cdot h_{\mathrm{CO_2}} - \nu_{\mathrm{H_2O}} \cdot h_{\mathrm{H_2O}}) \\ &\quad - T_0 \cdot (s_{\mathrm{waste}} + \nu_{\mathrm{O_2}} \cdot s_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}} \cdot s_{\mathrm{CO_2}} - \nu_{\mathrm{H_2O}} \cdot s_{\mathrm{H_2O}}).\end{aligned} \tag{21}$$

The first term of the equation is equal to the higher heating value of the dry ash free waste material, HHV, so the exergy of the waste is equal to Eqs. (18) plus (21):

$$\varepsilon_{\mathrm{waste}} = \mathrm{HHV} - T_0 \cdot (s_{\mathrm{waste}} + \nu_{\mathrm{O_2}} \cdot s_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}} \cdot s_{\mathrm{CO_2}} - \nu_{\mathrm{H_2O}} \cdot s_{\mathrm{H_2O}}) + \nu_{\mathrm{CO_2}} \cdot \varepsilon_{\mathrm{CO_2}} + \nu_{\mathrm{H_2O}} \cdot \varepsilon_{\mathrm{H_2O}(l)} - \nu_{\mathrm{O_2}} \cdot \varepsilon_{\mathrm{O_2}}. \tag{22}$$

To complete the calculation of the chemical exergy of the waste material, values are required for the HHV of the dry and ash free waste and the absolute entropy s_{waste}, both at T_0 and p_0.

The HHV of the waste material can be predicted or determined experimentally. In a case where the HHV of the waste material is not available or it is difficult to determine due to the form of the material, e.g. municipal solid waste, six predictive equations of HHV are reported from the literature. These equations have been applied for a characteristic waste material, i.e. sewage sludge, and the predicted values are presented along with the experimental value for evaluation purposes in Table 6.

Table 6
Prediction of HHV for sewage sludge

Equation	$\mathrm{HHV_{dry}}$ (kJ/kg)
Dulong	16,506
Scheuer and Kestner	18,892
Steuer	17,744
Milne	16,532
Francis and Loyd	16,895
Meraz et al.	17,686
Experimental value	16,600

The results in Table 6 indicate that the available equations predict fairly well the HHV of sewage sludge. It appears that the predicted values by the original Dulong formula and Milne's formula are closer to the experimental value. It is worth mentioned that the original Dulong formula is an equation with a theoretical background, and the next two equations are two modified forms of Dulong's [20]. Additionally, the Milne's [21] (Phyllis database) as well as Francis and Loyd's equations [22] were developed by correlation of experimental data, while the last equation [23] is the most recent one and it is based on thermochemical concepts.

Regarding the absolute entropy of the dry and ash free waste, this is calculated by using a correlation reported by Bejan et al. [19]:

$$s_{\text{waste}} = c \cdot \left(37.1653 - 31.4767 \exp\left(-0.564682 \cdot \frac{h}{c+n}\right) + 20.1145 \frac{o}{c+n} + 54.3111 \frac{n}{c+n} + 44.6712 \frac{s}{c+n}\right), \tag{23}$$

where c, h, o and n are expressed in kmol/kg daf waste material.

The above calculation of chemical exergy results in a value close enough to the heating value, which means that the chemical exergy is determined mainly by the heating value term. The use of the heating value of a fuel material (in this work the waste material is actually considered as an organic composed fuel) for the calculation of its chemical exergy is frequently observed in the technical literature.

Therefore, two statistical correlations are also presented here that will be used for calculation of the chemical exergy of the waste. The first correlation is the one of Kotas [24] that is shown below:

$$\varepsilon^0/[\text{kJ/kg}] = (\text{LHV} + 2442 \cdot w) \cdot \phi_{\text{dry}},$$

$$\text{where } \phi_{\text{dry}} = 1.0437 + 0.1882\frac{H}{C} - 0.0610\frac{O}{C} + 0.0404\frac{N}{C} \left(\text{valid for } \frac{O}{C} \prec 0.667\right) \tag{24}$$

LHV is the lower heating value of the waste material, and H, C, O, N and w denote the weight fractions of hydrogen, carbon, oxygen, nitrogen and moisture, respectively, in the waste material.

In addition to the above expression, the chemical exergy of solid fossil fuels is given also by Prins et al. [10]:

$$\varepsilon^0/[\text{kJ/kg}] = (\text{LHV} + 2442 \cdot w) \cdot \beta, \tag{25}$$

$$\text{where } \beta = \frac{1.0412 + 0.2160\frac{H}{C} - 0.2499\frac{O}{C}\left[1 + 0.7884\frac{H}{C}\right] + 0.0450\frac{N}{C}}{1 - 0.3035\frac{O}{C}} \tag{26}$$

(valid for $\frac{O}{C} \leqslant 2.67$).

5.2. Efficiency based on the first and second thermodynamic laws

The first law efficiency can be calculated in two ways. The first one, the so-called "hot gas efficiency", is the ratio of the energy of the synthesis gas, including the sensible heat of the gas, to the heating value of the waste material and the electricity used. This efficiency value would be equal to 100% because the process is adiabatic, and no losses were considered. The second one, the cold gas efficiency, excludes the sensible heat of the produced gas and is obtained by dividing the heating value of the synthesis gas by the lower heating value of the waste material and the electricity used:

$$e = \frac{\text{HV}_{\text{Synthesis gas}}}{\text{LHV}_{\text{Waste}} + \text{Electricity}}. \tag{27}$$

On the other hand, the second law efficiency is calculated in the same way, by dividing the exergy of the produced synthesis gas (chemical and physical exergy) by the chemical exergy of the waste material plus the electricity used. Furthermore, the exergy efficiency based only on the chemical exergy of the produced gas is calculated in a similar way to the cold gas efficiency.

$$\varepsilon = \frac{\text{Chemical exergy}_{\text{Synthesis gas}}}{\text{Chemical exergy}_{\text{Waste}} + \text{Electricity}}. \tag{28}$$

Concerning calculation of the chemical exergy of the waste material, it has to be reported that the values predicted by the three different ways described in the previous paragraph give similar results. For example, for sewage sludge and by applying the conventional exergy calculation method, which includes the standard molar chemical exergy values (Table 5) and predicts the entropy of the waste material, the obtained chemical exergy of sewage sludge is calculated to be 15.90 MW (for a feed rate of 0.635 kg daf/s). This value for chemical exergy is selected in this study, which is also in agreement with the values calculated with the help of statistical correlations by Prins et al. [10] and Kotas [24], i.e. 15.85 MW for both cases.

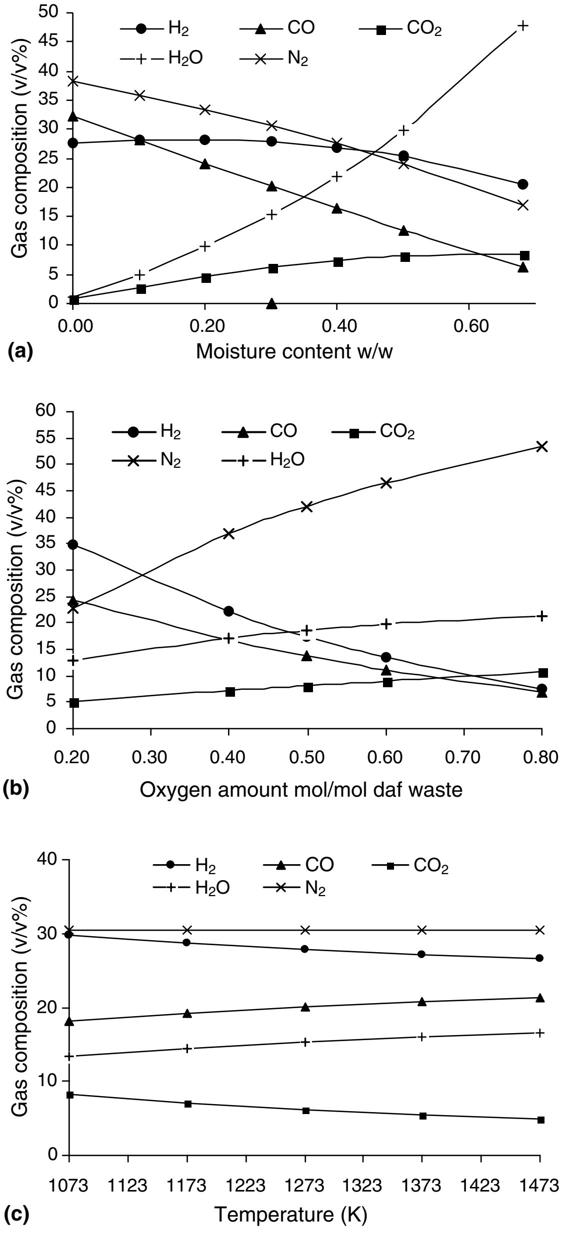

Fig. 3. Moisture, oxygen and temperature effect on synthesis gas composition. (a) Feed moisture: variable, oxygen: 0.3 mol/mol dry waste, temperature 1273 K, (b) feed moisture: 30% w/w, oxygen: variable, temperature 1273 K, (c) feed moisture: 30% w/w, oxygen: 0.3 mol/mol dry waste, temperature: variable.

The difference between the first and second law efficiencies is, in fact, the difference between the theoretically calculated efficiency of the process and the "real" efficiency of the process.

5.3. Parametric analysis

In process analysis studies, the study of each operational parameter's effect is required in order to decide which is the optimum scenario for high energy efficiency to be achieved. In this work, parametric analysis

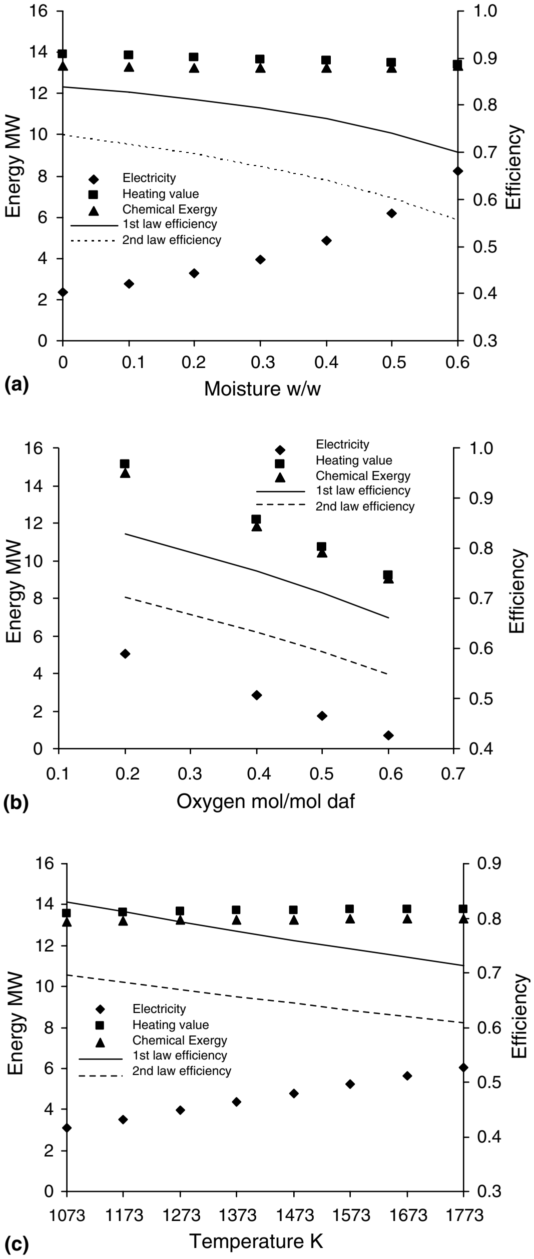

Fig. 4. Moisture, oxygen and temperature effect on process' energy performance. (a) Feed moisture: variable, oxygen: 0.3 mol/mol dry waste, temperature 1273 K, (b) feed moisture: 30% w/w, oxygen: variable, temperature 1273 K, (c) feed moisture: 30% w/w, oxygen: 0.3 mol/mol dry waste, temperature: variable.

has been conducted for a characteristic waste material, i.e. sewage sludge and for feed rate of 0.635 kg daf/s. Three parameters are considered: feed moisture content, oxygen and gasification temperature and their effect on the synthesis gas composition and the first and second law efficiencies of the process as demonstrated below.

The effect of each of these parameters, while holding the other two constant, on the gas composition predicted by the GasifEq model is presented in Fig. 3, and they are in agreement with the pertinent literature. Thus, it is shown in Fig. 3a that moisture content (up to 25%) is essential for the gasification chemical reactions as it contributes to the increase of hydrogen's concentration in the produced synthesis gas. This agrees with the findings of Pinto et al. [25], who state that the increase of the steam amount has proven to be advantageous because reforming reactions (such as $CH_4 + H_2O = CO + 3H_2$ included in the GasifEq model) are favored, and thus, the hydrocarbons concentrations decreased and the hydrogen release increased; and of Gil et al. [26], who presented results for three different cases of gasifying agent, i.e. air, steam and a mixture of air and steam, where the best results are obtained when a mixture of steam and air or steam alone is used.

Fig. 3b indicates that an increase of air flow rate is disadvantageous in all cases, as presented also by Pinto et al. [25] and Gil et al. [26], mainly due to the dilution of the produced gas with the nitrogen introduced by air. This should be avoided as it led to a substantial reduction in the synthesis gas HHV.

Regarding the temperature effect, Fig. 3c, it is shown that an increase of gasification temperature leads to an increase of the carbon monoxide concentration and to a small decrease of hydrogen concentration at temperatures over 1073 K. The total of these two main synthesis gas components concentration is increasing at high temperatures.

The aforementioned three operational parameters affect—through the synthesis gas composition—the energy performance of the process as demonstrated in Fig. 4 only for the central part of the process, the plasma gasification section. It is apparent that for an increase in moisture content, oxygen amount and temperature, both the first and second law efficiencies decrease.

The choice of the parameter values does not only depend on the H_2 and CO percents of the produced synthesis gas or on the thermodynamic efficiency of the process but also on the future application of the produced synthesis gas. The main commercial uses of synthesis gas are as a fuel for electricity generation, as a source for molecular hydrogen, in the synthesis of methanol and in the Fischer–Tropsch synthesis. Consider, for example, the use as a fuel, which is the typical case.

It is apparent here that for maximum efficiency, the electricity input must be zero and the operating temperature at the minimum possible. The operation requirements and environmental limitations of the process, e.g. destruction of dioxins, lead to a temperature of 1273 K. The variation of process efficiency with moisture content in this case is shown in Fig. 5. Notice that in order to maintain the temperature at the level of 1273 K, an increasing moisture amount of air is required. It is apparent that the lowest moisture content in the feed is desirable for maximum efficiency. Furthermore, the heating value of the synthesis gas is required to be at least equal to 1 kW h/N m^3 for most engines, which corresponds to a moisture content below 0.15. This indicates

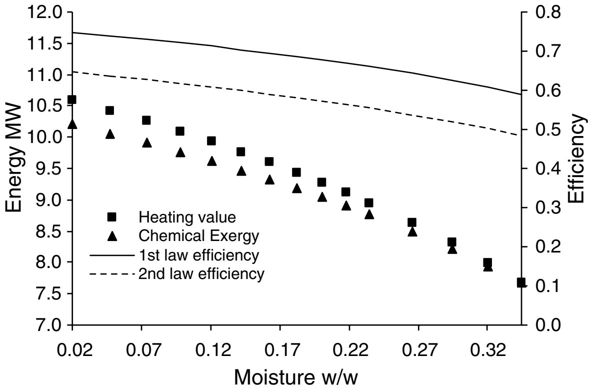

Fig. 5. Moisture effect on energy values and efficiencies of the process for the case of zero electricity supply for completion of gasification reactions (temperature 1273 K and oxygen range: 0.52–0.70 mol/mol daf).

that if the moisture content is higher, electricity must be utilized to maintain the temperature at 1273 K, either that or pre-drying of the waste material must be performed.

6. Conclusion

Plasma gasification offers an attractive alternative option for the treatment and energy utilization of solid waste. In this study, an equilibrium model is developed, called GasifEq, that incorporates recent thermodynamic data along with a detailed energy and exergy analysis in order to predict the performance of the plasma gasification process. Analysis of the process includes the effect of each operational parameter: moisture content, oxygen amount and gasification temperature, on the synthesis gas composition as well as the energy and exergy efficiencies of the process. The predictive capability of the model contributes to the selection of the optimum operation conditions based on both the processes first and second thermodynamic law efficiencies and some selected process parameters such as the quality of the produced synthesis gas and the need of possible waste drying prior to the plasma gasification furnace.

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