

GASIFICATION OF REFUSE-DERIVED FUEL (RDF)

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Abstract

In this work, the gasification of a fraction of municipal solid waste, MSW, generally separated from inorganic materials and biodegradable components, the so-called refuse-derived fuel (RDF), was studied using material characterisation methods, and the modelling of an industrial scale process was presented. The composition of RDF was determined by the separation of a representative sample into its basic components (paper, foils, hard plastics, textiles). All RDF components as well as a representative mixed sample of the RDF were studied using a thermogravimetric analysis (TGA), elemental analysis and bomb calorimetry to determine their proximate and elemental compositions, and a higher heating value. An industrial scale gasification process was studied by mathematical modelling and computer simulations. All techniques, gasification with air, gasification with oxygen, and gasification with both oxygen and steam were investigated under different conditions. The RDF conversion of 100 % was achieved by the gasification with air at the air to RDF mass ratio of 3.2. The gas heating value was 4.4 MJ/Nm³. The gasification of RDF using oxygen enables the production of gas with the heating value of around 10 MJ/Nm³ at the oxygen to RDF mass ratio of 0.65. By increasing the steam to the RDF mass ratio, the contents of H₂ and CO₂ increased, while the content of CO, reactor temperature and the gas heating value decreased.

1 INTRODUCTION

Many countries, including Slovakia, still landfill the majority of their municipal solid waste (MSW). Such landfilling results not only in significant environmental challenges, but also in wasting valuable resources. MSW represents a valuable source of material and energy. However, the heterogeneity and composition variations are important challenges for mechanical recycling of MSW. On the other hand, feedstock recycling methods such as pyrolysis and gasification have a big potential to be used for recovery of valuable chemicals and energy from MSW. The fraction of MSW generally separated from inorganic materials and biodegradable components is called refuse-derived fuel (RDF). The gasification of RDF results in the production of a combustible gas containing mainly H₂, CO, CO₂, and N₂ if air is used as the gasification agent. Some methane, light hydrocarbons, H₂S, NH₃, and tar are also present in the gas [1].

A number of power generation plants based on gasification technology are in operation worldwide. A list of operating and planned gasification plants has been provided by Higman and Van der Burgt [2]. The modelling of gasification enables predicting optimal process conditions and reducing the number of experiments in the processes of design and operation. A simple equilibrium mathematical model based on the minimisation of Gibbs free energy was used by some authors to model the gasification of RDF. Materazzi et al. [3] used the equilibrium model to evaluate a two-stage waste gasification system. It results from their work that except for H₂ the predicted composition of gas is in good coherence with the experimental data. The equilibrium model was also applied by Barba et al. for RDF gasification [4], and Jarungthammachote and Dutta [5] for the gasification of charcoal and coconut shell. The authors found that the model data is in good agreement with the experimental one. However, Li et al. [6] applied an equilibrium model for coal gasification and declared that this model has some limitations in predicting gas composition. Generally, the equilibrium model provides good results at temperatures above 1000 °C, and it fails at the reactor temperatures below 800 °C [7-8].

In this work, the equilibrium model was combined with some empirical correlations based on laboratory experiments to predict the carbon conversion, reactor temperature, gas composition, gas heating value and the gas tar content under different types and amounts of gasification agents. The input data for the model was determined by the characterisation of single components of RDF such as paper, polyethylene foils, hard plastics and textiles.

2 RAW MATERIAL

The RDF samples used in this study were provided by a recycling company based in Slovakia. The composition of the RDF was estimated by hand separation of a representative sample of RDF into its basic material categories. The contents of individual components of RDF are shown in Table 1.

The sample of RDF with the composition shown in Table 1 was homogenised by grounding in a cryogenic mill. In addition, homogenised samples of individual material categories of RDF were prepared.

Table 1: Composition of RDF samples used

Component	Material	w_i [kg/kg]
Paper	White paper, recycled paper	0.6317
Foil	LDPE, HDPE	0.1578
Plastics	Rigid plastics, polystyrene, polyurethane	0.1910
Textile	Polyamide, polyester, cotton, wool	0.0194

Using simultaneous thermogravimetric (TG)/differential scanning calorimetric (DSC) measurements (Netzsch STA 409 PC Luxx, selb, Germany), a proximate analysis of individual components of RDF was done. The experimental conditions were met at the linear heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ in the nitrogen flow of $60 \text{ ml} \cdot \text{h}^{-1}$. The samples were heated from 293 K to 1073 K; at this temperature, they were maintained for around 30 min and then combusted by entering the oxygen to the system. Samples of individual components of RDF, of around 20 mg, were used in the TG/DSC measurements.

The dry basis elemental composition of individual components of RDF was estimated by a Vario Macro Cube ELEMENTAR elemental analyzer. A CHNS (Carbon, Hydrogen, Nitrogen, Sulphur) module with the combustion tube temperature of 1423 K, and the reduction tube temperature of 1073 K was used. The module did not enable the determination of the Cl content. The mass of the sample was around 1 g. The results of both proximate and elemental analyses are given in Table 2.

Table 2: Proximate and elemental compositions of RDF and RDF components

Component	w_i [kg/kg]	Moisture	VM	FC	ASH	C	H	N	S	O*
Paper	0.6317	1.77	78.22	6.15	13.85	43.58	6.46	0.42	0.11	35.59
Foil	0.1578	0.00	99.23	0.00	0.77	79.38	13.63	0.93	0.07	5.22
Plastics	0.191	0.00	70.67	6.32	23.00	55.60	13.06	1.24	0.00	7.10
Textile	0.0194	4.04	84.97	6.95	4.04	51.05	4.92	0.71	0.21	39.07
RDF	1	1.20	80.22	5.23	13.34	51.66	8.82	0.66	0.08	25.42

*-calculated to 100 %, VM- volatile matter, FC- fixed carbon

Based on the elemental composition of RDF shown in Table 2 and the molecular mass of elements, the summary formula of RDF (dry ash free) in the form of $C_a H_b O_c N_d S_e$ was proposed. The values of a , b , c , d , and e are given in Table 3.

Table 3: Dry ash- free formula of RDF

C	H	N	S	O*
a	b	c	d	E
1	2.034454	0.010955	0.00058	0.369391

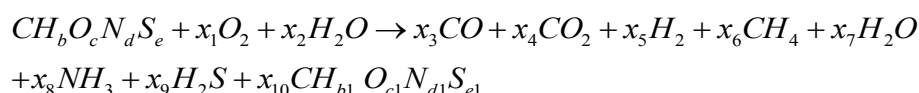
The final molecular formula of the RDF used is $CH_{2.03446}O_{0.3694}N_{0.010955}S_{0.00058}$ and its molecular mass based on one carbon is $20.143 \text{ g} \cdot \text{mol}^{-1}$.

3 GASIFICATION MODEL

Let us assume that:

- steady state flow is considered inside the gasifier
- no temperature and concentration gradient exist inside the reactor
- the residence time is long enough to reach the complete decomposition of RDF, and the unreacted part of RDF is only carbon
- only the major species are considered in the product gases, i.e. CO, CO₂, H₂, CH₄, H₂O, NH₃, H₂S, N₂, and Tar
- Nitrogen and sulphur presented in the RDF is converted only to NH₃ and H₂S.

Then the global material balance of RDF gasification can be written as:

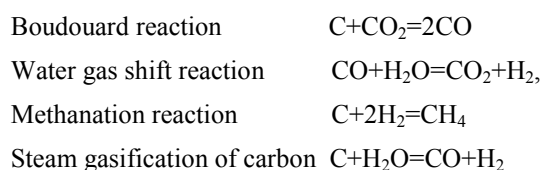


where, x_1 and x_2 are the numbers of moles of oxygen and steam used for each mole of the RDF and, $x_3, x_4, x_5, x_6, x_7, x_8, x_9$, and x_{10} are the numbers of moles of each corresponding species, obtained from each mole of RDF based on a single atom of carbon. $CH_{b1}O_{c1}N_{d1}S_{e1}$ is an empiric formula of tar that was estimated in the same way as that of the RDF using the results of the GC/MS analysis of biomass tar [9].

The following linear dependence between the tar content and the temperature based on biomass gasification experiments in [9] was assumed: $y = -0.0014(T - 273.15) + 2.0200$

where y represents the amount of tar in *mg* of tar per *g* of RDF and T is the temperature in K.

The mass balance of individual elements provides five algebraic equations. Together with the total mass balance, it makes six equations; however, to estimate all ten unknown stoichiometric coefficients, at least ten equations are required. The equilibrium constant of four gasification reactions should be added to the model. The following reactions were selected for this study:



The relation between the equilibrium constant and the equilibrium composition of the products of individual reactions is given by:

$$K_a = \left(\frac{P}{P^0} \right)^{\sum \nu_i} \prod \phi_i^{\nu_i} \prod x_i^{\nu_i} \quad (1)$$

where K_a is the equilibrium constant, P^0 the pressure at which K_a is defined [Pa], P the system pressure [Pa], ν_i the stoichiometric coefficient of component i , ϕ_i the fugacity coefficient of component i , and x_i the molar fraction of component i .

The value of equilibrium constant is calculated at constant temperature and pressure using the standard state Gibbs reaction energy $\Delta_r G^{298}$:

$$K_a^{298} = e^{\frac{-\Delta_r G^{298}}{RT}} \quad (2)$$

where K_a^{298} is the equilibrium constant at 298 K, $\Delta_r G^{298}$ the Gibbs energy at the standard state [$J \cdot mol^{-1}$], R the gas constant ($R = 8.314 J \cdot mol^{-1} \cdot K^{-1}$), and T is the temperature [K].

The fugacity coefficients were assumed to be equal to 1 in this work. The standard reaction Gibbs energy was calculated based on the standard reaction enthalpy, $\Delta_r H^{298}$ [$J \cdot mol^{-1}$], and the standard reaction entropy, $\Delta_r S^{298}$ [$J \cdot mol^{-1} \cdot K^{-1}$] as:

$$\Delta_r G^{298} = \Delta_r H^{298} - T \Delta_r S^{298} \quad (3)$$

The values of $\Delta_r H^{298}$ and $\Delta_r S^{298}$ were calculated using the standard reaction enthalpy and the entropy of formation:

$$\Delta_r H^{298} = \sum \nu_i \Delta_f H_i^{298} \quad (4)$$

$$\Delta_r S^{298} = \sum \nu_i \Delta_f S_i^{298} \quad (5)$$

where ν_i is the stoichiometric coefficient, $\Delta_f H^{298}$ the standard enthalpy of formation [$\text{J}\cdot\text{mol}^{-1}$], and $\Delta_f S^{298}$ the standard entropy of formation [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$].

The reaction enthalpy and the reaction entropy at the temperature of the system can be calculated by:

$$\Delta_r H = \Delta_r H^{298} + \sum \nu_i c_{pi} \cdot (T - 298) \quad (6)$$

$$\Delta_r S = \Delta_r S^{298} + \sum \nu_i c_{pi} \cdot \ln \frac{T}{298} \quad (7)$$

where $\Delta_r H$ is the reaction enthalpy at temperature T [$\text{J}\cdot\text{mol}^{-1}$], $\Delta_r S$ the reaction entropy at temperature T [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$], and c_{pi} the average molar heat capacity of component i [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$].

In the gasification reactor, the reaction temperature is obtained by partial oxidation of the feed. The global enthalpy balance of the reactor is:

$$H_{RDF} + H_{O2(air)} + H_{steam} + Q_R = H_{gas} + H_{ash} + H_C + Q_{loss} \quad (8)$$

where Q_R is the heat of reaction [J], H_{RDF} the enthalpy of RDF feed [J], $H_{O2(air)}$ are the enthalpy of oxygen and air, respectively [J], H_{steam} is the enthalpy of water steam [J], H_{gas} the enthalpy of gas [J], H_{ash} the enthalpy of ash [J], H_C the enthalpy of unreacted carbon [J], and Q_{loss} represents the heat losses from the reactor [J].

The heat of reaction can be calculated as the difference between the heating values of reactants and products:

$$Q_R = m_{RDF} \sum w_i Q_i - \sum (-\Delta_c H_i) n_i \quad (9)$$

where m_{RDF} is the mass flow of RDF feed [kg], n_i is the mole flow of component i in the products [kmol], w_i the mass fraction of component i in the feed (paper, foil, plastics, textiles) [-], Q_i the lower heating value of component i in the feed (paper, foil, plastics, textiles) [$\text{J}\cdot\text{kg}^{-1}$], and $\Delta_c H_i$ is the heat of combustion of component i in the products [$\text{J}\cdot\text{kmol}^{-1}$].

If the RDF feed and oxygen (air) are fed to the reactor at the same temperature which is selected as the reference temperature, T_{ref} , then $H_{RDF}=0$, $H_{O2(air)}=0$ and

$$H_{gas} + H_{ash} + H_C - H_{steam} = (T - T_{ref}) (\sum n_i c_{pi} + m_C \bar{c}_{pC} + m_{ash} \bar{c}_{pash} - m_{steam} \bar{c}_{psteam}) \quad (10)$$

where m_{ash} is the mass flow of ash [kg], m_C the mass flow of remaining carbon [kg], m_{steam} the mass flow of steam [kg], \bar{c}_{pash} the specific heat capacity of ash [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$], \bar{c}_{pC} the specific heat capacity of remaining carbon [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$], and \bar{c}_{psteam} is the specific heat capacity of steam [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$].

Substituting the equations (10) and (9) into the equation (8) for the temperature of products, the following results were obtained:

$$T = T_{ref} + \frac{m_{RDF} \sum w_i Q_i - (\sum (-\Delta_c H_i) n_i) - Q_{loss}}{(\sum n_i c_{pi}) + m_C \bar{c}_{pC} + m_{ash} \bar{c}_{pash} - m_{steam} \bar{c}_{psteam}} \quad (11)$$

The used heating values for products and components are shown in Table 4. The lower heating values of RDF components were measured experimentally [10] and the heat of combustion of the gas components was found in chemical engineering literature.

Table 4: Used heating values

<i>Component</i>	Q_i [J/g]	$-Δ_cH$ [J/mol]
Paper	13410	
Foil	43860	
Plastics	33570	
Textile	19770	
CO		282980
H ₂		241826
CH ₄		802362
C		393510

4 RESULTS AND DISCUSSION

The model described above was solved using MS EXCEL in the first step, then it was implemented into the ASPEN Plus simulation environment. The gasification with the following three different gasification agents was carried out:

- gasification of RDF using air
- gasification of RDF using pure oxygen
- gasification of RDF using pure oxygen and steam

The variable was the mass ratio of the gasification agent (air, oxygen or steam) and the observed output parameters were: conversion of RDF, reactor temperature, gas composition, and gas higher heating value (HHV).

a - Gasification of RDF using air:

Figure 1 shows the composition of produced gases at different air to RDF mass ratio. H₂ and CO are the most important components of the produced gas; the content of H₂ showed a maximum at $m_{(Air)}/m_{(RDF)}=2$ and that of CO at $m_{(Air)}/m_{(RDF)}=2.25$. The content of methane decreased to a value near zero at $m_{(Air)}/m_{(RDF)}=2.5$. However, it results from Figure 2 that at these values of $m_{(Air)}/m_{(RDF)}$, the adiabatic reactor temperature is around 850 K and the conversion of RDF is only 40-50%. A 100 % conversion was achieved at $m_{(Air)}/m_{(RDF)}=3.2$ at the reactor temperature of around 950 K. The gas heating value was relatively low, 4.5 MJ·N⁻¹·m⁻³, because of a high nitrogen content, and it remained practically constant for $m_{(Air)}/m_{(RDF)}$ ranging from 2 to 3.2, when it rapidly decreased because of the starting CO oxidation to CO₂ and a rapid increase of nitrogen content as a result of the decreasing contents of H₂ and CO. A low reactor temperature can cause a high content of tar in the produced gas. But increasing the reactor temperature requires the oxidation of H₂ and CO and also a rapid increase of nitrogen content in the produced gas which results in losing the energy content of the gas. Based on this observation, the optimal value of $m_{(Air)}/m_{(RDF)}$ for the gasification of RDF studied in this work was 3.2.

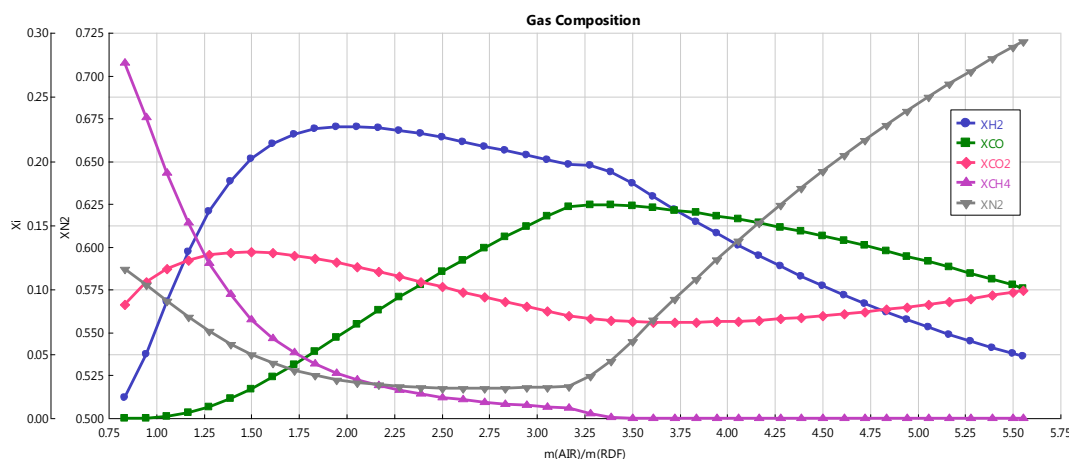


Figure 1: Gas composition at different $m_{(Air)}/m_{(RDF)}$ values using air as the gasification agent

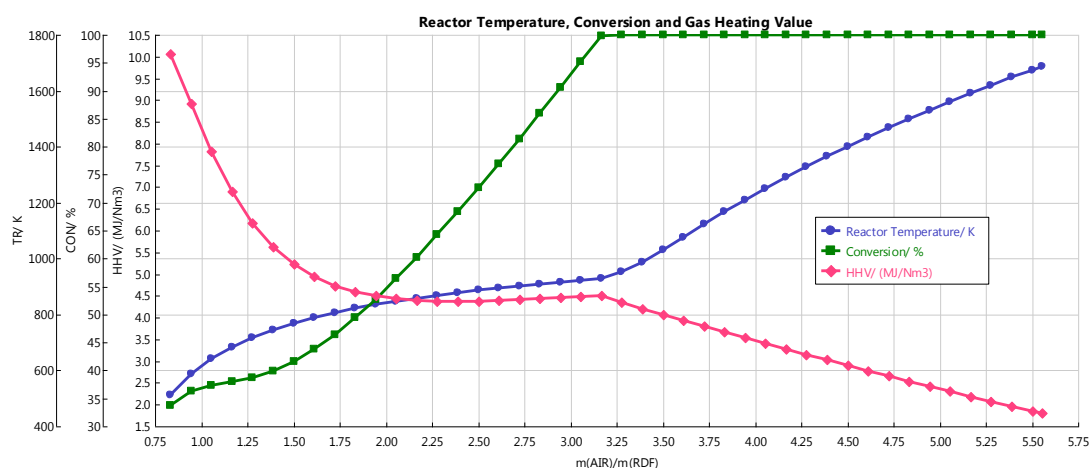


Figure 2: Conversion, reactor temperature and gas heating value at different $m_{(Air)}/m_{(RDF)}$ values using air as the gasification agent

The tar content of the produced gas decreased with the increasing reactor temperature and the air to RDF mass ratio. At optimum $m_{(Air)}/m_{(RDF)}=3.2$, the tar content was 280 mg/Nm^3 , which is not very high but still above the limit value of 50 mg/Nm^3 [2] for gas turbines.

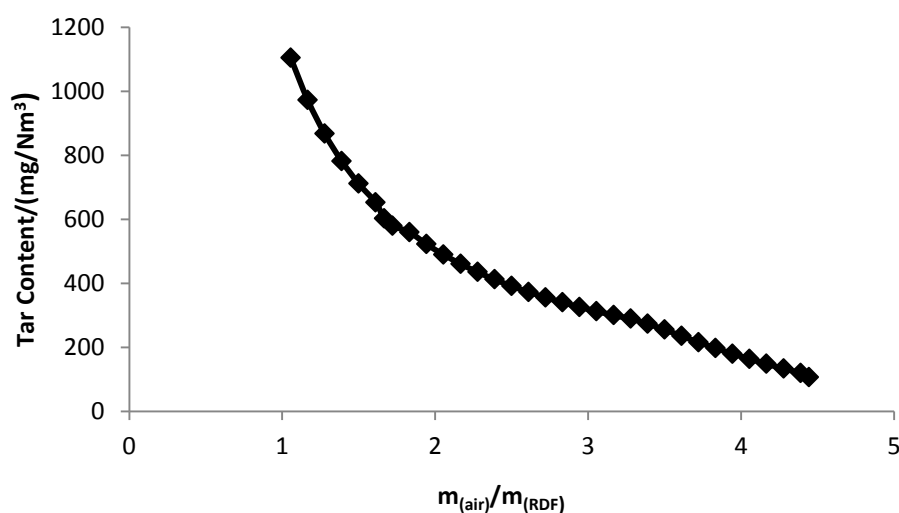


Figure 3: Content of tar in the produced gas at different $m_{(Air)}/m_{(RDF)}$ values using air as the gasification agent

The contents of H_2S and NH_3 decreased with increasing $m_{(Air)}/m_{(RDF)}$ (Figure 4); the content of H_2S at $m_{(Air)}/m_{(RDF)}=3.2$ was 0.015 mol \% . The combustion of such gas results in the SO_2 content in the flue gases of around 50 mg/Nm^3 , which is below the EU limit value for the combustion of solid fuels (200 mg/Nm^3).

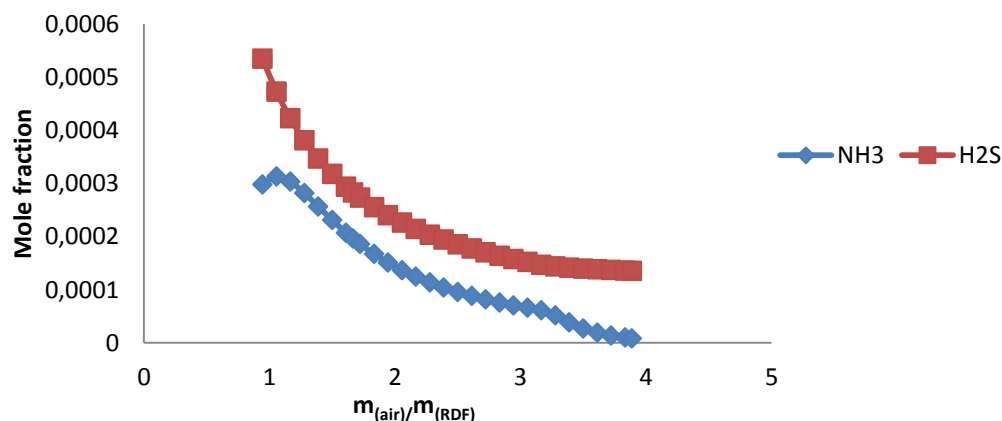


Figure 4: Content of H_2S and NH_3 of the produced gas at different $m_{(Air)}/m_{(RDF)}$ values using air as the gasification agent

b - Gasification of RDF using oxygen:

The oxygen blown gasification of RDF enables the production of gas with a 2-2.5 fold higher heating value. However, the gasification plant requires an air separation unit. The complete conversion of RDF was achieved at $m_{(O_2)}/m_{(RDF)}=0.65$; the adiabatic reactor temperature under these conditions was around 1100 K and the gas heating value was approx. 10 MJ/Nm³.

The content of H₂ showed its maximum at $m_{(O_2)}/m_{(RDF)}=0.38$ (50 mol.%), but the conversion at this point was only 50 %. The content of CO showed its maximum at $m_{(O_2)}/m_{(RDF)}=1.05$, (55 mol.%), but the H₂ content at this point was 25 mol.% and that of CO₂ was 18 mol.%, while its minimum value at $m_{(O_2)}/m_{(RDF)}=0.75$ was 10 mol.%. Based on these observations (Figures 5 and 6), the optimal value of $m_{(O_2)}/m_{(RDF)}$ for the gasification of the RDF studied in this work was 0.67. The equilibrium model based calculated gas compositions published by other authors showed a similar trend. However, the experimentally measured data showed lower H₂ and higher CO₂ contents of the gas. These differences are significant particularly at temperatures below 800 °C.

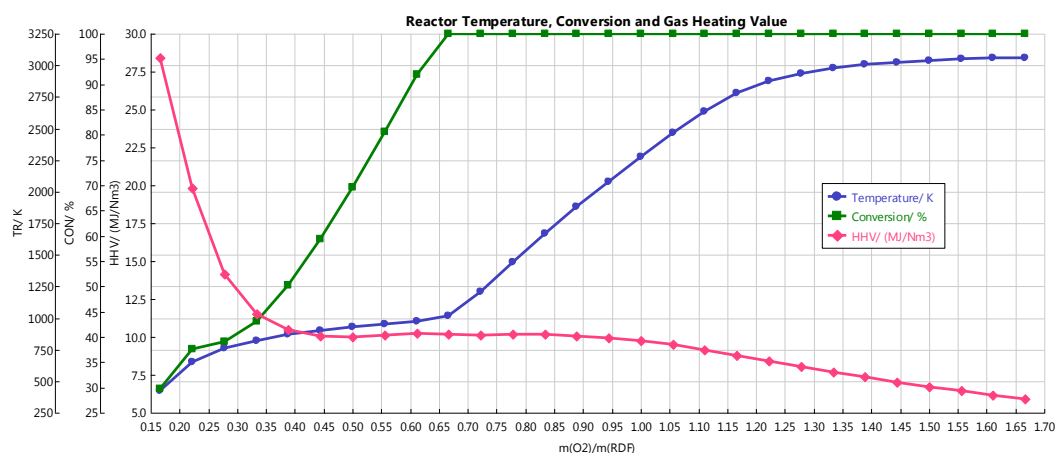


Figure 5: Conversion, reactor temperature and gas heating value at different $m_{(O_2)}/m_{(RDF)}$ values using oxygen as the gasification agent

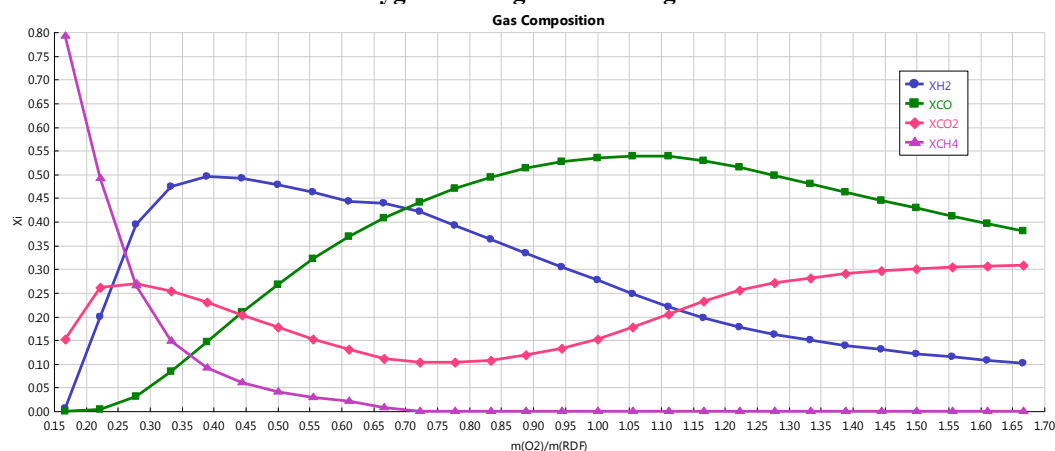


Figure 6: Gas composition at different $m_{(O_2)}/m_{(RDF)}$ values using oxygen as the gasification agent

c - Gasification of RDF using oxygen and steam:

The addition of steam to the gasification reactor enables taking care of the water-gas shift reaction and the steam gasification reaction of carbon. As a result of these reactions, a higher content of H₂ and CO₂ and a lower content of CO in the produced gas were obtained. At constant $m_{(O_2)}/m_{(RDF)}=0.67$, the gas composition, reactor temperature and the gas heating value at different $m_{(steam)}/m_{(RDF)}$ values were determined. Preheated steam with the temperature of 600 K and the pressure of 12 bar was considered. It was found that by increasing the mass ratio of steam to RDF from zero to 0.55, the content of H₂ increased from 44 mol.% to 51 mol.% and that of CO₂ increased from 10 mol. % to 22 mol.%. However, the content of CO decreased from 41 mol.% to 23 mol.%, the reactor temperature decreased by 40 K and the gas heating value decreased from 10.1 MJ/Nm³ to 8.7 MJ/Nm³. The effect of steam addition to a gasification reactor at $m_{(O_2)}/m_{(RDF)}=0.67$ is shown in Figure 7.

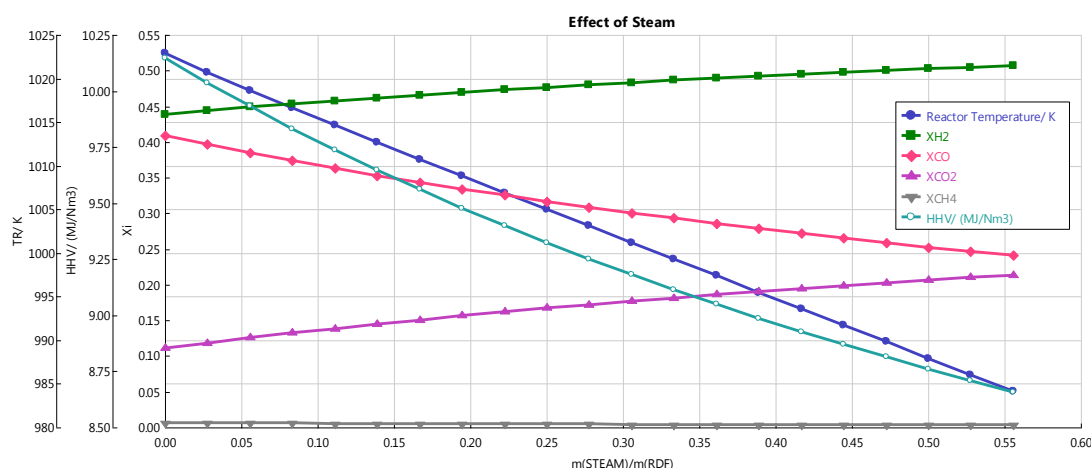


Figure 7: Effect of steam addition to gasification reactor at $m_{(\text{O}_2)}/m_{(\text{RDF})}=0.67$

5 CONCLUSION

The 100% RDF conversion was achieved in the gasification with air at $m_{(\text{air})}/m_{(\text{RDF})}=3.2$. However, the gas heating value was only 4.4 MJ/Nm³, and the reactor temperature was 950 K. The produced gas contained 19 mol.% of H₂, 16.5 mol.% of CO, 7.6 mol.% of CO₂, N₂, and a minor amount of other components.

The contents of H₂S and NH₃ did not exceed the EU limits for SO₂ and NO_x caused by the combustion of these components.

The gasification of RDF using oxygen enables the production of gas with the heating value of around 10 MJ/Nm³ at $m_{(\text{O}_2)}/m_{(\text{RDF})}=0.67$. Under these conditions, the content of H₂ was 44 mol.%, that of CO was 41 mol.%, and that of CO₂ was around 10 mol.%; the content of other components including methane was 5 mol.%.

By increasing the $m_{(\text{steam})}/m_{(\text{RDF})}$ ratio, the contents of H₂ and CO₂ increased. However, the content of CO, the reactor temperature and the gas heating value decreased.

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