

Numerical prediction of the chemical composition of gas products at biomass combustion and co-combustion in a domestic boiler

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Abstract. In recent years the numerical modelling of biomass combustion has been successfully applied to determine the combustion mechanism and predict its products. In this study the influence of the addition of waste glycerin in biomass wood pellets on the chemical composition of exhaust gases has been investigated. The pellets have been prepared from spruce- and pine wood sawdust without and with addition of waste glycerin. The waste glycerol is a undesirable by-product of biodiesel transesterification at oil manufacturing. The produced pellets were being burned in the 10 kW domestic boiler adapted to wood pellets combustion. The possibilities of pollutants generation (CO₂, CO, NO_x, SO_x and compounds containing chlorine) in the exhaust gases coming from the boiler were numerically calculated using the latest version of CHEMKIN-PRO software, introduced by the American company Reaction Design. The results of the calculations correspond to the data obtained on a real object, in particular: combustion temperature, gas pressure, residence time of fuel in the burner, air flow, fuel consumption, as well as elementary composition of fuel supplied into the boiler. The proposed method of predicting the chemical composition of exhaust gases allows proper control of the combustion process and can be considered as an important step in reducing the pollutants (lower emission of NO_x, SO_x and CO₂ neutral) and thus to contribute to the improvement of the environmental quality. In addition, knowledge of the amounts of Cl-based compounds produced in combustion process (under given conditions), can serve as an important hint in terms of corrosion prevention of boiler- and chimney steels.

1 Introduction

Since decades, the industry production in many European countries has been resting on fossil fuels. Combustion of such fuels as coal, crude oil and natural gas results in substantial

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emission of pollutants which, due to increasingly high environmental standards, requires continuous limitation [1-3].

There are many alternative new and renewable energy sources which can be used instead of fossil and conventional fuels. The most common form of renewable energy, widely used in the world is biomass [4-6]. One of the numerous advantages for the energy use of biomass is the reduction in the emissions of greenhouse gases, namely carbon dioxide, and, at the same time, toxic combustion gas components - sulphur dioxide, nitrogen oxides, carbon monoxide and chlorine compounds. It is often assumed that, in the overall balance, the carbon dioxide emission is zero [7]. This results from the fact that in the biomass growth process the plant absorbs a CO₂ gas, amount which is equal to that emitted during biomass combustion. However, considering the energy needed for biomass transportation and its preparation (breaking up), it is estimated that the amount of greenhouse gases formed in the biomass combustion process is smaller by over 90% compared to the combustion of coal [2].

Therefore, in recent years increasingly popular and environmentally friendly method of heating is use of the installation of biomass boilers that utilize wood pellets. Biomass boilers are becoming more and more modern, allow for acceptable combustion efficiency and are automated. In addition, fuels such as wood and biomass are broadly available and relatively cheap [8-10]. Because for the production of pellets water is normally used as binder, there is reasonable to consider the waste glycerin instead of water which can contribute to a higher calorific value of pellets. The waste (crude) glycerin is formed as a by-product in process of transesterification of biodiesel oil manufacturing [11-13]. Due to the relatively high calorific value of the waste glycerin (16.1–22.6 MJ/kg depending on the raw material used to biodiesel production [14-16]), a reasonable solution seems to be its utilization as a heating fuel [15-19]. Unfortunately, direct combustion of the waste glycerin is unprofitable due to its high viscosity and relatively high flash-point which requires a costly modifications of heating equipment [15,17-19]. The simplest and the cheapest method of the utilization of the waste can be its co-combustion with other fuels [20-22]. Glycerin co-combustion with the wood pellets can be a significant solution, because, besides the benefits of waste management, it also contributes to the reduction of harmful combustion products. It could be a cost-effective alternative without necessity of substantial modifications of the heating devices.

This paper presents modelling of wood pellets (WP) without- and with 7% addition of waste glycerin (WGP), during their combustion in a domestic MiniBio boiler adapted for this kind of combustion. The pellets contained glycerin additions have been compared in terms of applicable quality standards with these of glycerin free pellets. Effect of waste glycerin addition has also been examined in view of concentration of harmful combustion products.

2 Material and methods

2.1 Materials - specimens preparation

The waste glycerin used in the study has been delivered from Trzebinia Refinery (RT S.A.), Poland. The minimum content of glycerin in the waste was 80 mass%, ash content - below 5 mass%, MONG (Matter Organic Non Glycerol) - below 6 mass% and the balance - being water. Calorific value of the waste was 22.6 MJ/kg [15]. As the solid component, a spruce and pine wood sawdust with fragmentation of 2–4 mm and a bulk density of 180 kg/m³ has been used. Cylindrical, 5–15 mm long pellets, 6 ± 1 mm in diameter, have been machined with the use of MGL-200 pellet device, applying the wood sawdust without- and with 7 mass% of waste glycerol additions. In further parts of the paper, the abbreviation “WP” (wood pellet) and “WGP” (wood/glycerin pellet) is applied to name the two kinds of composite pellets tested. The appearance of the tested pellets, without- and with glycerol

addition, is visually shown in Fig. 1.

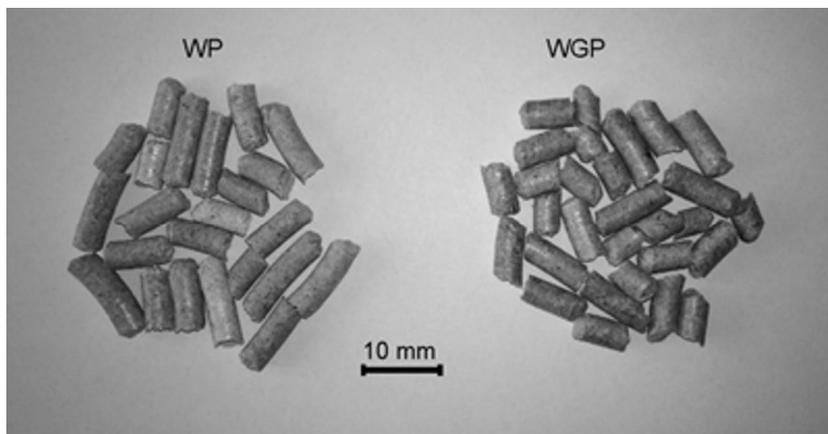


Fig. 1. Visual appearance of as prepared fuel wood pellets: without (WP) and with 7% of glycerin addition (WGP).

For the tested fuels the physicochemical characterization such as: calorific value, bulk density as well as moisture and ash contents have been determined. For simulations purposes also the elemental mass percentages of carbon [C], hydrogen [H], nitrogen [N], chlorine [Cl], phosphorus [P] and sulfur [S]. The detailed WP and WGP pellets characterization is presented in Table 1.

Table 1. Comparison of chosen physicochemical parameters and the elemental composition of the tested pellets. The numbers in brackets denote the confidential range of individual quantities.

Analyzed parameters	WP	WGP
Calorific value, MJ/kg (± 0.1 MJ/kg)	18.1	18.4
Bulk density, kg/m ³ (± 10 kg/m ³)	590	500
Moisture, % ($\pm 0.1\%$)	4.2	3.4
Ash, % ($\pm 0.2\%$)	0.8	0.8
C, % ($\pm 0.7\%$)	49.8	49.2
H, % ($\pm 0.32\%$)	5.85	6.24
N, % ($\pm 0.1\%$)	0.19	0.10
Cl, % ($\pm 0.04\%$)	0.20	0.02
S, % ($\pm 0.03\%$)	0.03	0.02
P, % ($\pm 0.01\%$)	0.01	0.01
O, % (bal.)	38.92	40.21

The resulting pellet parameters (diameter, bulk density, moisture- and ash content, and calorific value) are well matched with the German (DIN51731) and Swedish (SS187120) standards. To evaluate the permitted emissions for the analyzed fuels the EN 303-5 standard has been adopted.

2.2 Test stand description and modelling procedure

The 10 kW domestic biomass boiler, Mini Bio type, Kostrzewa (Poland) has been employed for pellets burning. The boiler has been equipped with a burner adapted for combustion of wood pellets having a diameter from 6 to 8 mm. The fuel feed rate ensuring the 7.5 kW

working boiler output was equal to 0.000414 kg/s for the WP, and 0.000404 kg/s for the WGP while the air flow was 0.00315 and 0.00308 m³/s for WP and WGP, respectively. The chamber's internal diameter was 0.35 m and its total length, 0.5 m. The temperature distribution inside of the combustion chamber (573 K to 1123 K, depending on the distance from the burner) was measured with the use of an NiCr-Ni thermocouple. The boiler water reservoir was installed around the combustion chamber and was equipped with a thermostat for keeping water in given temperature range. The temperature set point of the thermostat during pellets combustion was fixed on 333 K. The boiler parameters were employed for modelling purposes.

Numerical calculations of the chemical composition of products formed during combustion of the pellets were carried out with the use of CHEMKIN-PRO licensed software (*The American company Reaction Design*). For the calculations a simplified chemical mechanism involving 62 chemical elements and compounds and 255 chemical reactions has been applied. The mechanism has been developed using the databases of the universities of Leeds [23] and Milano [24] by the Gas Research Institute, University of California (GRI - Mech version 3.0) [25]. The selection of the chemical reactor and the combustion mechanism was based on the experience of other authors, who have modelled the processes of biomass combustion and co-combustion using older versions of the Chemkin application [2, 26-29]. For example, in paper [2], the processes of co-combustion of selected grades of biomass with natural gas have been investigated. In cited papers [2,3,29], the research comprised both laboratory experiments and numerical simulations with the use of the Chemkin-Pro. The comparison of chemical analyses with numerical calculations, shows that the values obtained from calculations were slightly lower than these coming from the experiment. Very close results have been obtained in Ref. [29] where numerical calculations were done for a wood biomass sample combusted in the heat chamber with a "Perfectly Stirred Reactor". Based on the above-cited [23-28] and our own experiences in the numerical modelling of the biomass co-combustion, the calculations for the WP and WGP have been carried out for the PSR (Perfectly Stirred Reactor) variant. In Fig.2 a simplified scheme of the variant is presented.

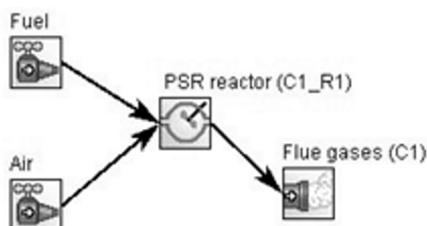


Fig. 2. Scheme of the PSR reactor used in the modelling calculations.

3 Analysis and discussion of the results

In modelling process, as maximum temperature the $T = 1123$ K has been assumed (the maximum temperature measured in reaction chamber during burning of the tested pellets), 1 atm as an external pressure and some different times of reactants spending in the chamber: 0.0001 to 1 s.

In the calculations, 62 products of combustion have been designated but a detailed analysis included the selected compounds. Among nitrogen oxides, the NO was the main burning product (concentrations of NO₂ and N₂O were relatively small, usually lower than 1

ppm). On the other hand, only traces of sulphur compounds were formed (the sum of H_2S , SO_2 and SO_3 concentrations was less than 0.001 ppm). Because of very small quantities of sulphur compounds in burning products, only $[\text{NO}]$ and $[\text{CO}]$ (Fig.3) as well as $[\text{CO}_2]$ and $[\text{O}_2]$ (Fig.4) have been presented on graphs illustrating reactant residence time in reaction chamber. It should be noted that some chlorine-rich compounds, like HCl , HOCl or Cl_2 are also formed during WP and WGP burning (Fig.5). These compounds can be a source of aggressive chloride ions that are responsible for accelerated corrosion of metallic elements of the chamber and boiler [30].

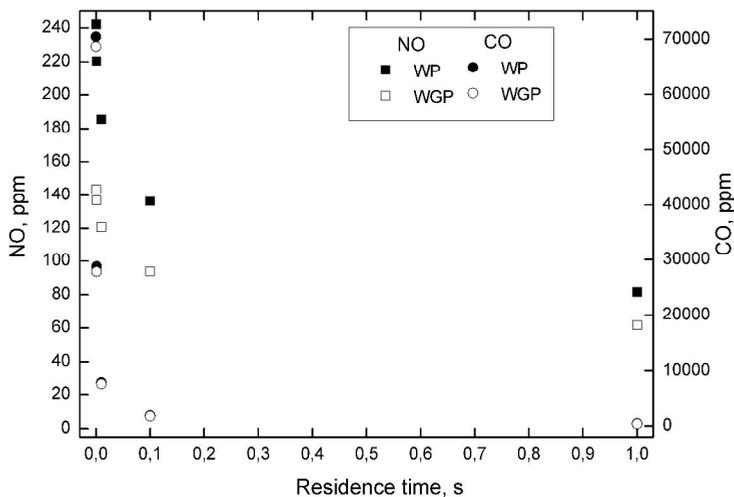


Fig. 3. Effect of waste glycerin addition on NO and CO concentration changes in burning products versus time of reactants residence in a reaction chamber.

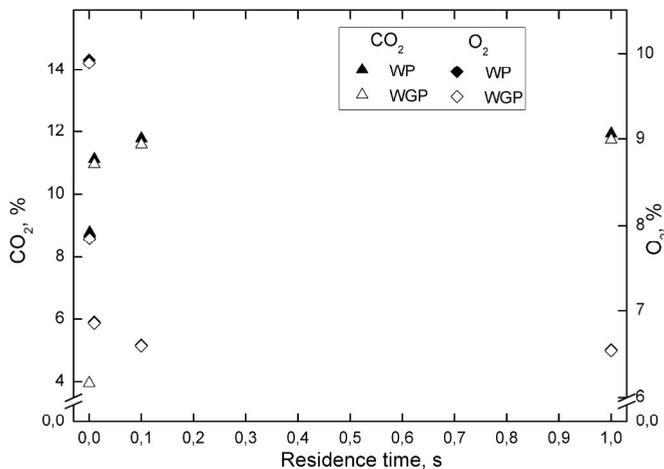


Fig. 4. Effect of waste glycerin addition on CO_2 and O_2 concentration changes in burning products versus time of reactants residence in a reaction chamber.

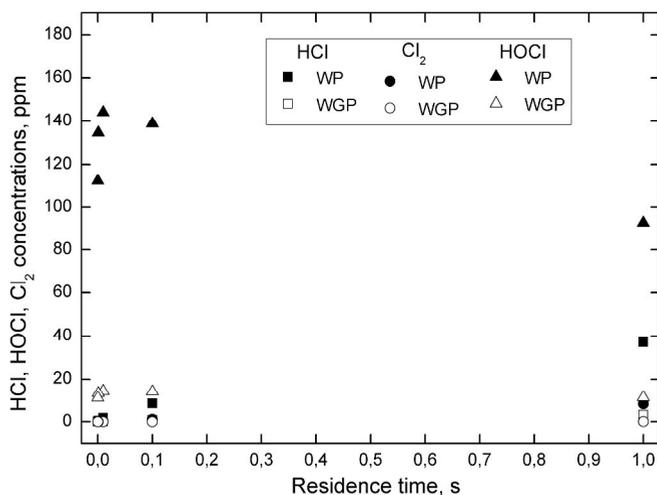


Fig. 5. Effect of waste glycerin addition on HCl, HOCl and Cl₂ concentration changes in burning products versus time of reactants residence in a reaction chamber.

It is seen from Figs 3 and 4 that NO and CO concentrations in the burning products are the greater the shorter residence time in the burner, irrespectively of presence of glycerin in the pellets. This behavior is strictly associated with limited O₂ concentration in flue gas. Concentrations of CO₂ is the greater the longer residence time in the burner due to carbon from wood oxidation (and, thus, O₂ disappearance in reaction products). The CO concentration after 0.0001 s is nearly 70000 ppm and does not practically depend on presence of glycerin in the pellets, which can be attributed to the similar carbon contents in both WP and WGP pellets (see Table 1). The situation is changed in the case of NO and results from twofold greater concentration of nitrogen in glycerin-free pellets. In fact, for the shortest residence times the NO concentration in flue gas is nearly 2 times greater for WP pellets. After 0.1 s the [NO] is still greater (by about 40 per cent) for the glycerin-free pellets. Evidently, glycerin reacts with nitrogen containing compounds present in wood with final formation of solid ionic deposits (e.g. nitrates). This most likely limits nitrogen oxidation to form NO.

Both HCl and Cl₂ concentrations increase a little with longer residence time in the chamber but they scarcely depend on glycerin presence in the pellets. However, in case of WP after time of 1s the HCl concentration is as large as nearly 40 ppm. For other cases it does not exceed several ppm. The situation becomes clearly unfavorable in view of emission of hypochlorous acid (HOCl). It should be stressed that the simulation indicates HOCl as a compound of the greatest concentration among possible chlorine agents in exhaust fume. Obviously, large HOCl emission is predicted for glycerin-free wood pellets only. Such prediction is an evident consequence of tenfold lower chlorine concentration registered analytically for the glycerin containing pellets. Possibly glycerin reacts with chlorine compounds at the stage of pellet formation and part of reaction products is not detectable by chemical analysis (Mohr method titration). In spite of ambiguity of chemical analysis relating appearance of chlorine in WGP, the present results confirm our earlier examinations [30] indicating decrease of chloride ions concentration in flue gas condensate being a result of glycerin addition to the wood pellets. The chlorides, even in small concentrations, accumulate during long-lasting boiler exploitation and cause local corrosion of steel boiler elements. This way, glycerin presence in the fuel ultimately inhibits corrosion of carbon- and stainless steel elements of the boiler.

The mechanism of possible reaction between glycerin and chlorine-rich agents present in wood is still an open question but the advantageous action of glycerin towards limitation of chlorine content in flue gas deserves further, systematic investigations.

4 Conclusions

Numerical modelling enables the evaluation of hazardous gaseous pollutants forming during the biomass combustion. Concentration of burning products depends on both the fuel chemical composition and parameters of burning process.

Co-combustion of wood pellets with the waste glycerin does not practically affect CO and CO₂ concentrations in flue gas. However, the addition of glycerin satisfactorily reduces the share of chlorine- and nitrogen-rich compounds that enter the fume. Consequently, glycerin indirectly limits concentration of both HOCl and NO in exhaust fumes.

Because of documented protection of boiler steel elements against corrosion and evident limitation of air pollution, the use of waste glycerin as a binder (instead of water) for the production of wood pellets can serve as a cost-effective solution of its use.

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