ANALYSIS OF THE BIOMASS COMSUSTION PROCESS BY THE NUMERICAL CALCULATIONS

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Abstract

This paper presents the numerical calculations of the biomass combustion process using the CHEMKIN program. The pollutants generated (NO_x, CO, SO_2) in the exhaust gases coming from boilers were calculated. The results of the calculations were noted taking into account the influence of temperature, pressure and residence time. The sample of biomass was tested with respect to physicochemical properties. Thermogravimetry studies of biomass were carried out. The computer simulation makes it possible to analyse complex phenomena which are otherwise difficult to observed.

Introduction

Combustion of biomass has received a lot of attention in recent years due to its fuel flexibility, high combustion efficiency, high heat transfer, and low emission of NO_x, SO_x and CO_2 neutral. The use of biomass as a fuel in existing coal fire power plants has been considered as an important step in reducing environmental emission (lower emission of NO_x, SO_x and CO_2 neutral). In recent years the numerical modelling of biomass combustion has been successfully used to predict the combustion process and its product [1-5]. Numerical analysis of the combustion process is useful. Experiments on real devices are expensive and difficult to be do, and in extreme cases even hazardous, therefore an alternative way to test the behaviour of the furnace is mathematical modelling. Computation methods help in the design of new process and technology technical devices. Numerical simulations of combustion, in addition to more conventional scale-up and design applications, can be regarded as a tool for the fundamental investigation of several, complex phenomena governing combustor performance. There are different kinds of computer programs modelling the chemical combustion process [6,7].

Biomass properties

Biomass energy or bioenergy is an important energy resource in the world and it has been extensively employed in many countries [8-10]. Biomass is utilized in a variety of conversion techniques such as physical, thermal, chemical and biological methods. Thermal conversion is the most commonly used technique. Combustion, gasification and pyrolysis of biomass as well as co-firing of biomass and coal have been widely studied and applied for the purpose of getting heat and power. Thermal conversion of biomass also generates synthesis gas, so called syngas, and biofuels. Currently energy consumption of biomass accounts for about 14% of total energy consumption. The conversion of solar energy by plants photosynthesis yields the food energy supporting animal life on earth. Biomass fuel is often wooden and agriculture residues, as well as waste material produced by industrial processes. Biomass is a renewable, CO_2-neutral energy resource, widely available and increasingly used as alterative to fossil fuel

for energy supply. Many elementary properties of biomass have been determined for a wide range of fuel types. These properties include moisture content, heating value, element composition, bulk density, specific gravity, thermal conductivity, and mechanical properties. Many such properties have only been determined for biomass in its original state at ambient temperature. High temperature properties relevant to the modelling of biomass combustion has only been partly developed. Difficulties arise in the determination of such properties because of the decomposition of the biomass under heating and reaction.

Biomass is not a homogenous chemical compound, but is a mixture of a wide variety of compounds. In addition to volatile and non-volatile combustible compounds, biomass contains compounds which do not burn and stay in a solid form, called ash. The components of biomass include cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water and other compounds. The concentrations of each class of compound varies depending on the species, type of plant tissue, stage of growth and growing conditions. Due to the carbohydrate structure, biomass is highly oxygenated with respect to conventional fossil fuels including HC liquids and coal. The principal component of biomass is carbon from 40 – 55 wt.% of dry matter. The second is oxygen from 41 – 50 wt.% of dry matter. Hydrogen is the third major component from 5 – 7 wt.% of dry matter. Nitrogen, sulphur and chlorine can also be found in quantities, usually less than 1%, but are very important in the formation of pollutant emissions. Sulphur and chlorine can lead to furnace corrosion in certain ash reactions. Combustion of biomass can cause hazards and operating problems. Alkali metals (Na, K), as well as sulphur and chlorine can lead to fouling and slagging [11].

Combustion of biomass
Combustion is a complex phenomenon involving simultaneous heat and mass transfer with chemical reaction and fluid flow. By analogy to coal combustion, the combustion of biomass can be considered as three step: devolatilisation to char and volatiles, and combustion of the volatiles and of the char [12-14]. The water content is significant and important and in some instances may dominate the in biomass combustion process. Pollutant emissions generated by combustion are particular matter (PM), CO, HC, oxides of nitrogen and oxides of sulphur. Nitrogen oxides (NO_x) are one of the most important substances resulting from the combustion of fuels. Typical combustion gases contain two kinds of oxides: NO and NO_2. Other kinds of nitrogen oxides are N_2O, N_2O_3 and N_2O_5, but they do not play any essential role. In typical combustion gases from a boiler, the volumetric share of NO amounts to about 95% or even more, the rest being NO_2. Nitrogen oxides are environmentally - the most harmful substances, which is why researches study how to reduce NO_x emission. This requires knowledge of the mechanisms of the formation and reduction of NO_x emissions based on the kinetics of chemical reactions. The concentration of fuel NO in the global emission of nitrogen oxides grows with the decrease by the heat release of the combustion chamber [15,16]. Carbon oxide is a very harmful substance for live organisms especially above permissible air emission standards. Carbon oxide with its property of superseding the oxygen in the oxyhemoglobine of the blood forms bonds with the haemoglobin generating carboxyhaemoglobin leading to suffocation. Sulphur dioxide is considered to be one of the fundamental air pollutants. SO_2 is assumed to be the only representative of sulphur oxides in combustion gases (at least 98 % of whole amount of sulphur oxides). SO_2 is the main constituent of the London type smog and is the main component of acid rain (reacting with rain water it may form sulphuric acid). During combustion some specific pollutants, such as Cl_2, HCl, salts, dioxins and furanes can occur. The emission of particulates is a significant problem in the combustion of biomass.

An increased interest in biomass including waste wood, has been observed in the fuel market due to the depleting recourses of fossil fuels and environmental pollutions. Wood

biomass is present as woodworking industry by-products [17]. Its combustion provides thermal energy and electricity enables the reduction of coal combustion and at the same time emission of CO_2. The aim of this work was to model of biomass combustion to predict the amount of pollutants generated (NO_x, CO, SO_2) in the exhaust gases coming from boilers . Numerical simulations using CHEMKIN are presented in following paper.

Characteristic of tested biomass
The numerical calculations were done for a wood biomass sample. The tested biomass sample was commercially available fossil fuel. Wood biomass was made by pressed dry wood wastes and a sawmill under high pressure without any kind of binder, or so called "pellets". The chemical composition of the biomass was carried out by Leco analyzer. Volatile matter, ash and moisture were done in accordance with PN-80/G-04511, PN-80/G-04512, PN-81/G-04516 standards (polish codes).

Table 1 shows the physicochemical properties of tested biomass. The quantities given in the tables such as: chemical composition of combustible mass and mineral matter contents, volatile matter contents and ash are decisive to in the combustion process. Carbon is the main component of that fuel, and the concentration of carbon amounts 47,16 wt. %. The concentration of oxygen is up to 48 wt. %. In comparison with coal (bituminous coal) the concentration of carbon is two times lower, but the concentration of oxygen is four times higher. The concentrations of sulphur and nitrogen in the tested biomass are low, causing low emission of NO_x and SO_x pollutants. Analyzed chemical composition explains the high amount of volatile matter and the high reactivity of the tested biomass. The determined net calorific value is 14,6 MJ/kg.

Table 1. Ultimate and proximate analyses of biomass.

C, wt.% daf	H, wt.% daf	O, wt.% daf	N, wt.% daf	S, wt.% daf	VM, wt.%	Ash, wt.% db	Moisture, wt.%	Q_i, kJ/kg
47,16	4,36	48,227	0,097	0,156	73,37	2,09	10,3	14 594

Table 2. Elemental composition of ash (%) of biomass.

SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	Na_2O	K_2O	Cl^-
17,3	34,74	8,14	2,27	2,72	2,94	3,92	9,92	11,7

The main components of ash are SiO_2, CaO, K_2O i MgO (Table 2). It can be seen that there are high concentrations of calcium oxide (CaO) and chlorine in the ash. Alkali metals, sulphur and chlorine present during the combustion process may be a factor generating corrosion of boilers. High-temperature corrosion is a main problem of boilers operating during biomass combustion. Despite this negative quality, biomass is a low-emissions, renewable, commercially available fuel. The combustion process of wood biomass is operated in many kinds of boilers. Technical and economical conditions existing in Poland lead to the application of biomass boilers in smaller power plants and especially in private households.

In the present study thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on the tested biomass. A sample was placed in an aluminium crucible (Al_2O_3) in the NETZSCH STA Jupiter 449F3. 31 mg of sample were heated from an ambient temperature up to 1010 °C at a constant rate of 10 °C/min in 40 ml/min flow of synthetic air. The resultant of TG and DTA curves are shown in Figure 1.
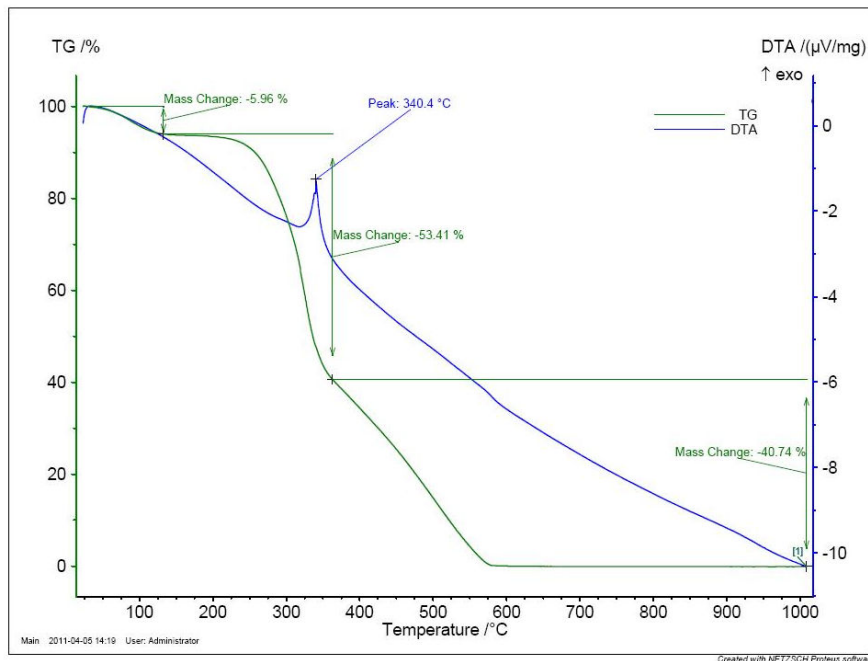
Figure 1. TG and DTA curves for tested biomass.

The correlation between the TG and DTA curves contributed to the interpretation of the thermal effects. Thus, one exothermal effect with a temperature maximum of 340 °C was determined. The TG curve represents the instantaneous weight percentage of the tested biomass in contrast to the initial weight. The TG curve can be divided in to three different stages. For the temperature below 200°C the slight decay of the tested biomass weight is due to the drying process and the release of some light volatiles. The weight loss of the tested material is less than 6 %. In the second stage (200 °C – 575 °C) a significant drop in weight is observed caused by the thermal decomposition of chemicelluose, cellulose and lignin. Once the temperature is higher than 575 °C weight loss is brought to an end by thermal decomposition.

Numerical modelling
All numerical calculations were done using the CHEMKIN program. CHEMKIN is the product of Reaction Design, which evolved from its origin as a Sandia National Laboratory combustion code Chemkin II. Currently CHEMKIN is commercial-quality software enables the simulation of complex chemical reactions for modelling and surface phase chemistry. It is uniquely qualified to lead the Clean Technology approach to design and improvement of combustors, engines and chemical reactors. CHEMKIN-PRO is specifically designed for large chemical simulation applications requiring complex mechanisms [18,19]. The numerical analysis of the biomass combustion process was made using CHEMKIN-PRO program application. The heat chamber of the furnace was a "Perfectly Stirred Reactor" (Fig. 2).
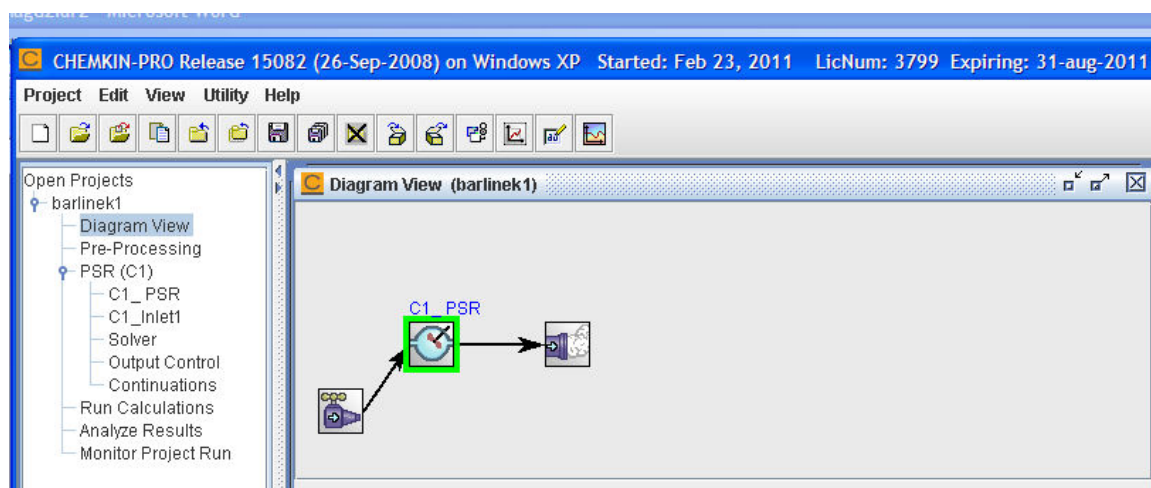
Figure 2. Model of the furnace used in the received to calculations.

The main aim of the present work was the modelling of the tested biomass combustion process inside the combustion chamber of a boiler (Pelletstar Bicontrol 20). The NO and CO emission were calculated as the most significant pollutants coming from the combustion process. Calculations were done for 5 kg of wood biomass combusted in a grade furnace, the combustion process was done under the air excess ratio ca. 2. Calculations were made including the influence of temperature, pressure and residence time. Chemical file "chem.inp", the thermodynamic file "therm.inp" and the chemical reactions were obtained from Leeds University website [19]. The chemical model includes 152 reactions together with sulphur oxides formation and 46 elements and compounds H, O, N, C, S, H_2, O_2, OH, HO_2, H_2O, N_2, NO, NH, NH_2, NH_3, HNO, NO_2, N_2O, CO_2, CO, CH, HCO, CN, HCNO, HCN, HOCN, HNCO, NCO, SH, H_2S, SO, SO_2, SO_3, HSO_2, SN, S_2, CS, COS, HSNO, HSO, HOS, HSOH, H_2SO, HOSHO, HS_2, H_2S_2.

Results and discussion

The figures show the calculated concentration of the main combustion gases NO, CO and SO_2 inside of a combustion chamber. The figures present the results of calculations which were made including the influence of temperature, pressure and residence time.

Figures 2 and 3 show NO, CO and SO_2 concentrations as a function of temperature in the range of 600 up to 1800 K calculated at a pressure of 1 atm and with a residence time 1 second. The range of temperature was chosen taking into account the behaviour of the tested biomass. The influence of temperature on the oxidation tested biomass in the air was measured by the thermogravimetric method (TG, DTA). It was observed that biomass was oxidized from c.a. 600 K. The calculated CO molar fraction was obtained in the range of 0,0123 to 0,000289. Decreasing CO concentration via temperature can be seen in Figure 3. The decreasing of the CO molar fraction is significant up to 1000 K. Above 1000 K it is only slightly observed. The CO rapidly reduced due to oxidation to CO_2.

The character and rate of change of NO concentration within the studied range of temperature was initially at a very low level between 600 to 1000 K and then significantly increased from 1000 K. The increase of NO concentration is connected with an increase of temperature level in the combustion chamber. The calculated NO concentration at a temperature of 1200 K is relatively low c.a. 75 ppm ($7,51 \cdot 10^{-5}$ molar fraction) and what was expected when compare with the results from the TG analysis. At high temperatures (above 1500 K) NO concentration was significantly higher (615 ppm). So high NO concentration, called "thermal NO", depends only on process temperature, and not from fuel-N

concentration. The calculated concentration of SO_2 does not change significantly with increasing temperature (Fig.4). The amount of SO_2 concentration is c.a. 155 ppm, which can be caused by the initial amount of sulphur in the fuel (0,156 wt. %). It can be seen that the tested biomass is a well chosen low-emission fuel.
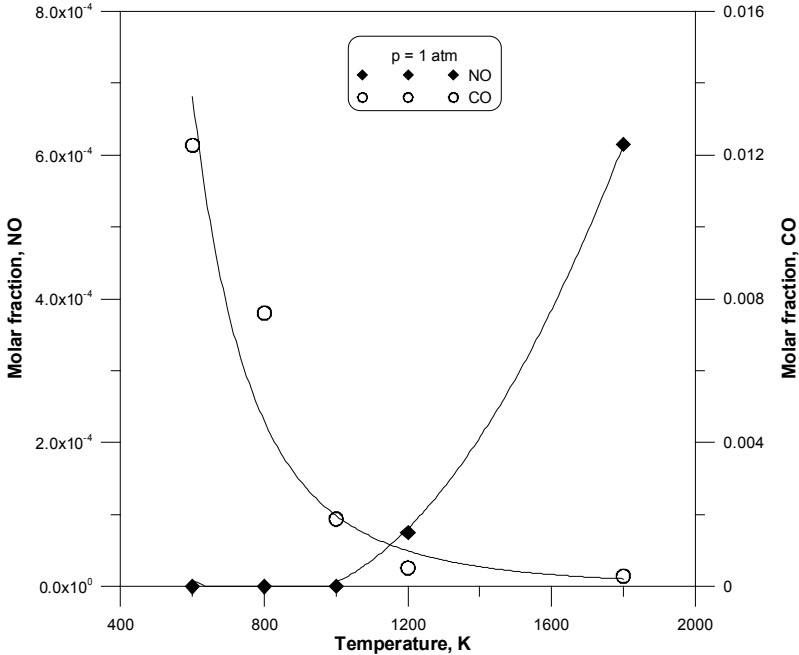

Figure 3. Molar fraction of NO and CO as a function of temperature, pressure 1 atm, residence time 1 s.
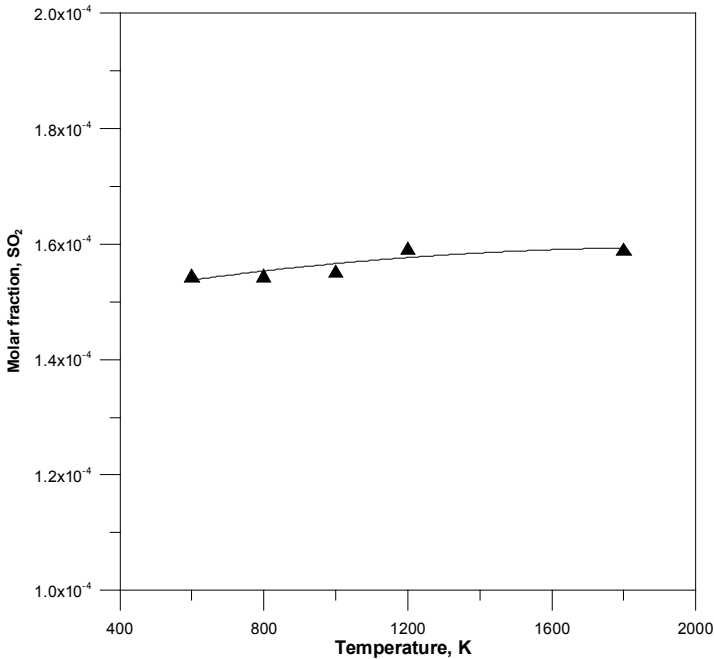

Figure 4. Molar fraction of SO_2 as a function of temperature, pressure 1 atm, residence time 1 s.

Figure 5 shows NO and CO concentrations as a function of temperature in the range of 600 up to 1800 K calculated at a pressure 2,9 atm and with a residence time of 1 second. Calculations done at 2,9 atm were caused by defined operating conditions specified by the

producer of the tested boiler (maximum operating pressure is 2,9 atm). The character and rate of change of the NO and CO concentrations with the increasing temperature is similar to results obtained for 1 atm pressure. NO concentration calculated at a pressure of 2,9 atm is evidently higher than for 1 atm below 1200 K, but above 1200 K the obtained NO is slightly lower. Thus, increasing pressure generates higher NO concentration in the biomass combustion (below 1200 K). On the other hand, the increase of pressure (2,9 atm) causes decreasing of CO concentration in the same range of temperature. The calculated concentration of SO_2 does not change with increasing temperature for this condition (159 ppm of SO_2), which is why SO_2 concentration is not presented in the figure.
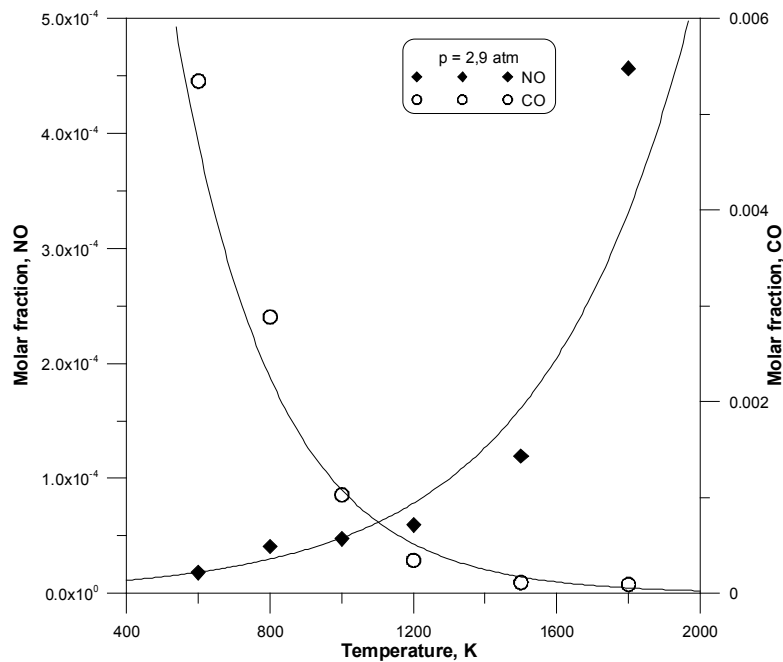

Figure 5. Molar fraction of NO and CO as a function of temperature, pressure 2,9 atm, residence time 1 s.

Figure 6 and 7 show NO and CO concentrations as a function of residence time at temperatures of 600 and 800 K and calculated at a pressure of 1 atm. The residence time of the pollutants in the combustion chamber strongly influenced their concentrations. The presented results indicate that in both cases there was a decrease in CO concentration with an increasing residence time from 1 to 10 s. In turn NO concentration is lower at 600 K, and an increase in temperature (800 K) generates a higher NO concentration. The change in NO concentration as a function of residence time was close to linear for 800 K, but for 600 K it was different. Between 1 to 8 s of residence time NO concentration changed only slightly, but for 10 s it was 4,5 times higher than that for 1 s.
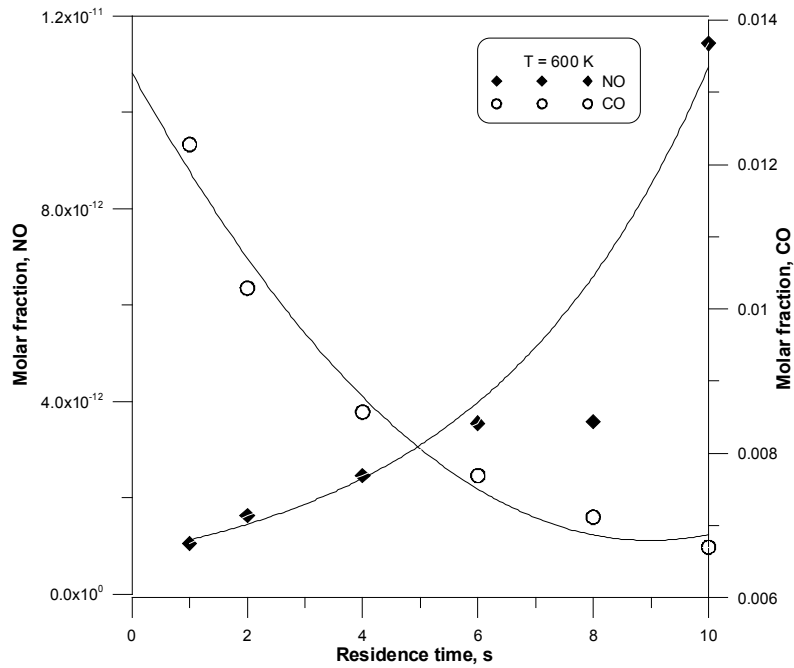
Figure 6. NO and CO concentrations as a function residence time, temperature 600 K, pressure 1 atm.
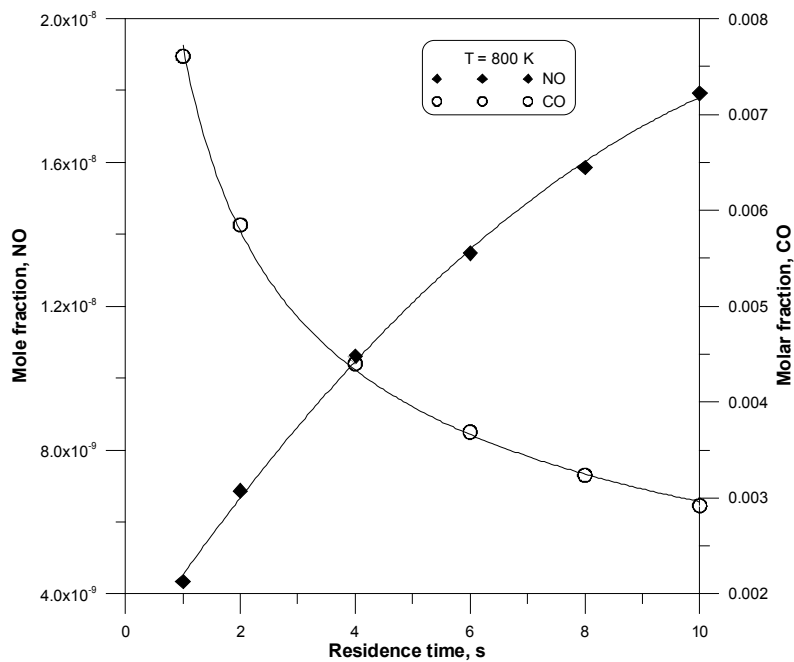

Figure 7. NO and CO concentrations as a function residence time, temperature 800 K, pressure 1 atm.

Summary

This paper presents modelling of biomass combustion which is currently very popular recently due to modern methods which are seeking to provide solutions to the complexity of problems related to the combustion process. Calculations were undertaken on known wooden biomass, on which physicochemical properties and thermogravimetry analysis were carried out. This data was input into numerical calculations. Numerical modelling enables the identification of hazardous gaseous pollutants which form during the biomass combustion

process such as NO, CO, SO_2 and others. The results of the calculations were noted taking into account the influence of temperature, pressure and residence time. Comparing results for modelling done at 1 and 2,9 atm, residence time at 1 s the character and rate of change of NO and CO concentrations with the increasing temperature were similar. The influence of residence time was evidently observed. NO, CO and SO_2 concentrations were relatively low when the temperature was below 1200 K (biomass combustion process). The obtained data shows that the tested biomass is a renewable, commercially available fuel.

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