

Waldemar GADEK\*, Angelika LYCZKOWSKA\*\*, Alexander SCHERRMANN\*\*\*, Hans-Joachim GEHRMANN\*\*\*\*, Andrzej SZLEK\*\*\*\*\*, Helmut SEIFERT\*\*\*\*\*, Dieter STAPF\*\*\*\*\*

CHARACTERIZATION OF BIOMASS FUELS IN ISOTHERMAL PLUG FLOW REACTOR  
(IPFR)

CHARAKTERIZACE PALIV Z BIOMASY V IPFR REAKTORU

**Abstract**

Combustion of fossil fuels is one of the most important source of energy. However low carbon politics and environmental commitments, affects developing combustion and co – combustion technologies. Utilization of biomass fuels can be answer for new challenges, although more research on effective utilization of these fuels are needed. Nowadays, combustion of biomass fuels, especially straw, causes many technical problems, mainly slagging formation, fouling of heat exchangers inside combustion chamber and insufficient fuel burnout. This paper focuses on analysis of biomass combustion. Better knowledge of behavior during biomass combustion may help to optimization of PF (Pulverized Fuel) boiler of and avoid some technical problems. The results of investigation shows that temperature and oxygen concentration in reactor play significant role in process of devolatilization and char burnout. For instance during char burnout experiments at temperature 850°C at 14% oxygen concentration after 200 ms more than 80% of mass loss were achieved. Compared to 700°C at 14% oxygen concentration this same level of mass loss were completed after 500 ms. Experiments performed on Isothermal Plug Flow Reactor (IPFR) at Institute of Energy Process Engineering and Fuel Technology (IEVB) at TU Clausthal were a part of project between IEVB and the Karlsruhe Institute of Technology (KIT) in Germany.

**Abstrakt**

Spalování fosilních paliv je jedním z nejdůležitějších zdrojů energie. Nicméně nízkouhliková politika a environmentální závazky ovlivňují vývoj spalovacích a spolu-spalovacích technologií. Využívání paliv z biomasy může být odpovědí na nové výzvy, i když je zapotřebí více výzkumu o efektivním využití těchto paliv. V současné době spalování paliv z biomasy, zejména slámy, způsobuje řadu technických problémů, zejména tvorbu strusky, zanášení výměníků tepla uvnitř spalovací komory a nedostatečné vyhoření paliva. Tento příspěvek se zaměřuje na analýzu spalování

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\* Silesian University of Technology; Institute of Power Engineering and Turbomachinery., address: Konarskiego 20, 44 – 100 Gliwice, tel. (+48) 32 237 23 79, e-mail: Waldemar.Gadek@polsl.pl

\*\* Clausthal University of Technology; Institute for Energy Process Engineering and Fuel Technology., address: Agricolastr. 4, 38678 Clausthal-Zellerfeld, tel. (+49) 5323/72 3583, e-mail: Lyczkowska@ievb.tu-clausthal.de

\*\*\* Karlsruhe Institute of Technology; Institute for Technical Chemistry., address: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, tel. (+49) 721 60823707, e-mail: Alexander.Scherrmann@kit.edu

\*\*\*\* Karlsruhe Institute of Technology; Institute for Technical Chemistry., address: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, tel. (+49) 721 60823342, e-mail: Hans-Joachim.Gehrmann@kit.edu

\*\*\*\*\* Silesian University of Technology; Institute of Thermal Technology., address: Konarskiego 22, 44 – 100 Gliwice, tel. (+48) 32 237 11 63, e-mail: Andrzej.Szlek@polsl.pl

\*\*\*\*\* Karlsruhe Institute of Technology; Institute for Technical Chemistry., address: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, tel. (+49) 721 60822655, e-mail: Helmut.Seifert@kit.edu

\*\*\*\*\* Karlsruhe Institute of Technology; Institute for Technical Chemistry., address: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, tel. (+49) 721 60829270, e-mail: Dieter.Stapf@kit.edu

biomasy. Lepší znalost chování procesů při spalování biomasy může přispět k optimalizaci návrhu práškového kotle a vyhnout se tím technickým problémům. Výsledky výzkumu ukazují, že teplota a koncentrace kyslíku v reaktoru hrají významnou roli v procesu tvorby prchavé hořlaviny a vyhoření tuhého zbytku. Například během experimentů s vyhořelým tuhým zbytkem při teplotě 850 ° C při 14% koncentraci kyslíku po 200 ms bylo dosaženo více než 80% úbytku hmotnosti. Ve srovnání se 700 ° C při 14% koncentraci kyslíku byla stejná úroveň úbytku hmotnosti dosažena po 500 ms. Experimenty provedené na izotermickém reaktoru (IPFR) v Institutu energetických procesů a technologií paliv (IEVB) na TU Clausthal byly součástí projektu mezi IEVB a „Karlsruhe Institute of Technology (KIT)“ v Německu.

## **Keywords**

Biomass combustion, Devolatilisation, Char burnout, DTF Drop Tube Furnance, Pulverised Fuel (PF) boiler.

## **1 INTRODUCTION**

Utilization of coal to produce electricity has around 40% share in total world electricity generation, and did not change much for over 40 years [1]. Nowadays 70% of antropogenic CO<sub>2</sub> emissions come from burning of fossil fuels. Furthermore concentration of CO<sub>2</sub> in preindustrial period in the second half of XIX century was about 280 ppm. It has risen continuously since then, reaching 396 ppm in 2013 [2]. It does mean 40 % increase of concentration in two centuries. Carbon dioxide belongs to group of greenhouse gases, and is one of the factors of global warming. The global warming changes led to establishment of new energy policy. One of the most important new political regulations was Kyoto Protocol, entered into the force in February 2005. Every member country pledged to reduce their emission of greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>x</sub>, HFC, PFC and SF<sub>6</sub>) by at least 5% level to 1990 during the first committee period (2008 – 2012) [3, 4]. European Union has decided to extend Kyoto Protocol until 2020. A new agreement known as the Doha Amendment is not yet ratified by EU countries [5].

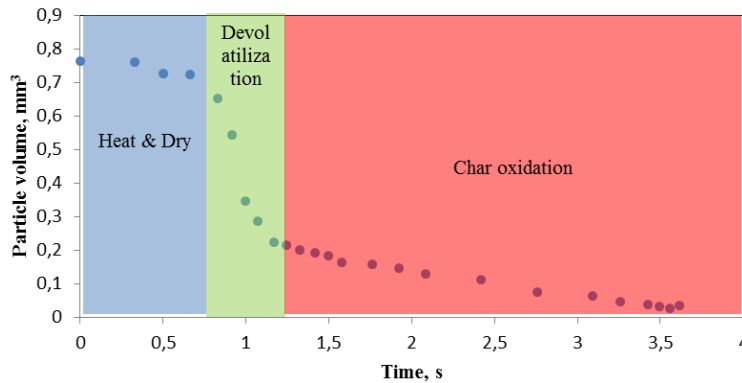
Poland as EU member has signed the Doha agreement. This kind of international regulation affects polish environmental politics. One of the most known EU law regulations is energy package (3x20). This document envisaged reduction of greenhouse gases up to 20%, increased energy use efficiency and increase of 20% in the share of renewable in final energy consumption. In addition European Commission recommends a 10% share of biofuels in transport fuel consumption [6]. Biomass is “carbon neutral fuel”, because it does not add to the Earth’s carbon dioxide inventory [7]. Thus biomass combustion may be an answer for new challenges. Nevertheless, combustion of biomass fuels causes many technical problems, mainly slagging formation, fouling of heat exchangers inside combustion chamber and insufficient fuel burnout. The research on this field is still needed.

The purpose of this study is to investigate the behavior and characteristic of the straw combustion performed on different conditions (temperature, oxygen concentration, residence time of particles) in Isothermal Plug Flow Reactor. Experiments were conducted in three stages: straw devolatilization, char production, char burnout. Collected samples are analyzed to determine mass loss of particles. The results from this study may be used for CFD simulations of biomass combustion.

### **1.1 Process during biomass combustion**

The real combustion process in the burner is highly complex including chemical and physical aspect of the process. Combustion process of small particles is shown on Fig. 1. Generally, can be divided into several parts:

- drying and heating
- devolatilization
- ignition
- volatile matters oxidation
- char oxidation



**Fig. 1** Scheme of combustion process of small biomass particle, own elaboration based on [8]

During combustion fuel is losing volume and mass. The rate of biomass combustion depends on composition of oxidizer, burning atmosphere and properties of the fuel. After few second a large quantity of energy is emitted. Better understanding of combustion process is required to achieve high combustion efficiency and to design and operate the combustion furnace [8]. Furthermore the process should be performed so as to minimize emission of harmful contaminants:

- unburnt pollutants such as CO, C<sub>x</sub>H<sub>y</sub>, H<sub>2</sub>, HCN, NH<sub>3</sub> and N<sub>2</sub>O, PAH (Polycyclic Aromatic Hydrocarbons), tar, soot, unburnt carbon,
- pollutants from complete combustion such as: NO<sub>x</sub>, CO<sub>2</sub>, ash, PM10, PM2.5 (Particulate Matters) and contaminants such as ash particles (KCl, etc.), SO<sub>2</sub>, HCl, PCDD/F, Hg, Cu, Pb, Zn, Cd etc [9, 10, 11].

## 1.2 Heating and drying

Moisture (and ash) content is one of the most important parameters of the fuel. Process of drying starts at temperature lower than 100°C [8]. However complete dehydration does not occur below temperature 350°C [12]. If moisture content is higher than 60% there may be problem with a fuel ignition. Significant amount of moisture slows combustion process. Drying is heat transfer limited process: radiation, convection from furnace environment and conduction inside particle [8, 13]. For complete drying process, a large quantity of heat must be transferred to the fuel particle. When temperature 120°C is achieved, the moisture is converted to the vapour phase [12]. There are many variables that affect on process such as: particle size, particle porosity, particle moisture content and furnace temperature.

## 1.3 Devolatilization

Devolatilization is also known as pyrolysis. Is a process of thermal destruction of organic materials in the absence of an oxidizing agent. When fuel is heating up the volatile matters is driven off. In this step intensive reduction of fuel volume and mass is observed for a biomass up to 70% [8]. The main products of pyrolysis process are [7]:

- Char
- Liquid (tars, heavier hydrocarbons and water)
- Gas (CO, CO<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, etc.)

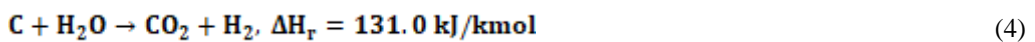
From fuel which has a high content of oxygen, e.g. biomass, appreciable quantities of CO or CO<sub>2</sub> can be produced. The heat for this process has to be supplied from the outside from external source of energy. Volatilities help ignite the carbonaceous char because volatilities have a lower ignition temperature. For a biomass fuel pyrolysis typically starts at 350°C [7]. Three forms of heat transfer occur. Radiative and convective heat from environment to the fuel particle and also conduction, pore convection inside particle. Devolatilization depends mainly on heating rate, initial temperature and residence time [14]. Following differences between biomass and coal pyrolysis can be observed [15]:

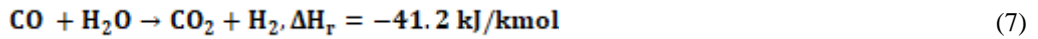
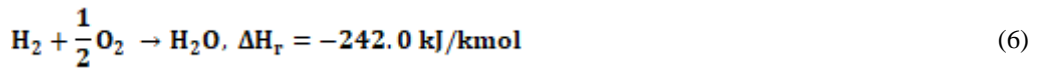
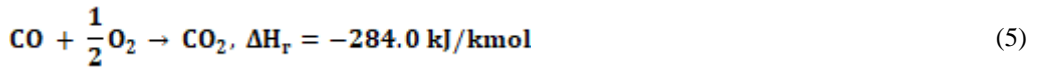
- Biomass devolatilization start earlier
- Biomass volatiles has a lower heating value
- Char produced from biomass has a higher oxygen concentration

#### 1.4 Char burnout

The char burnout is the last stage in combustion process. The aim of this process is to oxidize char (also known as active carbon) into gaseous form. Char produced in previous pyrolysis process is strongly reactive because of the trapped free radicals, and the porous structure [15]. Char is characterized by residual or non volatiles matter content, extremely large internal surface about 100 m<sup>2</sup>/g and apparent density 800 kg/m<sup>3</sup> [16]. Furthermore active carbon has remarkable adsorption properties [15].

The process of burnout can be defined as oxidation of elemental carbon into carbon dioxide. Char particle lose mass and volume [16]. In ideal stoichiometric reaction all carbon changes into CO<sub>2</sub>. Reaction of carbon oxidation is strongly exothermic, which means release large amounts of heat. Opposite endothermic absorbs energy (heat) from surroundings [17]. Heterogeneous chemical reaction of carbon oxidation is shown on equation (1). Reaction (1) becomes more important at lower temperature, e.g. under ignition conditions. Next primary heterogeneous reaction (2) dominates at higher temperature around combustion conditions. Because, carbon oxidation on particle surface is very fast and oxygen supply is insufficient. Reaction (2) emits lower amount of energy than reaction (1) and produce CO. As a result, oxidation is two step reaction, with CO is oxidized to CO<sub>2</sub> away from char particle. Moreover char can react also with CO<sub>2</sub> and H<sub>2</sub>O, reactions are shown in equations (3), (4) and they are known as gasification reactions [12]. Reactions (3), (4) are endothermic and occur at temperatures above 705°C [12]. Both reactions are very slow and have a small importance at temperatures under 1650°C [12].





The gaseous products of reactions (2), (3), (4) react with steam and oxygen away from char particle. The reaction (5), (6), (7) are called homogenous and occurs in gas phase [12]. Char oxidation is the slowest process in combustion, it takes a few seconds depends of various parameters (size of particles and structure, temperature, pressure, correct mixing with oxidizer agent, residence time) [11, 18]. Besides time needed to reaction is coupled with rate at which char particles are burned after pyrolysis and on quantity of combustible material which is remained in char [19]. All of the issues are extremely important and directly affect the proper fuel burnout and efficiency of the combustion process [8].

## 1.5 Research on combustion of solid fuels using DTF

The Isothermal Plug Flow Reactor (IPFR) also known as Drop Tube Furnace (DTF) is widely used for characterization of pulverized solid fuels [20, 21, 22, 23, 24, 25, 26]. Typical heating ratio of fuel for IPFR reactors reaches  $10^4 - 10^5$  K/s which is similar range as in PF boiler  $10^3 - 10^6$  K/s [19]. Thus using IPFR for advanced fuel characterization is an appropriate method to reproduce the conditions of combustion in PF boiler. Drop Tube Furnaces are often used for determine the behavior of solid fuels during pyrolysis, gasification and combustion process. Combustion behavior of biomass particles were detailed investigated in ref. [27] The residence time of particles is strongly determined by the particle size. Thus particle burnout calculations should take into account particle size distribution. Moreover the higher volatile matter content increases the burnout and on the opposite higher moisture content and grater particle size decreases the burnout [27]. In ref. [28] different types of raw and torrefied biomass were investigated in DTF in  $1100^\circ$  in air conditions. Burnout of torrefied biomass occurs much faster compared to raw biomass. The main reason is that torrefied biomass is described by lower volatile matter content compared to raw biomass [28]. A good comparison between technique of pyrolysis experiments using DTF and TGA (Thermogravimetric Analysis) is presented in reference [29]. Experiments were conducted in N<sub>2</sub> and CO<sub>2</sub> atmosphere for 2 different fuels South African coal and woody biomass. The heating rate in the case of DTF experiments were at level  $10^4$ - $10^5$  K/s and for TGA experiments 20 K/s [29]. The results of investigation shows that char produced from coal at  $1300^\circ\text{C}$  under N<sub>2</sub> atmosphere in DTF and TGA has a different properties. Combustion analysis of both coal chars shows that char produced from TGA is described by  $12,2\%/min^{-1}$  maximum rate for thermal degradation obtained at  $630^\circ\text{C}$ . Char produced in DTF is described by higher rate  $13\%/min^{-1}$  obtained at  $560^\circ\text{C}$ . It can be explained that char produced in DTF has a higher reactivity because of larger internal cavities and more open structure compared to TGA char [29]. It can be concluded that heating rate has a significant impact on produced char.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

One biomass fuel was used in this study. Tab. 1 shows proximate and ultimate analysis, and calorific data according to DIN (German standards). In the order to determine the particle size

distribution fuel samples were sieved. All of the fuel particles were smaller than 500  $\mu\text{m}$  and more than 80% of biomass particles were slighter than 200  $\mu\text{m}$ . In the first stage of experiments char from biomass was produced. Tab. 1 shows fuel analysis for char samples. Basic investigation of char is made according to German (DIN) standards. Char from straw was produced in the following conditions: temperature 900°C, gas velocity 3.01 m/s and residence time 706 ms in oxygen free environment (100% concentration of nitrogen). Biomass is characterized by low total moisture (TM) content 4.63% (ad) and high volatilities matter (VM) content 69.94% (ad). Moreover biomass is described by low fixed carbon content and high ash content. Which is directly related to low level of LHV 15.93 MJ/kg (ad). Low LHV parameter and high VM content are typical for biomass fuels [30].

Table. 1 Properties of straw and char produced from straw at temperature 900°C in IPFR - (DIN) standards

	Straw	Straw char
Proximate analysis		
Property	ad, %	ad, %
TM	4.63	0.00
Ash	7.39	32.16
VM	69.94	9.07
FC	18.04	58.77
Calorific value		
HHV	17.25	19.31
LHV	15.93	18.99
Ultimate analysis		
w	4.63	0.00
a	7.39	32.16
c	43.49	55.22
h	5.55	1.49
s	0.10	0.00
n	0.43	0.49
cl	1.07	3.50
o	37.34	7.14

Designations: ad – air dried

Biomass has relatively high content of chlorine 1.07% (ad), which may pose a problem with chlorine corrosion during combustion [31]. As one can observed biomass char has is described by very high ash content 32.16% and relatively low concentration of fixed carbon 58.77% (ad) which is directly related to low LHV parameter 18.99 MJ/kg (ad).

## 2.2 Experimental facility and method

The IPFR installed in IEVB institute is a furnace especially designed to carry out experiments on behavior of solid fuels during combustion process. The IPFR is characterized by flat temperature and oxygen profiles along reactor length, therefore combustion of particles is carried out in this same condition. The heating system is provided by 10 heating elements (together 20kW). Maximal temperature which can be achieved in the reactor is 1400°C. The IPFR can be divided in four main parts:

- gas preheating section
- vertical combustion chamber
- gas cooling and particle collecting section
- feeding system

Reactor chamber is vertical cylindrical ceramic tube with inner diameter of 0.12 m and 2.5 m length. Inside reactor is maintained overpressure around 20 – 50 Pa to protect suction from outside. The reactor is fully equipped by measure equipments to control all reactor conditions (temperature, oxygen/nitrogen mixture and flow). In order to achieve required residence time for char burnout/char production experiments feeding probe can be installed in different sampling ports. In the case of devolatilization experiments to the reactor is installed vertical sampling. Analyzer Rosemount NG 2000 ensures oxygen concentration control in the reactor. Particle burnout data were obtained by equation (8) as follows:

$$B = \frac{1 - \frac{A_0}{A}}{1 - A_0} \quad (8)$$

where B is particle burnout,  $A_0$  is the ash content in the input fuel, A is the ash content in the collected sample. In the case of devolatilization experiments mass loss formula may be calculated from equation (9) as below:

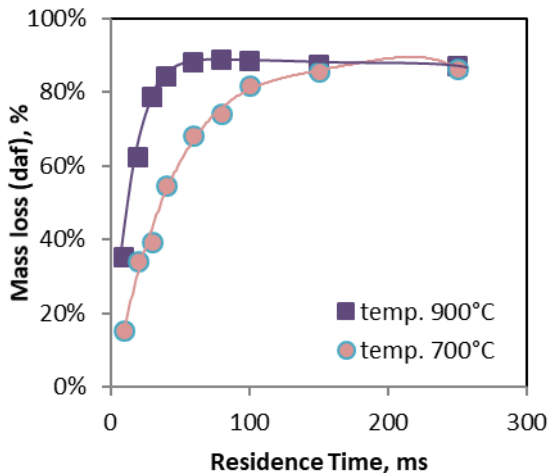
$$M_l = 1 - \frac{a_0}{a} \quad (9)$$

where  $M_l$  is particle mass loss,  $a_0$  is ash content of initial fuel and a – ash content of the sample.

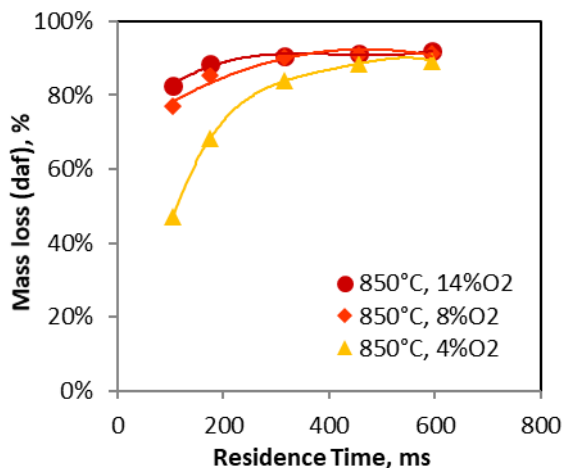
## 3 RESULTS AND DISCUSSION

The results from investigation are shown in Fig 2 – 5. The devolatilization experiments (Fig. 2) were conducted in oxygen free environment under two selected temperatures 700°C and 900°C at range 0 – 250 ms of particles residence time. Biomass devolatilization process occurs rapidly because of high VM content and tight porous structure of particles and high reactivity. One can conclude devolatilization of biomass occurs much faster at higher temperature. At temperature 900°C after 60 ms achieves mass loss at level 84%, finally after 250 ms obtains 83%. What could have been caused by measurement error. It can be concluded that, after 80 ms devolatilization process was finished. Decreasing temperature to level of 700°C slows devolatilization process. After 60 ms 65% of mass loss is achieved. Compared results to coal devolatilization performed in IPFR, biomass devolatilization occurs in lower temperature [19]. The results from char burnout experiments are shown in Fig. 3 – 5. Measurements were carried out in different condition including temperature

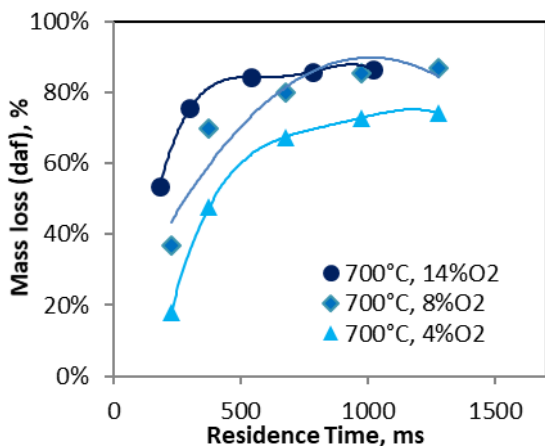
(600°C, 700°C, 850°C) and oxygen concentration (14%, 8%, 4%). Both of parameters are directly coupled with char burnout level. There is more factors associated with burnout rate such as: heating rate, char properties, char intrinsic reactivity, char morphology and surface area [29]. Generally at highest temperatures the process occurs quickly. However, in the case of high temperature combustion cannot exceed the ash melting points because of slagging and fouling problems in combustion chamber and convection area. Usually biomass ash contain high content of calcium oxide, alkali (mainly potassium) and phosphorus. These components are mainly responsible for the formation of deposits in PF boilers [33]. Higher oxygen concentration allows oxidizer penetrates precisely extensive, porous, internal particle surfaces affecting on rapid fuel degradation which can be easy observed in the charts. At lower temperature 600°C, 700 °C at 4% oxygen concentration oxidation process occurs slow and it is not finished.



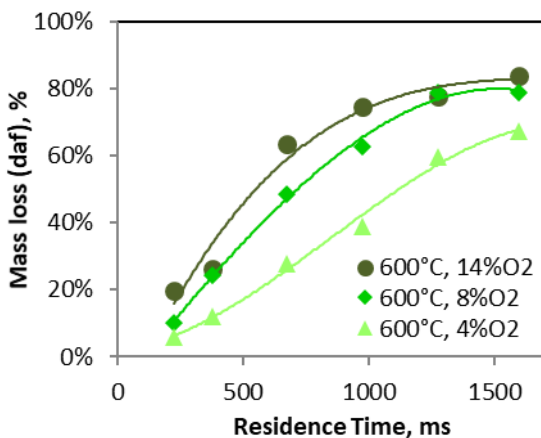
**Fig. 2** Devolatilization profile of biomass at temperature 900°C and 700 °C.



**Fig. 3** Burnout profile of biomass char at temperature 850 °C.



**Fig. 4** Burnout profile of biomass char at temperature 700 °C.



**Fig. 5** Burnout profile of biomass char at temperature 600 °C.



### 3.1 Operating problems and solutions

During the investigation with biomass, problems with slagging and fouling on reactor wall were encountered. At all stages of investigation this was observed. When level of deposits was very high, the reactor was stopped and carefully cleaned by brush and compressed air. The deposit formation is coupled with ash composition and ash melting points. Decreasing combustion temperature may help to avoid those problems. On the other hand low combustion temperature may be insufficient to ensure proper temperature of steam in real PF boiler.



**Fig. 6** Photo of the interior of the reactor before devolatilization measurements (cleaned)



**Fig. 7** Photo of the interior of the reactor after devolatilization measurements with visible foulants.

During devolatilization process installed vertical sampling probe after 30 minutes was clogged. Deposits were formed on devolatilization probe opening. It was necessary to pull out the probe and clean it with compressed air. Fig. 6. and Fig. 7. show foulants inside the reactor walls. The reason of fouling and slagging formation is high volatiles content in biomass fuel and high alkali content, and low melting point of this kind of fuel. This is serious challenge for combustion biomass fuels in PF boilers [15, 33, 34]

## 4 CONCLUSION

In this work researches on characterization of solid fuels are presented. Study includes basic characterization of biomass fuel according to German (DIN) standards and advanced characterization performed in Isothermal Plug Flow Reactor (IPFR). Advanced characterization is divided into three stages of measurements: char production, char burnout and biomass devolatilization. The aim of this research was to determine behavior of fuel during combustion process. The results of this investigation will be used for determine reactivity kinetics constant and CFD modeling of pulverized fuel combustion.

One of the biggest challenges of biomass combustion is slagging and fouling formation. However benefits such as zero carbon dioxide balance affect on increase interest technology of biomass combustion. One may conclude that, better understanding of fuel behavior and properties may avoid many of disorders during combustion process and affect to optimization of process. Improving combustion efficiency by minimizing loss of incomplete combustion (not burned solid

carbon particles in fly ash and slag) is one of method to improve boiler efficiency which is coupled with quantifiable benefits like fuel saving. It is directly translated with lower CO<sub>2</sub> emission, what is particularly important in the case of coal combustion. Additionally it influences to reduction harmful pollutants hazardous to human health and environment such as: NO<sub>x</sub>, SO<sub>x</sub>, CO, PM2.5, PM10, heavy metals, dioxins et. al.

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