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EFFECTS OF CONTENTS AND COMPONENT COMPOSITION OF ASH AND ORGANIC CONSTITUENTS ON FUEL CHARACTERISTICS OF SOFTWOOD AND WHEAT STRAW HYDROLYTIC PROCESSING RESIDUES

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Processing of biomass for obtaining of liquid ethanol, platform chemicals and solid biofuel, is topical biorefinery schema intensively developing. Acid hydrolysis, separated hydrolysis and fermentation, and simultaneous saccharification and fermentation are integrated with other treatments for the advanced technology development. The aim of this work was estimation of effect of softwood and wheat straw hydrolysis type on fuel characteristics of rich-in-lignin residues with emphasis on content and component composition of ash and feedstock. Elemental Analysis; Atomic absorption spectroscopy; calorimetric method; Klason lignin determination were used. Laboratory scale pellet mill KAHL 14-175 and original small pilot-scale gasifier were used for study of residues granulation ability and combustion behavior of pellets obtained. The ash content in softwood residues slightly increase but does not exceed 1%, for wheat straw residues it is >14% (0,2% and 10% for feedstock, correspondingly). The ashing temperature of 650ºC is experimentally established as optimal. Detection of ash component allows to foreseen possible contamination connected with materials of the devices and chemicals used in the technological stream. Combustion mechanism of solid residues differs from that of feedstock by increasing of ratio duration of glue combustion to flame combustion steps, that is more characteristic for coal. The efficiency of biomass combustion was regulated by changing the ratio of primary and secondary air supply. Direct correlation established between higher heating value and Klason lignin content for samples, allows to recommend these analyses for evaluation of biomass potential as a fuel. Residues under study meet the requirements of EU Standard CN/TS 335.

Keywords: biofuel, calorific value, combustion characteristics, inorganic admixtures, lignocellulosic hydrolysis, rich-in-lignin residues, softwood, wheat straw

INTRODUCTION

Catalytic chemical/biochemical processing of biomass directed on obtaining of liquid fuel (alcohols), platform chemicals, solid fuel (rich-in lignin hydrolytic residues) is topical biorefinery schema intensively developing during last decades. Currently bioethanol is produced mainly from sugar and starch-rich food crops (first ethanol generation), i.e. from corn in the US, sugar cane in Brazil and mix of grains of wheat, barley, corn and sugar beet in the Europe or through hydrolysis and subsequent fermentation of lignocellulosics (second ethanol generation) (Sanchez, 2008; Limayem, 2012). The latter processing is much more difficult for realization, but lignocellulose potential regarding feedstock supply is far larger, cost is lower and, in addition, it is used instead of food resource. Utilizing of lignocellulosic biomass is still in a relatively early stage of development. Waste based lignocellulosic ethanol production (e.g. from ash-rich straw of cereals) remains under technical development with a number of demonstrational and commercial sizes plants in operation across Europe (Hirschnitz-Garber, 2015).

Solid non-hydrolized lignin rich residues formed as a result of lignocellulosic ethanol production are recognized as a “green” fuel which study is an area of special research. They are proposed to use partly for energy supply for major technological processes, whereas another part is foreseen for manufacture of marketable granulated biofuel.

However, permanent improvement of biomass processing oriented on the enhancement of the ethanol yield, which in the laboratory scale at present achieved 84% from theoretical (based on both xylose and glucose) (Nielsen, 2017), lowering ethanol production costs, broadening of the feedstock assortment, leads to the changes in the fuel characteristics of reach-in-lignin processing residues.

Acid hydrolysis (AH), separated acid hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) processing are widely integrated with other chemical / biochemical treatments for the development of advanced ethanol production options.

The aim of the present work was estimation of effects AH, SHF and SSF processing of soft wood and wheat straw realized in pilot scale conditions on fuel characteristics of rich-in-lignin residues with emphasis on content and component composition of ash and feedstock.

RESEARCH METHODS

Objects for investigations. The softwood (SW) samples before and after separated hydrolysis and fermentation (SHF) and after simultaneous fermentation and sacharification (SSF) process were obtained from pilot plants of Lund (L) University and Ornskoldsvik (O) – both from Sweden. The sample of softwood after two stage acid hydrolysis (AH) from Ornskoldsvik were obtained as well.

The wheat straw (WS) samples after separated hydrolysis and fermentation were obtained from Institute of France petroleum (IFP) (France).

All samples were obtained during the development of economically efficient hydrolysis processes for fuel ethanol production in the frame of 6FP NILE Project (contract 019882).

Samples preparation. Residues, received as partially frozen masses (straw-based specimens) or not frozen masses (softwood-based specimens) with water content of 55-81%, were dried at 20^{o}C until 4,5- 6,0 water content and then were crushed additionally using Cutting Mill SM 100 (Retch GmbH). Fraction with particles size of ≤ 0, 25 mm were used for analysis.

Ash content was measured after ashing at three different temperatures 550, 650 and 800^{o}C till to achieving of constant mass of samples.

Element composition. Content of Na, K, Fe, Mg, Ca, Mo, Cr in ash was determined by atomic absorption plasma spectroscopy method.

Klason lignin determination method was used to characterize the composition and calorific properties of residues according to Tappi Standard T222.

Combustion heat. Higher heating value (HHV) was determined by burning of dry (at 105°C) samples in the calorimetric bomb according to ISO1928.

Granulation of lignin residues. Flat die laboratory scale pelleting press KAHL 14-175 with output up to 50 kg/h was used for residues granulation. Before granulation lignins were air dried at 22°C up to water content 11-12% and grounded using Cutting Mill SM 100 to produce fraction with particle size ≤3.0 mm. The moisture of granules (d=6.0 mm) obtained was 5.5–6.2 %. Commercial softwood granules with diameter 6.0 mm and moisture content of 6.2% were used as a reference material.

LHRs granules combustion. The testing of combustion and emission characteristics of granules was realized using a small pilot-scale combustion system, consisting of biofuel gasifier with discrete mass load chamber for Granules (about 180g) and water-cooled combustor. The propane/air (0.78/15.7 L/min) burner with a heat energy release at rate 1184 J/s was used TO START gasification (of granules and) accompanied by ignition of volatiles. After biomass ignition the propane burner was turned off. The portable gas-analyzer Testo 350XL was used to study the composition of GAS emissions (CO, CO_2, SO_2, NO, NO_x, O_2).

The time-dependent measurements of the flame temperature and heat production rate were recorded on-line using the date recording plate PC-20 (Fig. 1).

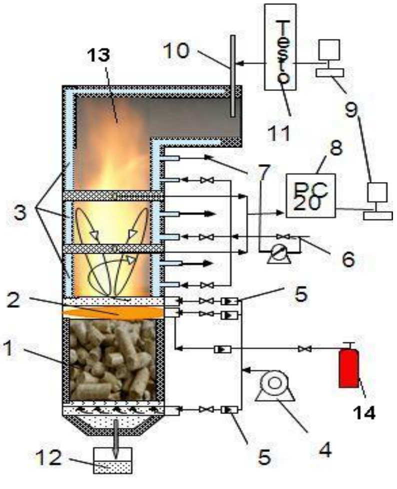


Figure 1. Scheme of the experimental set-up for granules combustion: *1* – gasifier, charged with biofuel pellets, *2* - swirling propane/air burner, *3* – water-cooled channel sections of the combustor, *4* – primary and secondary air supply, *5* – airflow meters, *6* – cooling water flow inlets, *7* – cooling water flow outlets, *8* – data recording plate PC-20, *9* – computers, *10* – gases, *11* – gas analyzer Testo 350-XL, *12* – ash container, *13* – combustions chamber, *14* – Propane bulb.

RESEARCH RESULTS AND DISCUSSION

The results of HHV and LHV determination for all samples of granulated rich- in lignin hydrolysis residues under study have shown that both groups of granules derived from softwood and wheat straw are characterized with higher energetic potential than parent samples. This is conditioned mainly by removal during biomass hydrolysis of carbohydrates which characterized by higher content of oxygen and, therefore, have less energetic value. The direct correlation between HHV and content of Klason lignin and carbon in residues is established (Fig. 2). This relationship is the basis for usage of lignin Klason content in lignocellulosic biomasses as criteria for the evaluation of their potential energetic value.

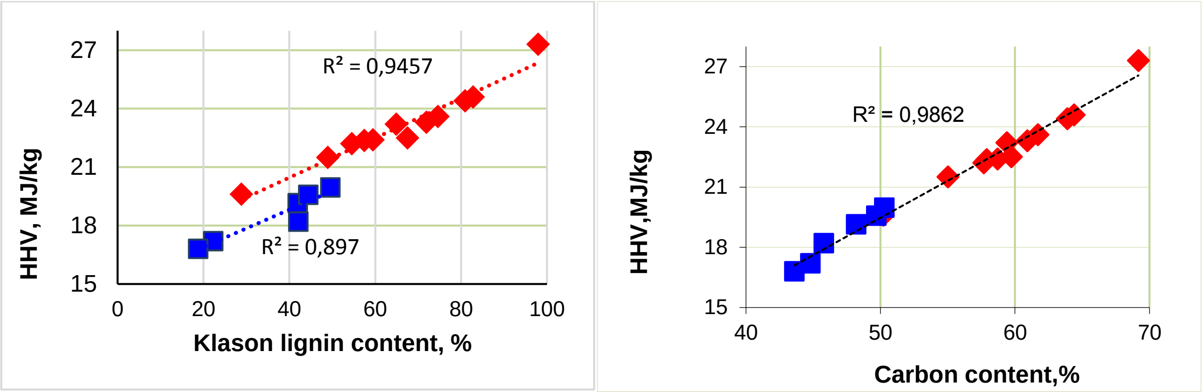


Figure 2. The correlation between Higher Heating Value (HHV) of softwood (rhombus) and wheat straw (square) hydrolysis residues and content of Klason lignin (A) and carbon (B) in them.

Due to high ash content in wheat straw residues, that varied in the range of 6-14%, and rather low lignin content (40-50%), carbon content in them does not exceed 50%, whereas for softwood residues (ash content 0.2-0.8%, lignin content 60-80%) carbon content achieved 68%. As the result, HHV calculated per weight of sample is higher for softwood residues, but the amount of ash produced in real combustion tests is significantly lower than for wheat straw hydrolysed residues.

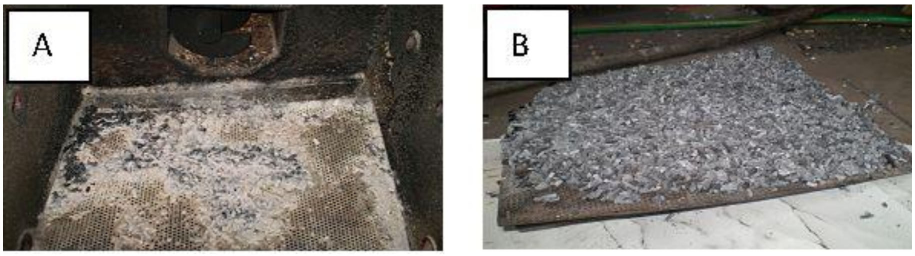


Figure 3. The ash residues collected in ash container of commercial pellet boiler (40 kW) after combustion of 10 kg of commercial wood pellets (A) and WS residue derived pellets (B).

Standards foreseen the possibility of chemically treated biomass application as a solid biofuel with ash content more than 6% if it will be preliminary declared (EU Standards CEN/TC 335, group A6+). However, high total ash content in fuel biomass create an additional problems for energy producers incl. high volume of ash by-stream (Fig. 3), that have to be managed, and a lot of ash-related operational problems arising during combustion (e.g. melting, enhancement of undesirable emissions etc.) due to incorporation in lignin residues inorganic elements derived from technological solutions.

Ash in biofuel is defined as unburned constituents, however, changes of biomass matrix structural characteristics as well as transition of inorganic elements from technological solutions into lignin-rich residues can significantly influence on volatalization of ash (elements). The range of temperatures proposed in standards for determination of total ash content in lignocellulosics is varied from 550°C (European Standard CEN/TS/14775) up to 815°C (ISO 1171, ISO 540, DIN 51719). For the samples under investigation the ashing temperature of 650°C can be recommended that is exemplified by the analyses of acid (AC), fermentative (SHF) and simultaneous fermentative and saccharification (SSF) hydrolytic processes residues (Table 1). Further increasing of analytical procedure temperature up to 800°C lead to decreasing of the ash yield connected with volatilization of some ash elements, e.g. potassium (Smeda, 2004).

In particularly, enhanced of alkali metals, Al and Si content and low content of Ca increase sintering tendencies (Ronnaback, 2006). Straw and grasses containing low concentration of Ca and high concentration of Si and K start to sinter and melt at significantly lower temperatures than ashes from wood samples. Fouling and sintering are promoted when temperature in furnace exceeds the temperature of ash melting. Part of the heat produced is expended for the ash melting. Adhesion of fly ash particles on the heat exchanger surface decrease heat transfer and, respectively, efficiency of boilers used.

Table 1. Effect of lignin residues ashing temperature on the results of total ash analysis

Sample	Ash content at different ashing temperatures, % on DM		
	550°C	650°C	800°C
Softwood pretreated by steam explosion	0.20	0.19	–
Softwood fermentative hydrolysis (SHF, Lund)	0.46	0.42	0.34
Softwood simultaneous saccharification and fermentation (SSF, Lund)	0.68	0.60	0.53
Softwood acidic hydrolysis (AH, Ornskoldsvik)	0.78	0.81	0.69
Wheat straw fermentative hydrolysis (SHF, Institute France Petroleum - IFP)	14.47	14.26	14.12

In general high relevance for the ash melting behavior and deposit formation is documented for Al, Ca, Fe, K, Mg, Na, P, Si, whereas for Cl, S, N, Na, K, As, Cd, Hg, Pb, Zn close connection with formation of gaseous and especially aerosol emissions are estimated although they are also influence on deposit formation and corrosion of constructions (Biedermann, 2005). For some of ash elements, namely for Cl, S, K and Na, concentrations making biomass (straw, cereals, grasses, waste wood) combustion unproblematic is established as <0, 1%, < 0, 1%, <7, 0% and <2, 0%, respectively.

Effect of hydrolytic treatments type (Table 2) and, respectively, chemicals used for its realization, process technological parameters (temperature, time) and corrosion stability of equipment materials (Table 3) is exemplified using softwood samples.

Table 2. Effect of different type of biomass hydrolytic processing on ash content and its composition in lignin-rich residues.

Sample	Ash content, % at 650°C on DM	Element content % on DM of ash				
		Na,%	K,%	Ca,%	Fe,%	Mg,%
Wheat straw	9.90	0.37	7.30	2.30	0.074	0.54
Wheat straw fermentative hydrolysis, (SHF, IFP)	14.3	1.25	0.17	0.10	0.28	0.05
Softwood fermentative hydrolysis (SHF, Lund)	0.42	17.7	2.10	16.70	2.17	0.68
Softwood simultaneous saccharification and fermentation (SSF, Lund)	0.60	11.9	3.30	18.80	1.37	1.08
Softwood acidic hydrolysis (AH, Ornskoldsvik)	0.81	10.00	1.37	1.19	0.86	0.32

Table 3. Enhancement of chromium and molybdenum content in lignin- rich residues obtained after different type of softwood hydrolytic processing.

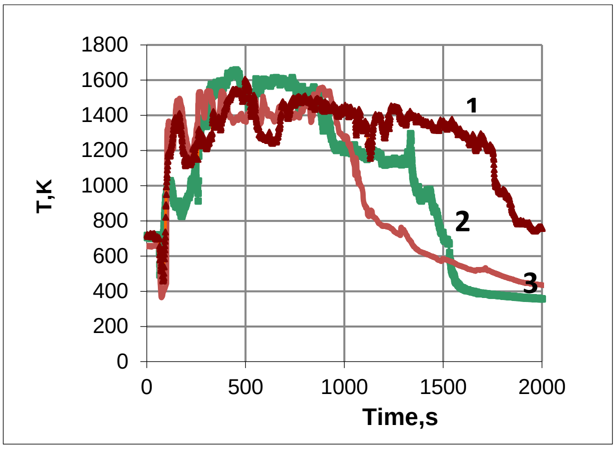
Sample	Element content, on oven dry matter, mg/kg	
	Cr	Mo
Softwood	1.46	n.d.
Softwood acidic hydrolysis (AH, Ornskoldsvik)	30,0	6.8
Softwood fermentative hydrolysis (SHF, Lund)	9.0	1.61
Softwood simultaneous saccharification and fermentation (SSF, Lund)	8.1	2.00
Softwood fermentative hydrolysis (SHF, Ornskoldsvik)	6.73	5.75

The high ash content in wheat straw residues are in compliance with this one in the feedstock, and, if necessary, it can be controlled by (i) usage of low ash straw only (that is depends on feedstock plant cultivation and storage management) (ii) application of special additives able to neutralize action of ash problematic elements or (iii) special formulation of mixtures with low ash biomass, incl. chemically treated.

Combustion profile of soft wood and rich-in-lignin residues after hydrolytic processing (exemplified by SSF) drastically differ (Fig. 4) that is displayed the different mechanisms of biomass burning (Fig. 5). Besides that, it was shown that the total heat release as result of combustion of the hydrolyzed residues, increases with initial feedstock, that coincide with the higher HHV value of the residues (Fig. 6).

Changes in structure and chemical compositions of biomasses under influence of hydrolytic processing lead to decreasing of duration of volatilizes combustion step, or so-called flame combustion, and, in parallel, to enhancement of duration of char combustion step, or so called glow combustion. The mechanisms are similar to fossil coal combustion. This similarity creates beneficial conditions for co-firing of hydrolyzed residues with the fossil coal that could be recognized as one of promising directions for utilization of biomass for energy purposes.

The combustion test has shown that the total heat released and the maximum heat release rate is increased in the raw LHR softwood – softwood – LHR wheat straw, coinciding with measured HHV values. Moreover, the heat release at the final combustion step of both LHRs exceeded that for softwood.



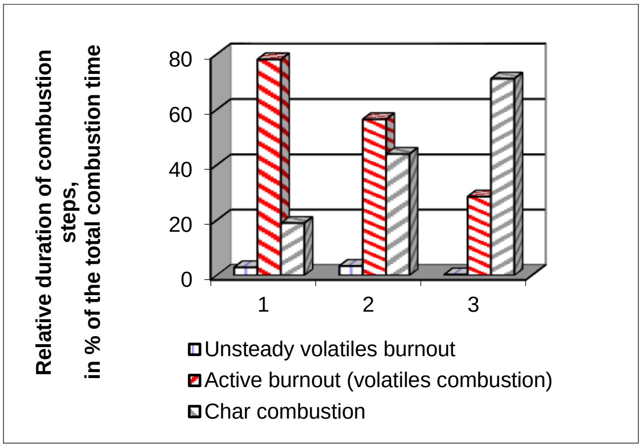


Figure 4. Variation of temperature in burning zone (T) depending on Time (Time) at burning out softwood (2) and rich- in-lignin residue after softwood SSF hydrolysis (1) and wheat straw SHF hydrolysis (3) samples in laboratory scale device.

Figure 5. Relative duration of unsteady volatiles burnout, sustainable (active) volatiles combustion step (flame combustion) and char combustion step (glow combustion) of lignocellulosic granules, in percent of the total combustion time in laboratory scale device. Softwood -1 , Softwood SSF (L) -2 , Wheat straw SHF (IFP) – 3.

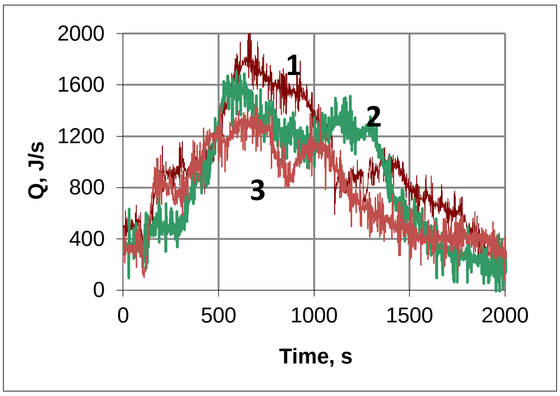


Figure 6. Heat release rate (Q) for rich- in-lignin residue after softwood SSF hydrolysis (1), softwood (2) and wheat straw SHF hydrolysis (3) samples.

CONCLUSIONS

Amount and composition of biofuel ash defined as unburned inorganic component of biomass, can create big problems for energy producers (sintering, fouling, emission). The ash content in hydrolysis lignin depends on biomass origin, type and quantity of chemicals used in processing as well as storage conditions. Even at low content in softwood hydrolysis residues, ash allows to reveal some ecological problems due to the presence of harmful contamination derived from materials of the devices and chemicals used in the technological stream.

Direct correlation established between HHV and Klason lignin content for all samples, independently on the types of plant feedstock and types of processing used, allow to recommend this analysis for evaluation of biomass potential as a fuel. The Klason lignin content taken into consideration together with combustion profiles detected for different biomass can serve for substantiation of choice of co-components for co-firing aimed improvement of fuel characteristics of high ash biomass.

Change in the structure and chemical composition of biomass taking place during processing for fuel ethanol production lead to formation of residues which combustion mechanism differ from that of feed stock by increasing ratio of glue and flame combustion step duration similar to that observed for coals. The efficiency of both steps biomass combustion can be regulated essentially by changing the ration of primary and secondary air supply. All residues under study meet the requirements of EU Standard CN/TS335.

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