THE COMPOSITION AND FUEL CHARACTERISTICS OF NON-HYDROLYZED RESIDUES FROM WHEAT STRAW ETHANOL PRODUCTION

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Abstract. The paper presents the results of the experimental study of composition, heating values and combustion characteristics of granulated non-hydrolyzed residues (LHR) of separated hydrolysis and fermentation (SHF) wheat straw bioethanol processing. The LHRs ash content at 1.4-1.7 times exceeds the values for the native wheat straw samples. It was established that higher heating values (HHV) of the granulated LHRs (on dry mass) exceed HHV of initial wheat straw and are some lower in comparison with that of softwood granules. Granulation was carried out using the laboratory scale flat die pellet mill KAHL. The higher plasticity of LHR results in lower energy consumption during the LHR granulation in comparison with softwood sawdust (most widely used for the production of biofuel granules). Combustion and emission characteristics of LHRs granules were tested using a small pilot-scale combustion system that is composed of the plant biofuel gasifier and water-cooled combustor. The test results were compared with characteristics of commercial softwood granules. Due to higher thermolability of LHR, granules on its basis are characterized with faster gasification and faster transition to the active burning stage, but the average rate of heat release and total heat output are slightly lower to that for softwood granules. LHR obtained by enzymatic hydrolysis of wheat straw show the higher nitrogen content than native wheat straw and softwood, resulting in higher NO_x emissions during the LHR combustion in comparison with softwood granules. Co-firing of LHR granules with propane flame, providing 10 % of the additional heat supply into the combustor allows decreasing the levels of CO emission, so promoting cleaner combustion of LHR.

Key words: wheat straw, non-hydrolyzed residues, granulation**,** combustion.

Introduction

Today the bio-ethanol production by hydrolysis of lignocellulosic materials, mainly from wheat straw and softwood, is considered as a real alternative to gasoline for transport needs.

The pilot plants for the wheat straw ethanol production are under operation today in Denmark, Canada, Spain, and France [1]. Utilization of the high amounts of LHR (for wheat straw 40-60 % from raw material) for the heat and energy production will make a valuable contribution to the process economy, decreasing dependence from the fossil fuel. In this account, there is a high need to estimate the main characteristics of LHR produced as by product of the bio-ethanol production to optimize technologies of the large scale heat energy production.

Today the biomass granulation is considered as the most effective way of biomass application for heat and energy production. Granulation allows enhancing the efficiency of the plant biofuels because of increased energetic density, simplification of transportation and storage, providing facilities of automatic fuel supply for the systems of heat and energy production [2].

With the aim to promote the large-scale usage of LHR for clean and effective heat and energy production, the present study is carried out in detailed investigations of the chemical composition and calorific values of two LHR wheat straw samples, realized on the SAFISIS pilot plant in France, by estimating the feasibility and the main parameters of granules, produced from these materials. Moreover, the evaluation of the main combustion characteristics (ignition time, emission characteristics, heat production rate and total heat output) is carried out using the laboratory pilot set up by comparing the obtained characteristics with those for softwood, including the commercial softwood granules.

Materials and Methods

1. Materials

Two samples of the native wheat straw and LHRs that were obtained by enzymatic SHF hydrolysis of the wheat straw samples in the pilot plant of SAFISIS (France) were used to estimate the main characteristics of wheat straw and LHRs. The main steps of the process of enzymatic SHF hydrolysis are as follows: steam explosion in the presence of sulphuric acid as catalyst, enzymatic hydrolysis of pretreated wheat straw, LHR separation step, fermentation of C6 sugars, ethanol distillation.

As a reference material in the granulation process the softwood sawdust, obtained from Latvian wood-sawing plants with initial water content 45 %, was used. Before granulation the softwood sawdust and LHR were air dried, decreasing the water content to 10±0.5 % and sieved through a 2 mm sieve. For the combustion tests the commercial softwood granules of 6 mm in diameter were used as reference materials.

2. Tests for determination of composition and characteristics of LHRs.

Water content and ash content in dispersed and granulated samples of biofuels were determined according to CEN/TS 14774-1 and CEN/TS 14775 correspondingly. Determination of Klason lignin (KL) was accomplished according to [3]. C, N H, S total was determined using Analysis System Vario Macro CHNS. Higher heating values (HHV) were estimated in accordance with ISO1928. Lower heating values (LHV) of granules were calculated according to [4]:

$$LHV = HHV - 0.0251 \cdot (9 \cdot H + W) \text{ MJ/kg} \quad (1)$$

where H – hydrogen content in sample, %;
W – water content in sample, %.

The combustion sulphur content (S comb) was measured spectrophotometrically after burning of granules in calorific bomb.

The net air supply (V_o) into the combustor to provide the stoichiometric combustion of granules ($\alpha = 1.0$) was estimated from the data of elemental composition of fuel samples using the equation [4]:

$$V_o = 0.0889 * C + 0.266 * H + 0.033 * (S\text{ comb.} - O) \text{ Nm}^3/\text{kg}, \quad (2)$$

where C, H, S-comb., O – carbon, hydrogen, combustion sulphur and oxygen content in fuel samples, correspondingly.

Particle and bulk densities of granules were determined according to CEN/TS 15150 and CEN/TS 15103, correspondingly.

3. Granulation of LHRs

To compare the ability to compress LHR in comparison with softwood sawdust and initial wheat straw, the moving piston compression mould was used. The piston diameter was 8.0 mm, sample mass 0.45 ±0.01 g. Compressing was conducted with the universal testing machine ZWICK ROELL Z100 up to pressure 150 MPa. Relaxation ratio [5] was determined after 2 min and 24 hours after the sample unloading.

The laboratory flat die pellet mill KAHL (14-175) with 3 kW engine power equipped with the die of 24 mm thickness and bore diameter 6 mm was used for LHRs and softwood samples granulation. The rotation speed of the pelleting press 90 rpm at idle run capacity 0.33 kW has been chosen for all experiments. The material loading mass was 1500-2000 g. Before testing the die temperature was up to 80-85 ˚C by pressing of softwood sawdust (handle supply). The output power of the engine in the range 1.5-2.0 kW was regulated with the material automatic feeding system. The main process characteristics, such as specific energy consumption (kWh/kg), the press productivity (kg/h), energy consumption in percent of obtained granules lower heating value were determined. The average values of power (one measurement each 10 s) were used for calculation.

The produced granules were characterized in terms of particle and bulk densities, heating values, volumetric energy densities.

4. Combustion test

The testing of combustion and emission characteristics for the different types of LHRs granules was conducted using a small pilot-scale combustion system, composed of biofuel gasifier with discrete mass load (220 g) of the biofuel granules and water-cooled combustor with the surface of heat exchanger 0.174 m^2 [6]. The total air supply in the system for the gasification of softwood and LHRs granules and complete combustion of volatiles was 118 l/min with a relation between the primary air/secondary air supply rates about 0,6. The propane/air (0.78/15.7 l/min) burner with a heat energy release at rate 1184 J/s was used for fuel ignition. Exposition of the heat input by propane flame flow into the biomass was 170 s. After that time the heat input by propane flame was switched out and the biofuel combustion developed due to self-sustaining gasification of granules and burnout of the volatiles.

In co-firing regime the additional heat supply by propane flame into the gasifier was carried out during all stages of biofuel combustion - up to complete combustion of the volatiles (2400 s).

The diagnostic tools for the complex on-line measurements of the combustion and emission characteristics included Pt/Pt-Rh thermocouples for the local time-dependent measurements of the flame temperature and portable probe for the gas sampling. The portable gas-analyzer Testo 350XL was used to study the effect of biofuels type on the composition of emissions (O_2, CO_2 CO, NO_x, NO_2), providing the estimation of air excess values. For characterization of the emission processes the average concentrations of O_2, CO_2 CO, NO_x, and NO_2 were calculated for the active burning zone (air excess ≤200 %).

The calorimetric measurements of the cooling water flow were used to estimate the time-dependent variations of rate of heat energy production at different stages of the biofuel granules burnout and the total amount of the produced heat. The time-dependent measurements of the flame temperature and heat production rate were recorded on-line using the date recording plate PC-20.

Results and Discussion

1. LHRs composition and fuel characteristics

Two processes influencing the heating values of LHRs are taking place during of wheat straw hydrolysis. Removal of cellulose and hemicellulose in wheat straw hydrolysis process lead to increased Klason lignin content in LHRs and correspondingly to increasing of the carbon content in them, promoting the increase in HHV (Table 1) and simultaneously the increase in ash content in LHRs (due to concentrating effect) decreases the positive effect of carbohydrates removal.

. Table 1

Composition of a dry plant biofuel samples, their heating values and air supply (Vo) for the stoichiometric (α = 1) combustion

Sample	Ash content %	Klason lignin content %	Element content, %					HHV, MJ/kg	Vo, Nm^3/kg
			C	H	N	S			
						Tot.	Comb.		
Wheat straw-A	9.9	18.7	43.6	5.8	0.62	0.20	0.12	16.8	4.11
Wheat straw-B	5.3	22.3	44.8	5.0	0.84	0.35	0.31	17.2	3.88
LHR A	14.3	42.1.	45.8	5.5	0.98	0.24	0.10	18.2	4.44
LHR B	9.3	41.9	48.2	5.4	1.17	0.43	0.30	19.3	4.55
Softwood	0.55	28.8	50.2	6.2	0.33	0.14	0.02	19.6	4.64

Therefore, due to the increase of the ash content in LHRs samples, the effect of an increase of their HHV in comparison with parent wheat straws was not so high as it could be expected from the alteration of KL content. As the result, the HHV of LHRs not more than 10 % exceeds the HHV of parent's wheat straw and is slightly reduced in comparison with softwood that has higher carbon content. The problem of higher ash content in LHRs, as well as behaviour during combustion, determining its further useful application, will be important at large scale LHR combustion and is considered by a lot of specialists [1].

As follows from Table 1, the calculated value of air (V_o) that must be supplied for the stoichiometric LHRs combustion, exceeds that for the wheat straw, but is some lower then that for the softwood.

The usage of enzymes in hydrolysis leads to higher nitrogen content in LHRs and higher NO_x emission can be predicted during the burnout of LHR in comparison with the levels of NO_x emissions during the burnout of native wheat straw and, especially, softwood. Negligible increasing of sulphur content is observed in both samples of LHRs (obviously to gypsum formation), but combustible (organic) sulphur amounts in these samples are practically equal to that of wheat straw (Table 1). The addition of limestone to the LHRs before combustion with the aim to provide bounding of organic sulphur into gypsum can be used as a conventional method for SO_2 emission decreasing [1].

2. LHR granulation with laboratory pellet mill

The investigation of LHRs granulation process using Laboratory pellet mill KAHL 14-175 allows to simulate the process of biomass granulation with application to industrial scale flat die granulators. It is well-known that a lot of factors show strong influence on the properties of granules and energy consumption during the granulation, including the origin material, the particle size, the water content in the material before granulation, so as the technological factors: (speed of the pelleting press, speed of the proportion screw, working gap, the ratio of the die thickness to bore diameter).

During the densification of dispersed material gradually decreases the free space between the particles of dispersed material. Moreover, during the densification of dispersed material three types of deformation can take place: elastic, fragile and plastic [7]. These factors all together can show the direct influence on the relationship between the sample densities, applied pressure and energy consumption during the granulation. In total, the energy consumption increases with an increase of material elasticity. The experiments with the moving piston compression mould have shown that the relaxation ratio calculated for LHR sample is reduced in comparison with that for the initial wheat straw and softwood (Fig. 1).

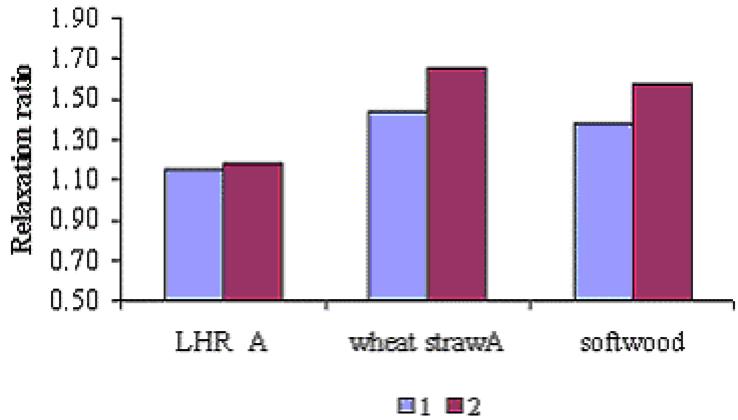

Fig. 1. **Relaxation ratios after 2 min (1) and 24 h relaxation (2) for granules by pressing the disperse biofuels at 150 MPa**

These results testify that the relaxation processes for the straw and softwood samples are more prolonged, and the value of elastic (reversible) deformation is higher then that for LHR. It means that native wheat straw and softwood sawdust are materials with higher elasticity then LHR. Consequently, the results show that hydrolysis of the plant materials results in degradation of plant cell walls, described as superposition of interpenetrated nets of main plant components: cellulose, hemicelluloses and lignin. Besides that the low molecular products formed in the result of lignocarbohydrate complex destruction and detected in LHR could reveal antifriction action on the pressing process.

This result correlates with the data that are obtained under investigation of LHR and softwood sawdust granulation with laboratory pellet mill.

It was shown, that for LHR wheat straw granulation the mean value of energy consumption is lower than that for granulation of softwood sawdust, determining the higher process productivity (Table 2).

. Table 2

Parameters of softwood sawdust and LHR B granulation with laboratory pellet mill KAHL (14-175) application and properties and characteristics of granules obtained

Parameters	Dimension	Value	
		Softwood	LHR B
LHV granules obtained	MJ/kg	17.8	16.8
Particle density	kg/m^3	1325±25	1255±18
Bulk density	kg/m^3	740	700
Volumetric energy density	MWh/m^3	3.7	3.3
The engine output power	kW	1.83	1.87
Productivity of pellet mill	kg/h	4.8	17.6
Granulation specific energy consumption	kWh/kg	0.382	0.106
Granulation specific energy consumption in percent on LHV granules obtained	%	9.3	2.3

Hence, the results presented in Table 2 prognosticate lower energy consumption and higher process productivity for industrial scale LHR granulation in comparison with softwood sawdust granulation using pellet mill technology.

3. Combustion and emission characteristics of LHR granules

The LHR granules with particle density 1255 kg/m3, water content 5.9 % and LHV 16.8 MJ/kg were used in combustion tests. Commercial softwood granules with particle density 1185 kg/m^3, water content 7.2 % and LHV 16.9 MJ/kg were used as a reference material.

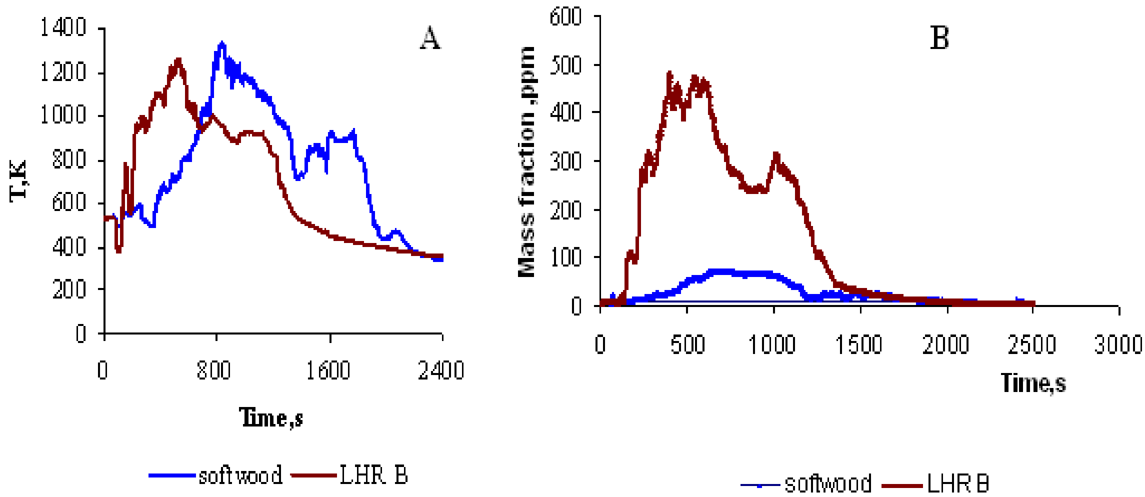

Fig. 2. **Time dependence variations of the burning zone temperature (A) and the formation of NO_x (B) emissions during the burnout of LHR and commercial softwood granules**

The granules on LHR wheat straw basis that were produced using the pellet mill method are characterized by significantly faster volatilization and shorter burnout time in comparison with those for commercial softwood granules (Fig.2-A).

The results show that LHR wheat straw differs with higher thermolability than that for softwood. In fact, such result correlates with the data of thermogravimetry. The minimum values of the temperatures to initiate the intensive thermal destruction of biofuel established by this method were 260 ˚C and 170 ˚C for the softwood and LHR samples, correspondingly.

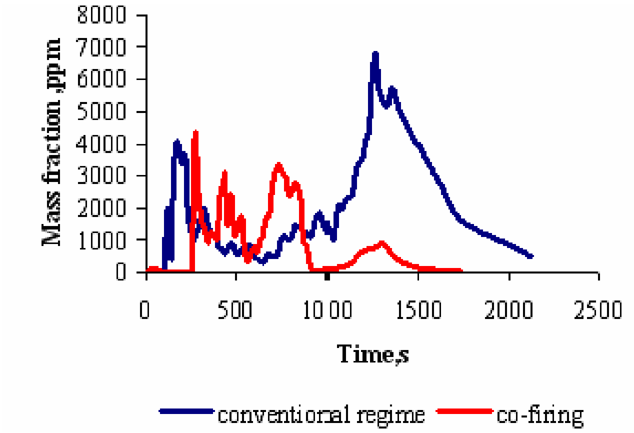

Fig. 3. **Time dependence variations of CO emission during the burnout LHR B granules for the self-sustaining and co-firing regimes**

As one can see from Fig.2-B, the negative feasibility of LHR has enhanced NO_x emission during the burnout in comparison with the result of softwood combustion that can be related to the presence of enzymes in biomass. Hence, the conventional technological measures could be undertaken to decrease the NO_x emission below to the levels of NO_x emission during the burnout of the softwood granules.

Table 3

Emission characteristics of LHR (B) and commercial softwood granules combustion

Biofuel	Regime	Emission				Air excess,%
		$O_{2, VOL.}$ %	$CO_{2, VOL.}$ %	NOx, ppm	NO_2, ppm	
Softwood	Self-sustaining	12.3	8.5	66	1.9	188
LHR B	Self-sustaining	12.7	8.1	338	10.5	158
LHR B	Co-firing	7.9	12.8	326	3.6	74

The output of heat energy during the burnout of biomass is significantly lower than that for the fossil fuels. Besides that, the dissimilar structure and variations of the density and moisture content in the granulated samples can result in the formation of incomplete and unstable process of biofuel burnout. To avoid these disadvantages and provide stable, clean and effective burnout of granulated samples, co-firing of biofuel with fossil can be used [6]. The variations of emission characteristics confirm that co-firing of LHR granules with propane flame flow allows significantly to decrease the formation of CO emission at the final stage of the biofuel burnout, decreasing the total amount of CO emission as well (Fig. 3).

This fact together with the correlating decrease of the free oxygen concentration in the products and the increased rate of the CO_2 formation with higher CO_2 volume fraction in the products confirms that co-firing of the fossil fuel with biofuel granules with the additional heat energy supply up to 35 % from the total heat produced results in more effective and complete LHR combustion.

It should be noticed that for the conditions of propane co-fire a slight decrease of the total amount of NO_x emission is observed that mainly can be related to the reduced rate of NO_2 formation (Table 3).

Table 4

Balances of heat energy obtained in the result of LHR B and commercial softwood granules combustion in the experimental set up at different regimes of propane flame heat supply into biofuel mass[1]

Sample	Regime	Q propane, kWh	Q biofuel, kWh	Q sum, kWh	Qbiofuel/ Q sum,%	Q_{LHR}/Q softwood
LHR B	Self-sustaining	0.09	1.89	1.98	95.4	0.98
LHR B	Co-firing	1.10	2.08	3.18	65.4	1.08
softwood	Self-sustaining	0.09	2.02	2.11	95.5	1.00

[1]The heat output values calculated per 1 kg of biofuel

By co-firing biofuel with propane the total heat output during the burnout of LHR granules can be increased by 10 % in comparison with the self-sustaining biofuel burnout of biofuel samples that mostly can be related to more complete combustion of the volatiles. For such conditions the total heat output slightly exceeds the value of heat, fixed during the burnout of softwood granules. For the conditions of self-sustaining LHR combustion the total heat output slightly reduces and is lower than that for the self-sustaining burnout of the softwood samples (Table 4).

Conclusions

1. The wheat straw non-hydrolyzed residue after enzymatic hydrolysis is a prospective raw material for granulated biofuel production.
2. The wheat straw LHR contains relatively high ash concentration and relatively high concentration of nitrogen and total sulphur in comparison with native wheat straw and especially with softwood. The higher carbon content in LHRs provides higher heating values of residues then that for native wheat straw but some lower in comparison with extremely low ash containing softwood.
3. The ash content in LHR depends on the ash content in native wheat straw, so the dispersion of LHR fuel parameters can be expected for industrial scale residues.
4. Because of enhanced LHR plasticity in comparison with softwood sawdust, lower energy consumption for LHR granulation and higher productivity have been observed.
5. In comparison with softwood granules the LHR granules indicate lower additional heat energy supply and lower temperature to initiate the thermal degradation of biofuel samples, promoting faster ignition of the volatiles. Burnout of LHRs granules produces higher levels of NO_x in the combustion products. Additional measures should be undertaken to decrease NO_x emission up to the level of softwood granules.
6. Co-firing with propane significantly decreases the total amount of CO emission during the burnout of LHR samples. By co-firing LHR granules with propane flame flow the total heat output from the burnout of LHRs samples can be increased by 10 % in comparison with the self-sustaining process of the biofuel burnout that mostly refers to more complete combustion of the volatiles.

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