

Evaluation of properties of biomass used for energy purposes.

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Introduction

The need to counteract climate changes necessitates undertaking measures aimed at reducing emissions of greenhouse gases [1]. Poland by accepting Kyoto Protocol stipulations has committed itself to reduce emissions of greenhouse gases. One of the solutions (to reduce emissions) is the substitution of renewable energy sources, among others plant biomass, for fossil fuels. The level biomass utilisation depends on the resources available and on the processing technology.

The energy sector uses most often the wood biomass in a form of chips, sawdust, pellets and briquettes. Also are burnt bark, straw as well as energy crop plants, such as energy willow, *Miscanthus giganteus*, Virginia mallow (*sida hermaphrodita*), Jerusalem artichoke (topinambour). Executive Order of Minister of Economy from 14th August 2008 [2] with later amendments from 23 February 2010 [3], imposes the obligation to introduce in the total amount of biomass co-combusted with conventional fuels of the strictly defined share of biomass coming from energy crops, or wastes and residues from agri production and wood processing industry and industry further processing wood products, as well as part of the remaining wastes which undergo biodegradation and grains of cereals which do not conform to the quality requirements for cereals in the intervention purchases, and cereals that are not subject to the market intervention purchases. The wastes from forestry production and from industries processing the forestry products do not fall into this category. The draft of the Executive Order of the Minister of Economy from 17.02.2011 [4], the share of biomass outside of forestry and forestry processing products has been envisaged at 20% in 2011 and 50% (!) in 2020.

As a result of the obligation to increase in a biomass co-firing process ever increasing share of biomass from outside of forestry and because of lack of possibility to fulfil these needs from one or several sources only, the number of the new types of biomass burnt or co-fired in the energy sector has been on the rise. This biomass coming also from foreign countries exhibits diversified physical and chemical properties. Great variety of biomass offered by the suppliers requires a thorough examination of its properties and its impact on the process and installations when used in energy sector. The constant control of the biomass quality properties is then expedient. At the Institute for Chemical Processing of Coal the research of chemical and physical characteristics of different types of biomass used in Poland's power sector has been carried on for many years by using our own research procedures.

Physical and chemical properties of biomass

The biomass physical and chemical properties differ from those of bituminous coal most often burnt in utility boilers (Tab.1).

The differences are exhibited in:

- basic parameters characterising fuel's suitability for energy purposes such as: LCV-Lower Calorific Value, moisture content, ash content and total carbon content
- content of chlorine, total sulphur and nitrogen, which exhibit negative impact on the environment as well as on the installations being used for combustion of fuels
- chemical composition of ashes, especially content of silicone, calcium, phosphorus and potassium
- characteristic ash fusion and melting temperatures.

Table 1

Properties of coals and different types of biomass

Parameter	Bituminous coal	Lignite	Wood biomass	Agro biomass
W_t^r , %	3.2 - 19.1	10.9 - 54.6	4.9 - 68.5	6.1 - 82.2
A^d , %	3.5 - 27.9	7.8 - 20.3	0.3 - 6.9	0.5 - 44.4
S_t^d , %	0.32 - 1.17	0.69 - 1.10	< 0.02 - 0.08	0.03 - 0.67
Q_t^r , MJ/kg	21.1 - 27.7	7.8 - 18.4	4.4 - 18.4	1.1 - 24.5
Cl^d , %	0.020 - 0.159	< 0.005 - 0.029	< 0.005 - 0.057	< 0.005 - 1.168
C_t^d , %	49.7 - 78.4	41.7 - 56.8	45.2 - 51.7	27.2 - 59.1
N^d , %	0.54 - 1.51	0.31 - 0.98	0.12 - 0.92	0.16 - 6.45

W_t^r – total moisture content (in a as received state), A^d – as content (in a dry state), S_t^d – total sulphur content (in a dry state), Q_t^r – LCV-lower calorific value (in a as received state), Cl^d – chlorine content (in a dry state), C_t^d – total carbon content (in a dry state), N^d – nitrogen content (in a dry state)

In the power sector the share of „agro” biomass burnt or co-fired has been systematically on the rise. The variability of its chemical and physical properties can cause problems in proper operation of energy equipment. Table 2 presents values of the basic quality parameters of the exemplary types of biomass coming from: energy crops, from agricultural processes being analysed at the IChPW's Laboratory of Fuels and Activated Carbons [5].

Table 2

Basic parameters describing fuels suitability for energy purposes

Type of biomass	Parameter			
	W_t^r , %	Q_t^r , MJ/kg	A^d , %	C_t^d , %
Energy willow	4.5 - 52.9	7.0 - 19.2	0.3 - 10.8	49.0 - 53.8
Virginia mallow (<i>sida hermaphrodita</i>)	6.9 - 13.6	14.5 - 16.1	2.2 - 4.5	47.8 - 49.9
<i>Miscanthus giganteus</i>	7.7 - 31.0	11.1 - 16.1	1.6 - 5.1	47.4 - 49.9
Sorgo	12.0 - 81.6	1.1 - 10.9	6.6 - 44.4	27.2 - 46.7
Oil palm	2.5 - 17.7	14.9 - 24.5	1.2 - 6.5	48.6 - 59.1
corn – flasks	9.1 - 45.5	6.9 - 17.0	1.9 - 21.2	40.5 - 49.5
Rapeseed straw	10.1 - 17.3	13.0 - 15.4	4.0 - 10.2	46.0 - 49.6
Sunflower husks	6.0 - 41.0	10.0 - 19.3	2.6 - 11.2	50.7 - 53.8
Dried fruit	12.2 - 82.2	1.6 - 16.4	0.9 - 4.4	50.4 - 54.2
Olives pomace (residues from olives pressing)	5.1 - 53.8	8.5 - 17.4	3.2 - 12.4	49.1 - 52.1
Sugar beet pulp	9.9 - 11.9	13.4 - 15.0	3.7 - 9.5	44.9
Cocoa shells	7.6 - 12.3	14.9 - 18.4	1.7 - 10.1	47.3 - 54.5
Coconut shells	9.0 - 20.5	16.0 - 16.9	0.5 - 2.5	53.0 - 53.9
Cashew nut	6.1	21.7	2.8	58.7

W_t^r –total moisture content (in a as received state), Q_t^r – LCV-lower calorific value (in a as received state), A^d – ash content (in a dry state), C_t^d – total carbon content (in a dry state)

Table 3

Biomass constituents with detrimental effect on the environment and on technological installations

Type of biomass	Constituent		
	Cl ^d , %	S _t ^d , %	N ^d , %
Energy willow	<0.005 - 0.148	<0.02 - 0.32	0.16 - 2.27
Virginia mallow (sida hermaphrodita)	0.019 - 0.166	0.03 - 0.08	0.24 - 0.64
Miscanthus giganteus	0.030 - 0.363	0.04 - 0.12	0.22 - 0.79
Sorgo	<0.005 - 0.380	0.06 - 0.21	0.54 - 1.43
Oil palm	<0.005 - 0.220	0.02 - 0.26	0.39 - 2.82
corn – flasks	0.045 - 0.352	0.04 - 0.19	0.51 - 1.70
Rapeseed straw	0.295 - 0.713	0.14 - 0.35	0.32 - 2.73
Sunflower husks	0.048 - 0.215	0.10 - 0.59	0.15 - 6.45
Dried fruit	0.029 - 0.227	0.03 - 0.25	0.56 - 2.63
Olives pomace (residues from olives pressing)	0.174 - 1.168	0.08 - 0.17	1.33 - 1.87
Sugar beet pulp	<0.005 - 0.328	0.08 - 0.42	-
Cocoa shells	<0.005 - 0.130	0.03 - 0.19	0.44 - 2.31
Coconut shells	0.038 - 0.102	<0.02 - 0.06	0.46
Cashew nut	<0.005	0.11	1.24

Cl^d – chlorine content (in a dry state), S_t^d – total sulphur content (in a dry state), N^d – nitrogen content (in a dry state)

Lower Calorific Value, LCV

LCV is a basic parameter to evaluate fuels. It depends to a great extent on total moisture content. For the given fuel with ash and combustible elements constant content its LCV decreases with the rise of total moisture content (for example for biomass – Fig. 1).

Based on research conducted at IChPW it was established that LCV of wood biomass is lower than that of „agro” biomass with comparable total moisture contents. The biggest LCV figures exhibited samples of cashew (above 21 MJ/kg).

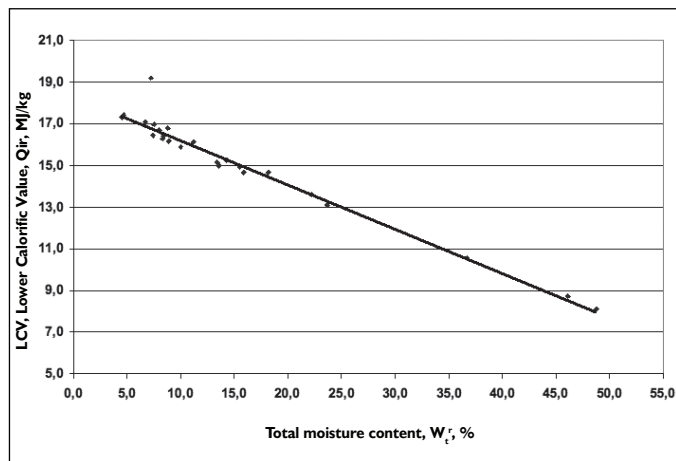


Fig 1. LCV of biomass versus it moisture content

Total moisture content

Moisture content of biomass has been a significant problem in combustion and co-combustion processes. Solid raw biomass exhibit high figures of total moisture content. Moisture in biomass reduces its LCV since portion of the heat generated is being lost for heating and then evaporation of moisture. Increase of moisture as a rule reduces capacities of the individual pieces of equipment; as an example can be biomass crushing where high moisture content leads to deterioration of dynamics of the hard coal pulverisers [6]. Moisture content depends among others on:

- part of the plant from which biomass is derived (e.g. bark, trunk, stems, leaves, bulbs, seeds, fruits)
- period of harvesting (higher moisture content exhibits biomass harvested in spring and summer, but lower moisture has the biomass harvested in autumn and winter)
- conditions of transport and storage.

In order to reduce moisture content and to increase its heating value the biomass is subjected to pelletisation or briquetting. These processes improve also the biomass heterogeneity and bulk density [7].

Dry biomass accelerates and stabilises lighting up (ignition), wet on the other hand shifts the flame nucleus to upper part of the combustion chamber. This influences the heat transfer in both combustion chamber and in convection pass of a boiler [6].

Content of chlorine, sulphur and nitrogen

Chlorine, sulphur and nitrogen are undesirable constituents of fuel because of their negative impact on the environment. In addition both chlorine and sulphur induce corrosion of technological equipment used in combustion processes [6, 8, 9]. Table 3 presents contents of chlorine, total sulphur and nitrogen in the selected types of biomass.

Chlorine content in wood biomass amounts from below 0.005% to 0.057%, total sulphur content from below 0.02% to 0.08%, nitrogen content from 0.12% to 0.92%.

In case of energy crops the content of chlorine can even reach 1.0%, sulphur up to 0.67%, and nitrogen to 6.45%. These figures are higher than those for hard coal. High concentration of chlorine in case of energy crops can be attributed among others to the application of the potassium based fertiliser which most often is the potassium

chloride (KCl). Substitution of potassium sulphate (K₂SO₄) for potassium chloride can lead to almost fivefold reduction of chlorine in the cultivated biomass. The proof of this is in the results of the research conducted on Virginia mallow (sida hermaphrodita) [1].

Co-firing of some types of biomass (e.g. straw, leaves, bark) can cause an increased risk among others of chloride corrosion of steam re-heaters due to increased concentration of chlorine in the fuel. This corrosion is inevitably connected with fly-ash deposits on boilers piping [6, 10]. Type of deposits, their shape and thickness depend on the fuel's S/Cl ratio. It is approved that at the molar ratio S/Cl > 2.2 the chloride corrosion ceases to be serious (but this condition does not prove itself in all combustion systems).

Applying in processes of combustion and co-firing of biomass with high content of nitrogen (such as sunflower husks) will have the effect of increased emissions of NO_x to atmosphere.

Ash and its chemical composition

Ash content (higher) has negative impact on energy (calorific) value of the fuel and on the process of combustion. The ash content depends on type of biomass and as a rule is equal to : for wood biomass from 0.3% to 10%, for „agro” biomass is higher and amounts to from 1.3% to 16.3%. The highest ash contents from biomass presented in table 2 exhibited sorgo (up to about 44%) and corn flask (up to about 21%).

Low ash content in samples of wood biomass is a factor that leads to reduced flyash emissions. In combustion and co-firing processes of biomass not only ash content is vital but the chemical composition of ash as well (Tab. 4).

Ash composition of „agro” biomass

Table 4

Constituent	Energy willow	Miscanthus giganteus	Sorgo	Sunflower husks	Corn chips	Dried fruit	cashew	Virginia mallow (sida hermaphrodita)	Straw briquettes
Ash chemical composition , %									
SiO ₂	12.51	56.14	45.79	17.49	32.65	16.81	16.53	2.37	32.99
Al ₂ O ₃	1.71	1.14	2.27	3.99	0.62	2.74	1.96	<0.01	2.78
Fe ₂ O ₃	0.27	0.96	0.88	1.39	0.67	3.57	2.40	0.42	0.74
CaO	31.46	11.03	11.09	13.17	8.04	11.93	6.04	48.74	2.70
MgO	6.89	2.78	2.52	3.58	2.29	2.59	3.27	2.40	3.78
P ₂ O ₅	12.65	3.45	6.62	8.79	14.64	13.17	16.89	4.36	7.97
SO ₃	6.06	3.50	2.20	3.02	0.62	5.64	2.24	2.80	7.64
Mn ₃ O ₄	0.72	0.23	0.06	0.10	0.14	0.12	0.30	0.09	0.27
TiO ₂	0.02	0.08	0.15	<0.01	0.06	0.23	0.18	0.04	0.08
SrO	0.07	0.02	0.02	0.03	0.02	0.06	0.03	0.09	0.03
Na ₂ O	0.29	0.51	0.61	0.26	0.21	1.01	1.57	0.34	0.67
K ₂ O	23.87	18.17	19.26	38.11	28.65	21.22	35.35	19.52	19.90
Characterisitic ash melting temperatures, °c									
Oxidising atmosphere (air)									
t _s	770	730	700	730	700	930	-	760	730
t _A	1180	790	920	890	840	1210	1130	1420	890
t _B	1450	1060	1140	-	1090	1420	1210	1450	1120
t _C	1550	1130	1230	-	1230	1490	1260	1480	1160
Semi reducing atmosphere (CO/CO₂ mixture in volume ratio of 3/2)									
t _s	730	730	790	660	720	730	-	740	690
t _A	790	840	920	890	950	1150	970	800	860
t _B	1540	1100	1150	-	1170	1250	1230	1540	1020
t _C	1540	1370	1250	-	1200	1360	1270	1550	1170

t_s – sintering temperature, t_A – softening temperature, t_B – melting temperature, t_C – ash flow temperature

The ashes from biomass used for energy production contain high amounts of calcium, potassium, and phosphorus. This derives mainly from the structure of biomass itself, type of soil where it is cultivated and types of fertilisers used during its growing. Behaviour of the mineral substance during biomass combustion is influenced by the presence of alkaline metals such as Na, K, Ca and chlorine and sulphur. Sodium and potassium evaporate at high temperatures of combustion, and in higher parts of boiler react with other constituents of the flue gases and create low melting compounds that foul steam reheating surfaces. This process differs slightly in a fluidised bed. Creation of deposits (boiler fouling) in presence of sulphates, especially of chlorine compounds significantly increases high temperature corrosion.

In the combustion processes the important fuel evaluation criteria comprise also indices characterising ash behaviour in high temperatures. This applies among others to characteristic ash melting/fusion. They depend on chemical composition of ash and on atmosphere in which the indicator is being established. It is worth noting that ash fusion temperatures established in laboratory conditions do not take into account boiler construction and operating conditions. Phenome-

non of ash fusion/melting runs differently in case when tested samples are exposed for the definite time period to constant temperature (e.g. maintaining of sample in a thermal equilibrium for one hour).

The ash fusion temperatures established in this way are lower [6].

Most types of „agro” biomass when compared with hard coal and wood biomass [10] exhibit lower ash softening (t_A) and melting temperatures (t_B) both in the oxidising and semi reducing atmosphere. Energy willow and Virginia mallow are the exemption from this rule since they exhibit higher ash melting temperature, in both atmospheres (> 1400°C) and dried fruit for which this temperature is higher only in the oxidising atmosphere.

Summary

Taking into account legislation requirements imposing systematic increase of „agro” biomass in total biomass being burnt one should pay special attention for its proper selection based on both quality and quantity.

Based on the results presented it has been established that basic differences between fossil fuels and biomass are as follows:

- higher moisture content in raw biomass which has negative impact on combustion process and increases costs of transport
- lower than for fossil fuels calorific value,
- comparative qualitative chemical composition (similar ultimate analyses) but
- differing contents of individual elements.

A significant improvement of biomass utility from energy crops can be reached by its pelletisation. This applies first of all to its homogeneity, reduction of moisture content and at the same time increase of its LCV and bulk density.

Due to introduction to co-firing processes of new types of biomass containing significantly higher amounts of chlorine, nitrogen and total sulphur than the wood biomass , it is necessary to systematically control the contents of these elements.

Reliable identification of combustion and co-firing processes, establishing chemical composition of ashes from the combustion of biomass and establishing of its characteristic fusion/melting temperatures will make the safe operation of boilers possible.

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odnawialnych źródłach energii oraz obowiązku potwierdzenia danych dotyczących ilości energii elektrycznej wytworzonej w odnawialnym źródle energii.

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Translation into English by the Author

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Events IYC'2011

June 2011

Eröffnungsveranstaltung - opening ceremony at ETH Zurich and University of Zurich, Switzerland - Jun 01, 2011

- Calatrava Library, Rämistrasse 74, Zurich, Switzerland

The Combined XII Spring Meeting of the Division of Synthetic Chemistry and XXXIII Finnish NMR Symposium

Synthetic Chemistry and NMR Symposium - Jun 07 - Jun 10, 2011 - Spa Hotel Rantasipi Laajavuori, Jyväskylä, Finland

Clusters: Physics and Chemistry in a Finite World Nottingham Chemistry Public Lecture Series - Jun 09, 2011

- Lecture Theatre XI, School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

75th Prague Meeting on Macromolecules Conducting Polymers - Jun 10 - Jun 14, 2011 - Prague, Czech Republic

Conferences “grand public” during the Week of Chemistry in Fribourg - Jun 14 - Jun 18, 2011 - Chemin du Musee 9, 1700 Fribourg, Switzerland

Chemspec Events - the fine and specialty chemicals connection - Jun 15 - Jun 16, 2011 - Hall I, PALEXPO, Geneva, Switzerland

Tag der Chemie, Universität Zürich and ETH Zürich, Switzerland - Jun 18, 2011 - ETH Hönggerberg und Universität Zürich-Irchel

4th International IUPAC Symposium for Trace Elements in Food (TEF-4) Trace Elements in Food - Jun 19 - Jun 22, 2011 - King's College, University of Aberdeen, Aberdeen AB24 3FX, Scotland, United Kingdom

Symposium of the Commission on the History of Modern Chemistry Renewing the Heritage of Chemistry in the 21st Century - Jun 21 - Jun 24, 2011 - ESPCI ParisTech, Paris, France

Joint 15th Annual Green Chemistry & Engineering Conference / 5th International Conference on Green and Sustainable Chemistry Green and Sustainable Chemistry and Green Engineering - Jun 21 - Jun 23, 2011 - Capital Hilton Hotel, Washington, DC USA

Schiff-Fahrt-Diskussion, Universität Zürich and ETH Zürich - Jun 23, 2011 - Zürichsee, Switzerland