CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Tropical AgriSciences

Department of Sustainable Technologies

Czech University of Life Sciences Prague
Faculty of Tropical AgriSciences

Quality evaluation of solid biofuels based on rice straw waste biomass

Master's thesis

Prague 2016

Supervisor:

Ing. Tatiana Ivanova, Ph.D

Consultant:

Prof. Ing. Bohumil Havrland CSc

Author:

Bc. Monika Špunarová

Declaration

I hereby declare that I have composed the present diploma thesis entitled Quality evaluation of solid biofuels based on rice straw waste biomass by myself and all the used sources have been properly quoted and acknowledged by means of complete references.

Prague, 25 April 2015

....

Monika Špunarová

Acknowledgement

I would like to thank everyone who helped me and supported me during the composition of this thesis as well as throughout the whole MSc studies. First and foremost, my thanks belongs to my supervisor Ing. Tatiana Ivanova, Ph.D. for her inestimable help, guidance, kindness and patience and to my consultant Prof. Ing. Bohumil Havrland CSc.

Equal thanks belongs to Alexandru Muntean, MSc. for helping me with the pelletizing of the material, and to prof. Ing. Milan Brožek, CSc. for providing the grinder. I would like to express my appreciation to Bc. Magdaléna Stavjarská and Bc. Christina Vlachosová for cooperation on the research.

I would also like to express my gratitude to all the people who have given me the opportunity to work on my research and have helped me during the research at the Research Institute of Agricultural Engineering. Special thanks goes to Ing. Petr Hutla, CSc and to Ing. Michel Kolaříková.

A thank you also goes to my dear friends Ing. Veronika Chaloupková for her time and vital advice, to Bc. Karolína Tomšová and Bc. Tomáš Starý for grammar corrections, and to Ing. Socheat Keo without whose help and provision of rice straw the thesis could not have been composed.

Last, but not least, I am grateful to Mgr. Jan Hurda for his never-ending support, to my dearest family and friends for their encouragement throughout the whole MSc studies at CULS. Thank you all.

The research was supported by Internal Grant Agency (IGA) of the Faculty of Tropical AgriSciences at Czech University of Life Sciences Prague (grant number 20165012).

Abstract

Biomass from plants, specifically agricultural waste and residues, can serve as a promising energy alternative to fossil fuels. It is an environmentally friendly and renewable source of energy even for solid biofuel production. Nowadays, there are huge amounts of produced agricultural biomass residues, particularly rice straw, which are not properly utilized and processed. This thesis demonstrated a possible way of processing rice straw and tested the appropriateness of the densification method in terms of pelletizing that transform these abandoned bio-wastes into pellets, products with a higher energy value. Generally, densification increases the bulk density of original biomass material which leads to the production of solid fuels uniform in size and shape. It brings with it the advantages of cheaper transportation and storage, as well as easier and more efficient handling. Rice straw material obtained from Cambodia was grinded and subsequently pelleted. The main mechanical, physical and chemical properties (moisture content, calorific value, mechanical durability, amount of heavy metals, C-H-N analyse, volatile matter, ash content and ash melting behaviour) were determined. Since rice straw exhibited a large production of ash during combustion, special emphasis was put on understanding the role of ash melting behaviour. This is because during the combustion of straw occurs ash sintering which can result in the damaging of the heating facilities. This negative aspect can be overcome by the addition of additives based on calcium. The additives containing calcium may be effective for certain biomass material but ineffective, or even with the opposite effect, for other types of biomass material. The effectiveness is also dependent on other conditions. Based on the research, additives of calcium hydroxide and calcium carbonate were mixed with rice straw. Generally, the pellet samples with the addition of calcium carbonate showed a better ability to abate the sintering of the rice straw ash. Thus, the present investigation was carried out in order to research the potential abatement of ash melting behaviour by using calcium carbonate additives in different ratios. The pellet's quality was evaluated by comparing their properties with the current EN and ISO technical standards and findings of other authors of scientific papers.

Key words: ash melting behaviour, calcium additive, rice straw, pellets, pressing process, standards

Table of contents

List of tables

List of figures

List of abbreviations

AC	Ash content
BEC	Biomass Energy Centre
CULS	Czech University of Life Sciences Prague
FAO	Food and Agriculture Organisation
FE	Faculty of Engineering
FTA	Faculty of Tropical AgriSciences
GHG	Greenhouse gas
IEA	International Energy Agency
IMC	Initial moisture content
MC	Moisture content
NRDC	Natural Resources Defense Council
Q_{gross}	Gross calorific value
Q_{net}	Net calorific value
RC	Rice straw
RES	Renewable Energy Resources
RIAE	Research Institute of Agricultural Engineering

1. Introduction

The current energy consumption is growing. Increasing population requires more and more energy sources and desires to improve the quality of life, economic and industrial expansion (Moskalík et al., 2008; Hiloidhari et al., 2014). This trend brings with it serious problems related to energy sector because the conventional fuels reserves have already become limited and their negative environmental impact has been leading world to search for other sources than fossil fuels (Fernández et al., 2012; Hiloidhari et al., 2014).

Thus, the population interest is focusing on renewable and sustainable energy sources which are still more required. Potentially, biomass seems to be effective and widespread resource of energy (Moskalík et al., 2008). The above mentioned declining reserves of fossil fuels and their fluctuating prices also give importance to biomass sources because it is an attractive alternative to replace or complement petroleum derivate as a fuel (Fernández et al., 2012; Said et al., 2013). The agriculture residue has become a source of fuel since the early 1970s (Lim et al., 2012). Nevertheless, due to the drop in oil prices in middle of 1980s, agriculture biomass source has lost its economic competitiveness to fossil fuels (Lim et al., 2012). Moreover, now Chen et al. (2009) marked biomass as the third largest primary energy in the world (of course after fossil fuels).

According to the above mentioned reasons, there is a growing interest in bioenergy as well as biofuels made from different biomass materials including energy crops or agricultural wastes as a perspective, alternative, sustainable and renewable energy (Tumuluru *et al.*, 2010).

One of the possibilities of processing biomass is by pressure - using densification. The densification of biomass into durable solid biofuels in the form of pellets or briquettes is an effective solution which improves properties of raw materials by increasing quality of final product (Kaliyan, 2008; Kaliyan and More, 2009; Tumuluru *et al*., 2010). According to Hutla and Jevič (2011) solid biofuels made of plant biomass will soon become increasingly important.

The emphasis of the present thesis was put on pellets because of their consistent quality and high burning efficiency (in comparison to other forms of biomass fuels); and the pellet's market has been grown considerably which gives pellets significant value (IEA, 2015). Therefore, pellets are the ideal possibility for sustainable solutions of energy supply of private homes and sometimes big plants. In addition, their further advantage is the fact that they can be made from different kind of biomass agricultural waste.

The rice grain is one of the world's most important food commodities and its production is the major component of agricultural residues (Missagia, 2011; Zhang et al., 2015). The rice straw is considered as the most abundant agriculture residue with great energy potential, which is one of the forms (biological) of renewable energy. It is easily obtainable biomass material due to the fact that it represents a major by-product through world, with annual production about 731 million tons (Said et al., 2015; Zhang et al., 2015). The worldwide biggest producers are in Asia where it is 90% of the total global rice output (Lim et al., 2012; Faostat, 2015).

The present thesis aims at two areas: first, to testing of a densified rice straw in the form of fuel pellets and determining its main physical, mechanical as well as chemical properties. The quality of pellets depends on two general factors: feeding material itself related to its chemical composition and operative variables of the pelletization process including physical and mechanical properties (Garcia-Maraver and Pérez-Jiménez, 2015). Disadvantage of straw pellets is generally high ash content 3-7% (Bejlek and Sladký, 2012) and also it shows poor combustion properties with regard to low melting point (Ewida et al., 2006; Bejlek and Sladký, 2012) and associated sintering. These phenomena bring with it a number of operational problems of fuel boilers (Moskalík et al., 2008). Thus, the second aim of the thesis is to improve the ash melting behaviour of rice straw pellets by addition of calcium additive. Therefore, Wang et al. (2012) state that by using the additives together with agricultural residues could be competitive for energy production in the future.

2. Literature review

2.1 Rice and rice straw

The rice is marked as one of the most popular plants in recent years. It is possible to find it through different regions of the world (see Figure 1). As demonstrate Figure 2, it is widespread especially in Asia where it created 90% of the total global rice production. This commodity is extensively consumed staple food. Thus, it is one of the world's most important food crops and their production is the major component of agricultural residues (Missagia, 2011; Zhang et al., 2015).

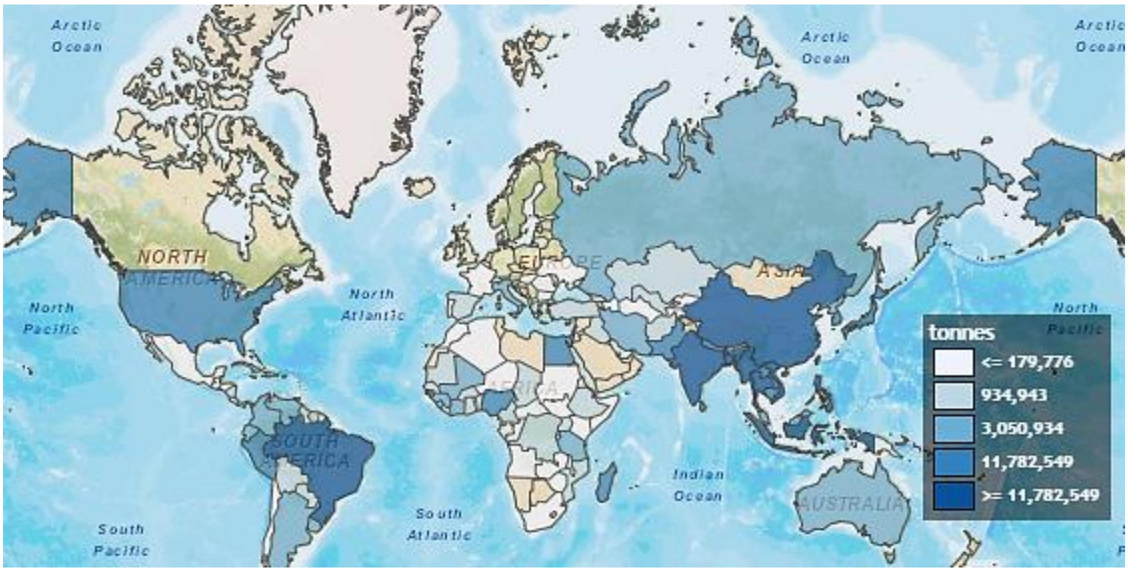

Figure 1 Production quantities of rice (paddy) in the world

Source: Faostat, 2015

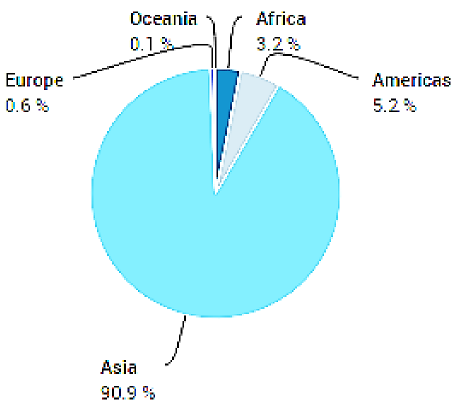

Figure 2 Production of rice, paddy – share by region in average 1993 – 2013

Source: Faostat, 2015

The rice straw annual production is about 731 million tons (Said et al., 2015; Zhang et al., 2015) and distribution through the world is showed in Table 1 below. For comparison, in 2012 the annual global quantity of rice straw was 685 million tons and rice husk 137 million tons (Lim et al., 2012).

Table 1 Distribution of produced rice straw and rice paddy in the world

distribution	Africa	Asia	Europe	America	Oceania
million tons of straw[1]	20.9	667.6	3.9	37.2	1.7
rice, paddy - area harvested (ha)[2]	10,931,051	146,462,731	648,320	6,562,328	117,233

Source: Demirbas et al., 2011[1]; Faostat, 2013[2]

Rice is botanically known as *Oryza* (Khush, 1997). It is seasonal crop, the production is standardly steady (Prasertsan and Sajjakulnukit, 2006). Morphology of rice plant is presented in Figure 3. The genus *Oryza* consists of two cultivated species originated from Asia and Africa (*Oryza sativa* and *Oryza glaberrism*) and 21 wild species (Khush, 1997):

- *Oryza sativa* – is characterized by superior yield and milling quality properties, commercially grown around 112 states throughout all continents (Khush, 1997)
- *Oryza glaberrism* – grows in the West Africa region, although it is categorized as a semiaquatic plant, the cultivated rice species can grow in dry land or in deep water of up to 5 m (Chang, 1985 in Lim et al., 2012)

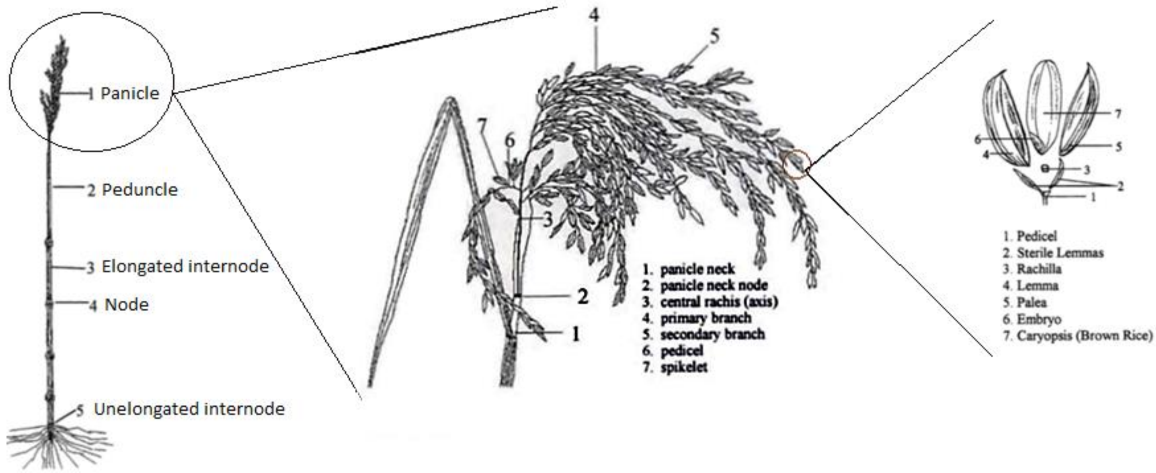

Figure 3 Morphology of rice: mature culm (left), parts of panicle (middle) and structure of a rice grain (right)

Source: Moldenhauer and Gibbons, 2003

2.1.1 Rice residuals

The required product of *Oryza sativa* is grain, the rest of the grass is agricultural by-product (straw and husk). The advantage of rice straw is that as by-product it does not threaten food supply. It is part of the plant - stalk (after the grain and chaff have been removed) (Said et al., 2015). The husk is the outer layer of rice, which accounts for about 20% - 33% of paddy weight and it is generated during the milling process. Thus, it could order to meet the countries' energy demands if residues will be used (Lim et al., 2012). Currently, it is widely used in stall mats, fillers, and compost but due to increasing demands for finding bioenergy source, researchers are actively involved in researching new ways how to use it as fuel (Yoon et al., 2012).

Lal (2005) argues that crops residuals are "*the non-edible plant parts that are left in the field after harvest*". The rice straw is considered as the most important agriculture residue with great energy potential. It is easily obtaining biomass material because represents a major by-product through world (Said et al., 2015).

In general, biomass residues are considered as agricultural waste. The residues can be divided into two categories namely the crop residues (plant residues after the collection of crops) and the agro-industrial residues (by-products of the post-harvest processes) (Tripathy et at. in Lim et al., 2012).

How to estimate quantity of rice straw?

- Straw-to-Grain Ratio (SGR) (useful while estimating the energy potential of rice straw) (Gadde et al., 2009)
- Residue-to-Product Ratio (RPR) (Gadde et al., 2009)

Rice straw has potential as a source of energy but is rather limited as compared to the use of rice husk (Lim et al., 2012; Yoon et al., 2012). Disadvantage of straw is logistic aspects of collecting or handling which leads to assess the economics point of view.

2.1.2 Composition of rice straw

The rice straw is mainly composed of hemicelluloses, cellulose (abundant source of carbon in biomass) and lignin[1] (grass lignin) as it is also shown in Table 2 below. To activate the natural binders are necessary moisture and temperature to create durable particle–particle bonding through softening (Liu et al., 2014). Lignin is an organic substance, which connects cells of plants and through the process of pelletization (pressure and temperature from 75 to 120 °C) binds raw material into form of pellets like nature glue. Lignin conducts water in plant stems and it is hydrophobic that helps to improve storage behaviour. In addition, it is good fuel even better then cellulose and allows pelletization without additional binders (Tumuluru et al., 2011b). There was also found another difference between stalk and husk i.e. standardly husk has lower content of alkali compounds and expose high melting points (Werther et al., 2000). The rice straw exhibits also a high content of ash, as it can be also seen in Table 2, it can reach up to ¼ of total composition amount. In generally, straw materials are shown to have a certain percentage of protein[2] content which can promote binding important for densification. During the process is leading to formation of new bonds with other available proteins, starches and lipids. Others

[1] According to Buranov and Mazza (2008) rice straw lignin is also called p-hydroxyphenyl–guaiacyl–syringyl (H–G–S) lignin and content of it is significantly higher than that of corn and wheat straw.

[2] *Raw protein improves the physical quality of the pellets compared to denatured proteins* (Tumuluru, 2011b).

components of straw are lipid or fat (lubricant during the pelletization) (Tumuluru 2011b).

Table 2 Composition of rice straw

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Extractive matter
Rice straw[1]	41–57	33	8–19	8–38	–
Rice straw[2]	35.7	32.0	22.3	18.67	24.4
Rice straw[3]	30–38.9	24–29.8	5.6–7.4	–	–
Rice straw[4]	41.30	18.21	18.11	11.99	–
Rice husk[2]	28.6	28.6	24.4	20.27	18.4

Source: Liu et al., 2014[1]; Jenkins et al. (1998) in Lim et al. (2012); Zhang et al., 2015[3]; Niu et al., 2016b[4]

2.2 Need of processing solution for rice straw residues

The rice residues are largely and abundantly unused agricultural waste (Islam and Ahiduzzaman, 2012).

The problem is that substantial amount of residuals is left on the field (Gadde et al., 2009). And in terms of seasonal by-product it is more than desired to use and processed it to usable form. The processed straw also facilitates storage for off-season utilization (Said et al., 2015) for example in form of solid biofuels. Silalertruksa and Gheewala (2013) described the rice straw in meaning that can could be also considered as a substitution of the grid electricity, LPG, gasoline and chemical fertilizer.

On the other hand the solid waste from rice straw has seldom been investigated (Chou et al., 2009a). Mostly the rice straw is abandoned on the field or burned there - that is the most common method of residue’s disposal (Said et al., 2015; Chou et al., 2009a). The process called open-field burning is connected with releasing of CH_4 and N_2O as GHGs (Gadde et al., 2009). Sometimes during the rainy season abandoned rice straw in the field may flow into the drainage. This causes an obstruction in the drainage system. Therefore by these obstructions is provided the place for propagation of the bacteria (Chou et al., 2009b).

Other way is ploughing which is related with problems like a reduction in yields due to binding of nitrogen from the soil on microorganisms decomposing straw, decrease seed germination (seed insufficient contact with the soil), the development of plant diseases and pests, including rodents or in acidic soils formed mould (Bejlek and Sladký, 2012). According to Matsumura et al. (2005) benefits come when the rice straw is ploughed during autumn and winter, allowing sufficient time for decomposition before the spring planting (in Japan location).

2.2.1 Post-harvesting utilization of rice residuals in different countries

Thailand

Lim et al. (2012) say that 90% of the rice straw collected during the peak harvesting season in Thailand is burned in the open fields. For other example and compering see below the case from Gadde et al. (2009), who claim that during the year is:

- 48% rice straw is burnt in the field
- about 30% is unused
- 15% is used as animal feed
- 5% is used as fertilizer
- 1.5% is traded (sold)
- 0.18% is used as fuel
- 0.27% not specified

Japan

Another case comes from Japan where about 9 million tons of rice straw is generated annually and it is also main agricultural residues there (New Energy Foundation, 2011, Matsumura et al., 2005). However, 70% of rice straw is stayed in paddy fields and it is left naturally degrades into the soil. There is no use of rice straw open burning because it was banned (Ishii and Furuichi, 2014). The problem also is that according to Matsumura et al. (2005) due to the high cost of collecting straw for animal feed use, farmers can actually import rice straw more cheap. As it was mentioned above, degradation on the field leads to some problems like as decreasing of germination of seeds or development of some kind of diseases.

Philippines

On the other hand the situation in Philippines looks like different way. It was found that about 95% of the rice straw produced is burnt in the field and only 5% of the rice straw is used for other activities like animal feed, mulching material or like a medium to grow mushrooms (Gadde et al., 2009). So it is possible to say that what comes from plant production is not eaten it is generally either broken down by activity of microorganisms but mainly is burned on the field and carbon is returned to the atmosphere as CO_2 – GHGs (BEC, 2011).

Egypt

Like next case could be introduced Egypt where has been estimated about 12.33 million tons of dry biomass produced from bioenergy crop residue sources per year. It is important to say that almost 64% is produced from rice straw. The source like this should represent the highest percentage 44.6% of the total theoretical energy potential in this country. Then it could be follow by municipal solid wastes (Said et al., 2013). Many of Egypt's agriculture wastes are burnt haphazardly and without energy recovery. Rice straw causes the most serious problem with their huge quantities. Therefore, direct open burning in the fields is a dominant choice for disposal and intensifying waste disposal problem and smoke cloud is easily detected during the harvest season (Okasha, 2007; Okasha et al., 2014).

China

China has huge agricultural residue resources, producing more than 630 million tons (Liu et al., 2014; Chen et al., 2009) and according to Zhang et al. (2014) in China is even available the amount about 820 million tons per year. The part of this, of course, is created by rice straw (over then 40% Chinese people using it like the primary food source). Niu et al. (2016b) state that 119.55 Mt of rice straw was produced in 2010.

Nowadays majority of these residues are burnt in situ after harvest that leads to serious environmental issues even precious resources particularly in rural areas (Liu et al., 2014). Thus, lack of forest areas is playing into the hands of non-wood pellets because conversely there is potential of use agricultural residues mentioned before.

Taiwan

In Taiwan, the average agricultural waste - rice straw is generated yearly at amounts from 1.3 to 1.8 million tons. The most of it is either burnt away or also abandoned in the field after the farmers harvest their rice (Chou et al., 2009a; Chou et al., 2009b). According to Estrellan and Iino (2010) burning rice residues there were found to be a significant source of air pollutant. Concentrations of some of them were measured in two Taiwan's areas. The ambient air in the two tested locations were approximately 4 and 17 times higher than those without biomass open burning.

2.2.2 Energy utilization of rice residues

One of the possibilities of energy utilization is densification which is defined according to Werther et al. (2000) "*as compression to remove inter- and intra-particle voids".* The different densification (of biomass) technologies exist, namely: pellet mills, balers, briquette presses, screw presses, and agglomerators (Hoover et al., 2014). Processing of rice straw through densification process is in detail described in chapter 2.3.4 solid biofuels –pellets.

According to Said et al. (2015) rice residues can be converted by techniques, such as direct combustion, gasification, pyrolysis, and anaerobic digestion. Other example is electricity that is generated through direct combustion technology (Gadde et al., 2009). Conversion technologies applicable to rice straw according to Matsumura et al. (2005) are direct combustion heating, direct combustion power generation (both of commercialized), gasification and power generation (gas engine, steam turbine, fuel cell), gasification and methanol production, flash pyrolysis, acid hydrolysis and ethanol fermentation, and co-firing. Okasha et al. (2014) investigated co-combustion of rice straw and natural gas in a novel configuration of fluidized bed. Gadde et al. (2009)

present possibility of using rice for the production of ethanol from grain (a solution to high consumption transportation fossil fuel, but there is big disadvantage because this is somehow competitor to food production and this also influence the price.

Biomass can be transformed to the energy by several processes according to requirements and use of produced fuel. Generally, there are two main types of biomass conversion to energy: thermochemical (combustion, pyrolysis, gasification) and biochemical (fermentation, anaerobic digestion) (McKendry, 2002a).

Another source notes two main techniques for burning rice residues (Ewida et al., 2006):

1 Indirect techniques has disadvantage compare with direct – lower energy conversion efficiency (gasification, liquid fuel production, pyrolysis, anaerobic digestion, thermo-chemical conversion)
2 Direct techniques means burning straw as a solid fuel often with disadvantage ash-related problems (co-firing, standalone)

In general, according to Lim et al. exists two processes of converting rice biomass into the energy:

1 Thermo-chemical process (involves direct utilization as fuel for combustion for heat and electricity generation and converting biomass into other useful forms of energy products)
2 Bio-chemical process (biomass conversion into value-added products include the production of ethanol, hydrogen and methane[3])

The easiest way dividing seems to be according to BEC (2011):

1 Thermal conversion (combustion, gasification, pyrolysis and other not so common conversion processes)
2 Chemical conversion (transesterification)

[3] Accortding to Zhang et al. (2015) the rice straw has a good potential for methane production.

3 Biochemical conversion and using enzymes of bacterias and micro-organisms (anaerobic digestion, fermentation, composting)

According to Silalertruksa and Gheewala (2013) it is possible to distinguish four utilization systems of rice straw, more shows Figure 4:

1 Direct combustion for electricity
2 Biochemical conversion to bio-ethanol and biogas
3 Thermo-chemical conversion to bio-dimethyl ether (DME)
4 Incorporation into the soil as fertilizer

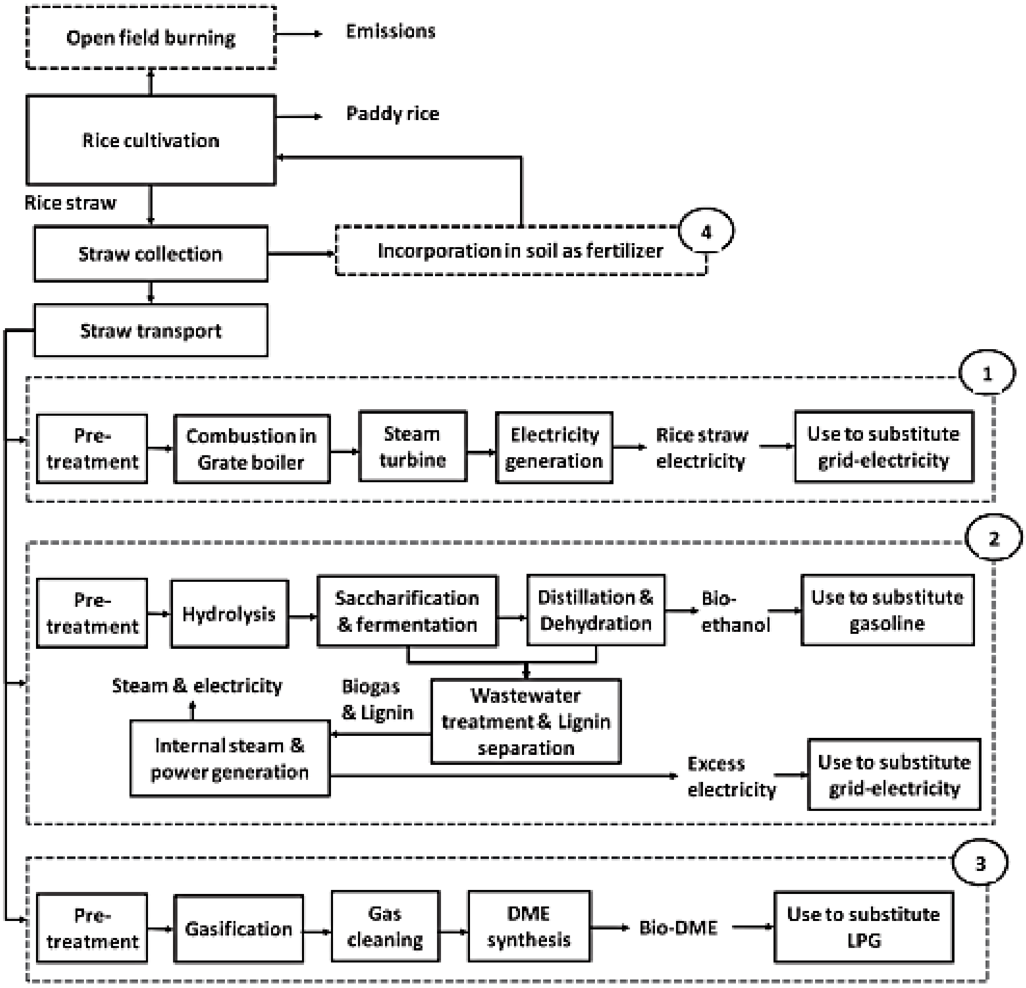

Figure 4 Bio-resources technologies (System boundary of the rice residues utilization systems)

Source: Silalertruksa and Gheewala, 2013

Rice straw from point of non-energy purposes could be use as covering material for fields (mulch), cattle house flooring, animal feed, and rice-straw handicrafts (Matsumura et al., 2005).

2.3 Renewable energy

Energy is crucial to almost every entity in nowadays world. It can also be called as an instrumental for improving our conditions. The access to energy is absolutely essential for us even in ordinary everyday life. We need it, we cannot exist without it. The main question is: Is the supply of energy amply? Is it there enough energy sources to satisfy the demand?

According to Lim et al. (2012) by the year 2030, the global energy demand is predicted to increase by 43.64%, i.e. from the current total of 472 quadrillion Btu (British thermal unit) it will rise by about 206 quadrillion Btu. Thus, the answer could be sustainable energy which transforms lives, planet and changing surrounding bonds. This also leads to the renewable energy like a source for our demand.

According to Said (2013) *"Renewable energy sources are natural resources such as sunlight, wind, biomass, and geothermal heat, which are naturally replenished".* It is possible to divide renewable sources into assorted types like wind energy, solar or biomass, biogas energy, geothermal energy, hydropower and offshore wind, wave and tidal energy (NRDC, 2015).

The utilization of renewable energy sources (RES) helps to contribute to one of Sustainable Development Goals, namely goal number 7: Ensure access to affordable, reliable, sustainable and modern energy for all (UN, 2015). This position puts renewable energy into higher awareness and gives it more importance and attention. Even Secretary-General of United Nation Ban Ki-moon is trying to highlight a sustainable energy to improve efficiency and support extension of using renewable sources (UN, 2015). Anyway, interest in renewable energy resources has increased in recent years (Hoover et al., 2014). The efficient utilization of huge amount of agro-residues is crucial for providing bioenergy (Chen et al., 2009).

2.3.1 Bioenergy

According to International Energy Agency (2015) bioenergy *"is energy derived from the conversion of biomass where biomass may be used directly as fuel, or processed into liquids and gases"*. If it considers biomass and biofuels together, it is called bioenergy. The current amount of bioenergy utilization is 10% of global primary energy supply. The bioenergy provides many advantages such as sustainability, socio-economic solutions to energy challenges or using many raw materials for bio-based fuels (wastes, agricultural and forestry residues, as well as energy crops) (IEA, 2015). The agriculture residue has become a source of fuel since the early 1970s. Thus, it is nothing quite new. Nevertheless, in 1980s, agriculture biomass has lost its economic competitiveness to fossil fuels (Lim et al., 2012).

From political point of view is put emphasis on deploy bioenergy including incentives such as renewable energy certifications, supporting research and development. The reason is clear, it is desired to ensure lower life-cycle greenhouse gas and others emissions, and supporting of some kind of cooperation between fields like agriculture, forestry and rural development. According to World Meteorological Organization (2015) these problematic gases reached yet another new record in atmosphere in 2014. This *"trend"* is continuing a ruthless rise which is leading to make the planet more dangerous and inimical for future generations. Nevertheless, the basic goal is to get environmentally sound, socially acceptable and cost-competitive bioenergy (IEA, 2015). Bioenergy has a high potential for the future because it was estimated that its growth could be about 3% per year on average for heating purpose mainly in OECD Europe (driven by the EU 2020 targets) (IEA, 2015). It makes biomass in Europe acknowledged as a main RES for achieving EU targets. Increasing utilization of RES is a part of energy strategies all over the world, causing higher demand of biomass (Welfle et al., 2014).

2.3.2 Biomass

The term biomass is used in meaning *"biological material derived from living, or recently living organisms, both animal and vegetable"* (Tumuluru et al., 2011a; BEC, 2011). Besides other things it also depends on a context. In context for energy production purposes the term often focus just to plant based material included origin - wood and herbaceous material (BEC, 2011). On the other hand it is possible to come across biomass in term "*biological material derived from living, or recently living organisms"* which means not just plant based materials but also equally materials of animal origin like manure, slurry and many others (BEC, 2011). It is part of the carbon cycle, during combustion is produced carbon dioxide but over a relatively short timescale, carbon dioxide is renewed from atmosphere thanks to new growth of vegetation (Islam and Ahiduzzaman, 2012).

Biomass is the source which includes a large variety of different fuels differing significantly from each other by chemical compositions even combustion characteristics (Said et al., 2013). Yoon et al. (2012) note biomass as *"one of the most important and most widely used renewable energy resources"*. Moreover, Said et al. (2013) marked the biomass as a theoretical potential for supply world's energy needs. According to Leeweonjoon (2012) biomass source is one of the most feasible and economical ways how to enhance the renewable energy production. It becomes an essential renewable energy resource because it has appealing properties besides other things (such as low production cost), it is low greenhouse gas and low acidic gas emissions (Chou et al., 2009b).

At present, still more and more developed countries discovered this type of source that will be appropriate to their purpose. Within near future, many types of biomass will be traded commercially and imported (Leeweonjoon, 2012). With growing population also increase food production which leads to increasing by-products and agricultural residues (Matsumura et al., 2005). Declining reserves and fluctuating prices of fossil fuels also give importance to biomass sources because it is attractive alternative to replace or complement petroleum derivate as a fuel (Fernández et al., 2012).

Biomass has also traditional form of using which refers to burning wood, charcoal, agricultural residues and animal dung for cooking and heating but with really low conversion efficiency up to 20% and often unsustainable supply (IEA, 2015; Yoon et al., 2012). That still exists mainly in developing areas and number of traditional biomass energy users and household expected to rise from year to year (Lal, 2005; Islam and Ahiduzzaman, 2012). However, dominant role of bioenergy in the developing countries is in needs to be modernized, mainly in terms of efficiency and emission (Islam and Ahiduzzaman, 2012).

According to Fernández et al. (2012) it was found that biomass compared with traditional fuels (fossil fuels) and presents advantage because contains low sulphur and nitrogen contents (lower content emissions of NO_x and SO_2 than fossil fuels).

Chemical composition of biomass

Stele et al. (2011) note biomass from plants is a cellular material of high porosity, consists mainly of large vacuoles which are filled by water in case of wet material or eventually by air in case of dried material. What is important to say - biomass is carbon based. It also contents a mixture of organic components containing hydrogen, often atoms of oxygen and usually nitrogen. Other components could be small quantities of atoms, such as alkali, alkaline earth and also problematic heavy metals (but usually is found in functional molecules which include chlorophyll obtaining magnesium) (BEC, 2011).

Categories of biomass materials

Biomass material for energy purpose can include a wide range of different material's types. However, the BEC (2011) says that in the world there are huge resources of residues or co-products and also enormous amount of waste. These sources could potentially become available; relatively low cost or even negative costs are anticipated because it is leading to avoiding pay for disposal. According to sources is based the following division of biomass materials:

- virgin wood, arboricultural activities, from forestry, waste from wood processing
- energy crops such as high yield crops grown specifically for energy applications
- food waste including food's and drink's manufacture, preparation and processing, and post-consumer waste
- industrial waste and its co-products from processes

- agricultural residues from harvesting and/or processing

Niu et al. (2016a) note that biomass can be classified into four major categories, according to its source: agricultural, waste, woody (the largest biomass energy source) and excrement. The wood residues, bagasse, rice husk, agro-residues, animal manure, municipal and industrial waste are main sources of biomass (Islam and Ahiduzzaman, 2012).

According to Zhang et al. (2015) lignocellulosic biomass (including stalks and leaves) is very promising for future. Therefore, development of new technologies for renewable energy production from it and especially from agriculture residues is important from the following reasons:

- it is abundant and renewable
- it does not compete with food production

2.3.3 Biofuels categories

According to IEA (2015) there are two main categories of biofuels:

- **Conventional** (first-generation) are well-established processes that are already produced on a commercial scale. The feedstock includes sugar-crops and starch-crops based ethanol (wheat), oil-crops and straight vegetable oil based biodiesel (sunflower seeds), in some cases animal fats even used cooking oils. Feedstock is seeds or grains. As well as it also includes biogas derived through anaerobic digestion (IEA, 2015; Demirbas et al., 2011)

- **Advanced** (second and third-generation) are still in the research and development. There are biofuels based on lignocellulosic biomass, cellulosic-ethanol, and biomass-to-liquids and bio-synthetic gas such as algae-based[4] (oilgae) (IEA, 2015). Second generation is made from non-food crops and wheat

[4] Algae are low-input/high-yield (Demirbas et al., 2011).

straw, corn, wood, energy crop using advanced technology (Demirbas et al., 2011). At the pilot stage are conversions of sugar into diesel-type biofuels using biological or chemical catalysts. The advanced biofuels promise more appropriate land-use efficiency even better greenhouse-gas balance with comparing biofuels used today (IEA, 2015). If it is consider dividing according to their production technologies, it is previously mentioned fourth generation. It is based in the conversion of vegoil and biodiesel into biogasoline (Demirbas et al., 2011). More shows Table 3.

Table 3 Classification of biofuels based on production technologies

	Generation	Feedstock	Examples
Conventional	1st	sugar, starch, vegetable oils, or animal fats	bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Advanced	2nd	non-food crops and energy crops, straw, corn, wood, solid waste	bioalcohols, bio-oil, bio-dmf, biohydrogen, bio-fischer–tropsch diesel, wood diesel
	3rd	algae	vegetable oil, biodiesel
	4th	vegetable oil, biodiesel	biogasoline

Source: Demirbas et al., 2011

Another classification of biofuels is based on their state of matter (IEA, 2015):

- liquid (Table 3)
- gaseous
- solid

This Thesis is focused on solid biofuels, specifically on pellets, thus next chapters provide more complex insight into this topic.

2.3.4 Solid biofuels - pellets

Solid biofuels are assessing according to the European (EN) and International (ISO) standards which are almost akin. The main distinction is that the European standards also focus on non-industrial uses and by way of contrast the international standards will include aquatic biomass as a raw material and thermally treated biomass. The standards can be divided according to related fuel specification, classes and quality warranty; the standards classify: wood pellets, wood briquettes, wood chips, firewood, non-woody pellets, non-woody chips (but just in case of ISO only) and also general requirements (Solid Standards, 2011).

According to standard EN ISO 16559 solid biofuels are made in the form of cubiform, polyhedral, polyhydric or cylindrical units with a diameter up to 25 mm with or without additives. Solid biofuels are densified (compressed) by mechanically compressing or thermally treated (into a specific size and shape such as pressed logs, cubes, briquettes or pellets). Tumuluru et al. (2001b) note that the briquette press, screw extruder and pellet mill are the most common used for solid biofuels production.

Pellets are divided as wood and non-woody. Non-woody pellets are crucial for present thesis. It is made from fruits, herbaceous, or aquatic biomass and may content additives (EN ISO 16559).

Production of pellets goes through process (pelletization) which consist of several stages included storying or compression of materials (more shows Figure 5). Pelletizing is a method of increasing the bulk density of biomass (more than 600 $kg.m^{-3}$) by mechanical pressure (Mani et al., 2006). It is process through which is reduced biomass material to a greater structural homogeneity, thus it is a form of mass and energy densification. It also includes reducing of handling costs and serves easier handling of product, transporting or store and utilizing (Stelte et al., 2011; Ishii and Furuichi, 2014). The most common biomass types for pelletization are hardwoods, softwoods and grasses, respectively. The drawback for straw materials are that the compression strengths is in general higher for pellets produced at higher temperatures, and also are much higher for wood pellets than for non-wood pellets (Stelte et al., 2011).

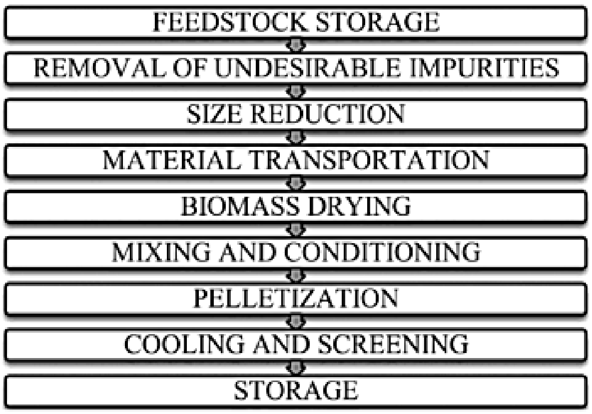

Figure 5 Stages of the pelletization process

Source: Garcia-Maraver and Pérez-Jiménez, 2015

Process of pelletization is conducted in pellet mills by pressing the materials through cylindrical shaped press channels where is material exposed to high pressure and heat that arises from the high friction between the feedstock and equipment's walls (Stelte et al., 2011). The raw materials for pelletization have to be chopping because straw have structural tubes of highly crystalline cellulose, which is protected by a waxy outer surface. Thus, it can be effectively pelletized only after destroying the structure. So, reason for using chopping or milling is clear (Werther et al., 2000). Feeding raw material is better to filter before grinding to remove impurity fragments, soil and stones (Garcia-Maraver and Pérez-Jiménez, 2015). The stage *"biomass drying"* is necessary in case of high content of water (in the raw material must be about 10% before the pelletizing process begins), thus by drying process it is achieve in case of higher moisture content (Hansen et al., 2009). Mani et al. (2006) state that about 8% of moisture content it is enough.

During pressure applying is the melting point of the particles reduced and particles are forced to move toward one another, which is following increasing the contact area (Tumuluru, 2011b). The effect of the pelletizing pressure is influenced by type of biomass, die size, temperature, and moisture content (MC) of feeding material (Said et al., 2015).

Tumuluru et al. (2011b) and Yoon et al. (2012) claim that biomass has low density and the difference in density causes difficulties in feeding the fuel into the boiler and reduces burning efficiencies. The densification overcomes this limitation through increase of biomass density (Stelte et al., 2011).

It was found some kind of trend in case of production, consumption and trade of wood pellets. They have grown strongly over the last decade. According to International Energy Agency (2015) pellets in comparison with other forms of biomass fuels, are of consistent quality and burn efficiently. Thus, pellets are ideal possibilities for sustainable solutions. There is also a fact that they can be made from different types of biomass include sawdust from the milling industry or agricultural waste (IEA, 2015). Nevertheless, according to Leeweonjoon (2012) biomass of woody origin fight with higher prices and its quantity is so limited that the electric generation cannot obtain enough quantities to fulfil their renewable energy obligation despite it is the most traditional biomass resources. According to Stelte et al. (2011) *"fuel pellets are used both in industrial sized heat and power production plants, thermal gasification units, as well as for heating in private households".* The global pellet market is growing considerably which gives the major component of agricultural pellets significant value (IEA, 2015).

From economic point of view the wet straw is economically nonsense to drying it because the cost of hay and straw, drying and pelletizing would have exceeded the sales price of pellets. For this reason, the harvest of straw *"dry"* operations crucial for efficient production of pellets (Bejlek and Sladký, 2012). Gadde et al. (2009) introduced thought that the seasonal variations have to be considered because of the availability pattern over a year – in means dry and wet seasons.

Tumuluru et al. (2011b) named process variables with typically impact in the densification process (briquetting, pelleting), which are:

- particle size - smaller size particles have more contact area and facilitate better binding between particles
- die rotational speed - retention time in a pellet mill/an extruder, which further influences the viscosity of the biomass
- preheating temperature

Sadehgi (2012) presented other interesting way how to use pellets - feed pellets in animal and aquatic farming industries. Advantages of feed pellets are in the physical and the nutritional benefits which it provides.

Comparing briquettes and pellets

Tumuluru et al. (2011a) claim that for pelleting is easier grinding. Moreover, pelletizing means dry feedstock which has better storage properties, reduced energy losses, reduced health risks and calorific value is higher.

Durability and particle density are the main parameters describing the physical quality for both of them (briquettes and pellets). There is problem related with susceptible on mechanical wear. Thus, this is leading to production of fine particles or dust during transport, transshipment, disturbing of feeding systems of boilers and may lead to inhomogeneous combustion processes and storage (Temmerman, 2006).

Bryol (2009) states several advantages of production pellets and their use:

- possibility of automatic heating[5] = heating with high user comfort
- compared to the rather coarse wood exhibit stable characteristics in terms of moisture and saved space needed for storage
- during their manufacture and distribution applies to the domestic labour force
- they are made of material definable composition renewable in nature

The advantage of briquette press is that it more flexible in terms of feeding material where higher moisture content and larger particles are acceptable for making good quality samples (Tumuluru *et al.*, 2011b). Moreover, possibility of spontaneous combustion during storage is reduced (Tumuluru et al., 2011a).

Tumuluru et al. (2011b) stated that unlike pellet mills, briquetting machines:

- can handle larger-sized particles and wider moisture contents without the addition of binders

[5] Offer automatic pellet boilers and related equipment is already so broad that it can be used in almost any condition - from family houses, industrial and agricultural establishments to special installation technology for various purposes, including brewing (Bryol, 2009).

- agricultural material briquettes can be formed at 22% moisture content

On the other hand, according to Tumuluru et al. (2011b) both of processes offer:

- better feed handling characteristics
- higher calorific value
- improved combustion characteristics
- reduced particulate emissions
- more uniform size and shape with specific characteristics for bioenergy applications

2.3.5 Parameters of pellets

Length and diameter

Both dimension - diameter and length, are important factors with respect to combustion. It was proved that thinner pellets allowed a more uniform combustion rate than others, especially in small furnaces. The pellets change of diameter could be due to the water migrating from pellets disrupting formed bonds in the pelletization process and changing diameter of pellets. On the other hand, length of the pellets affected the fuel feeding properties because the shorter one is easier the continuous flow could be arranged (Liu et al., 2014). According to EN ISO 16559 standard pellets are randomly length (3.15 mm to 40 mm) and diameter is less than 25 mm.

Unit density

It is determined by weighing the individual pellet and calculating its volume based on its length and diameter (Liu et al., 2014). Bejlek and Sladký, (2013) using the density of the pellets like a controlling through by the compression ratio (length: diameter of the pressure holes). The compaction pressure increases exponentially depending on the compression ratio and thus the density of the pellets. An influence of pellet density (pressing pressure) is also related with the raw material, water content, additive, chopped straw quality, and fraction melting matrix. Liu et al. (2014) investigated the unit density for rice straw pellets - 1.35 $g.cm^{-3}$.

Bulk density

It is calculated as the ratio of the material mass to the container volume. The container volume is calculated by measuring its length and diameter. Liu et al. (2014) also note bulk density for better handling, uniform shape and size after densification. The bulk density of densified biomass is significantly influenced by temperature (Tulumuru et al., 2011b). Liu et al. (2014) investigated the bulk density for rice straw pellets - 0.64 g/cm^3. Garcia-Maraver and Pérez-Jiménez (2015) state that the bulk density is an important consideration since the fuel is not fed by weight but volume which mean that variations in bulk density can cause considerable variations in combustion efficiency. The bulk density characteristic of non-densified biomass makes it difficult to transport over long distances and demands spaces for storage (Garcia-Maraver and Pérez-Jiménez, 2015).

Pellet strength

This factor is also connected with handling and transportation. According to Liu et al. (2014) it includes two parameters, durability and fine content which are showed

Figure 6. The important information from this research is that durability has increased by increasing rice straw content in mixture with bamboo. Rice straw improves bamboo's pellets properties especially bulk density, durability and fine content (Liu et al., 2014).

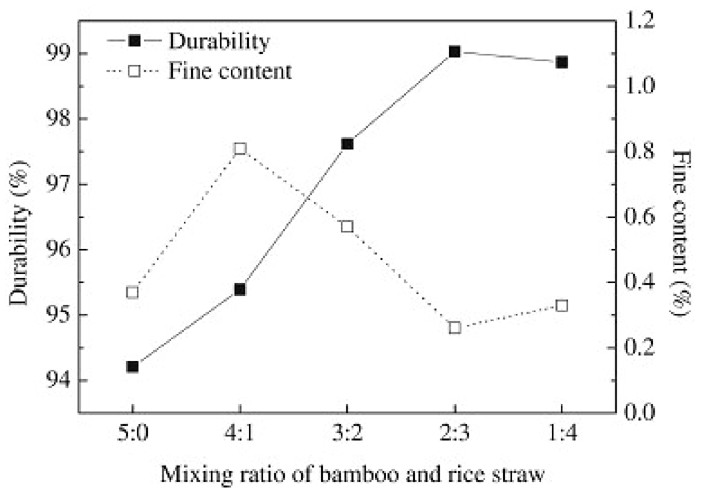

Figure 6 Graph of Durability and fine content of pellet
Source: Liu et al., 2014.

Generally factors affecting the strength are biomass constituents, moisture content, particle size and distribution, forming temperature including preheating, binders or additives, densification equipment variables (Ishii and Furuichi, 2014; Kaliyan and Morey, 2009).

Tumuluru et al (2011b) used variables which depend on strength and durability of the particle bonds.

- die diameter[6]
- die temperature
- pressure (plays an important role on the quality of pellets made from agricultural biomass)
- binders
- pre-heating of the biomass mix

Particle size

The recommended particle size for good pellet quality is 0.6–0.8 mm or 0.5–0.7 mm to produce durable pellet. Bigger size (more than 1 mm) leads to breaking point (Kaliyan and Morey, 2009). On the other hand, the particle size ranged from 5 to 20 mm did not significantly affect the yield ratio or durability (Ishii and Furuichi, 2014). Moreover, the particle size of the material to be granulated should not exceed 1/5 the diameter of the final granules (Kott, 2009). The finer structure of the material for granulate is leading to better resulting strength of the pellets. This is connected with the surface of the particles to be bonded (Garcia-Maraver and Pérez-Jiménez, 2015; Kott, 2009). According to Ishii and Furuichi (2014) the most important factors affecting the productivity (yield ratio) and quality (calorific value and durability) in case of solid

[6] *An increase in the length of the pellet die increases the pelleting pressure, whereas an increase in the diameter of the pellet die decreases the pelletizing pressure. Thus, press channels in the matrix have a strong influence on determining the pressure needed to press pellets through the matrix* (Tumuluru et al., 2011b).

fuel produced from biomass are the moisture content, forming temperature, and particle size.

Production efficiency

Ishii and Furuichi (2014) investigated the production efficiency, which could be found with help of yield ratio, as an important criterion for evaluating pellet. Calculation is follow: dividing the amount of (rice straw) pellets produced by the amount of material (rice straw) before shredding to account for the amounts of residues.

2.3.6 Advantages of solid biofuels base on rice straw

Why should be given an attention to rice straw as solid biofuels? Rice straw contains lower content of lignin but higher silica content (∼10%) and therefore is unsuitable for its use in animal feeding, papermaking and pulping (Buranov and Mazza, 2008). The demand of energy for rice processing increases every year (Islam and Ahiduzzaman, 2012). That is why there are many advantages for energy utilization:

I. The fact is that the rice straw is waste from agriculture production which can be used as bioenergy (Chou et al., 2009a; Ishii and Furuichi, 2014). It is an autonomous fuel resource, which partly avoids dependence on foreign energy supplies (Fernández et al., 2012). Additionally, it is by-product which does not threaten food supply (Said et al., 2015).

II. In some regions (mainly in Asia) is rice straw abundantly available (Ishii and Furuichi, 2014) which leads to stable amounts of material production each year, due to this fact it is possible to secure a raw material supply (Yoon et al., 2012). The point is that rice is produced in large volumes. According to Suramaythangkoor and Gheewala (2011) it is possible to cultivate two crops annually (with sufficient water supply for the whole year). Besides that, Chao-Lung et al. (2011) note it could be possible even in a three-season per year.

III. Solid biofuels based on rice straw could be substitute of coal or fuels (Chou et al., 2009a) which are causing global warming and climate change (Said et al., 2013). Furthermore, it was proven that 3 billion people depend on wood, coal, charcoal or different animal waste for cooking and heating in their households (UN, 2015). Furthermore, direct indoor combustion for cooking and heating in rural areas is related with detrimental effects of indoor air pollution (Chen et al., 2009). According to Ray and Kim (2014) burning of biomass materials instead of oil and coal reduce sulphur dioxide (SO_2) emissions which are produced by combustion of fossil fuel at power plants (73 %) and other industrial facilities (20 %), while the rest (7 %) are of natural origin.

IV. Decreasing local pollution during open burning (Said et al., 2015). Air pollutants from open burning can adversely affect human health, such as the asthma attacks even including causing cancer (Lim et al., 2012). The open burning may cause the traffic accident if the field is close to the freeway (Chou et al., 2009b).

V. Moreover, utilization of biomass reduces rate of fossil fuel depletion (Said et al., 2013).

VI. Utilization of renewable energy as a source of energy is important from an environmental viewpoint (Said et al., 2013).

VII. It is also a carbon-neutral energy source (with respect to the GHGs) because CO_2 emissions are negated by the process called photosynthetic contribution by new plants (Garcia-Maraver and Pérez-Jiménez, 2015; Chou et al., 2009a). This is happening during the growth cycle of plants, so it results in a net zero impact on the environment (Chou et al., 2009a; Said et al., 2013; Leeweonjoon, 2012).

VIII. Low production cost (Chou et al., 2009a). Another economical point of view is that using of rice straw biofuels is improving a country's trade balance and economical sustainability (Fernández et al., 2012). Chen et al. (2009) investigated that abundant agro-residues can provide the economical and sustainable raw material for densified solid biofuels development in China.

IX. It is known that biomass in original form is very difficult to handle, transport, store, because of different reasons as high moisture content, irregular shape or bigger size and low bulk density (Liu et al., 2014; Ren et al., 2012). The straw is characterized by considerable inhomogeneity and low bulk density (chopped straw) from 50 to 80 $kg.m^{-3}$ (Bejlek and Sladký, 2013), in case of machine-bailed rice straw density is 150 $kg.m^{-3}$ (Matsumura et al., 2005) and for comparison rice husk has bulk density 90–150 kg.m^{-3}(Chao-Lung et al., 2011). Thus, in case of final product like for example pellets, it is possible to find another advantage – pellets could be easily handled (because of uniform shape and size, high energy and bulk density), which should leads to reduce transportation and storage costs (Said et al., 2015; Ishii and Furuichi, 2014, Garcia-Maraver and Pérez-Jiménez, 2015). In some cases of biomass materials (f.e. peanut hulls) was reported a four-fold reduction of storage space due to the pelletization (Fasina, 2007).

X. Can be easily adopted for usage in different energy conversion systems (Said et al., 2015).

XI. In case of pellets was proven that a district-heating network linked to a biomass-fired boiler is economically and environmentally sustainable option (IEA, 2015).

XII. Also there is a way of usage the ash after burning. Fertilizing by ash is a well-known and very old method. The use of ash as a fertilizer is an excellent basic method with a high content of calcium, potassium, phosphorus and magnesium (Vassilev et al., 2013).

XIII. From social point of view developing of agriculture residues as biofuel permits the creation of employment and contribute to stopping the depopulation of rural areas (Fernández et al., 2012)

Generally, production of rice also leads to some inconveniences. One of the disadvantages of growing rice could be production of biogenic greenhouse gas (GHG) emissions as methane (Gadde et al., 2009; Ishii and Furuichi, 2014). The way how can we fight with it is using of residues like straw and husk produced from rice cultivation (Gadde et al., 2009). In case of pellets production and its following storing and burning contribute to greenhouse gas emissions as well. During the storing, pellets emit some amount of carbon and during combustion it can create particulate emissions such as ash. These disadvantages apply to all kinds of pellets (IEA, 2015). According to Leeweonjoon (2012) the rice straw is not good enough to use as a fuel. Not even authors Suramaythangkoor and Gheewala (2011) note rice straw like a qualitative fuel. According to them the rice straw does not have particular advantage regarding to its net calorific value, hence other fossil fuels and biomass with higher net calorific value are bigger competitors. According to Fernández et al. (2012) it was found that biomass compared with traditional fuels (fossil fuels) presents disadvantages that carbon composition is much lower than coal's (a lower gross calorific value).

Chen et al. (2009) state that unlike conventional energy feedstock, agricultural residues have complex of physicochemical properties (may include moisture content, ash content) that complicate the burning of densified agricultural residues.

One of the obstacles to biomass utilization is relatively low softening temperature and ash melting temperature (Moskalík et al., 2008).

3. Hypothesis and objectives of the thesis

3.1 Hypothesis

The biopellets produced of rice straw feature some negative properties related to combustion processes, which can be eliminated by use of appropriate additives.

3.2 Overall objective

The aim of the present thesis was to analyse and improve the properties of pellets made of rice straw biomass.

3.3 Specific objectives

Thesis goals of the Thesis were:

- To analyse the ash melting behaviour of rice straw and rice straw with additives ($CaCO_3$ and $Ca(OH)_2$)
- To determine appropriate additive and it is optimal ratio for improvement of ash melting behaviour of rice straw pellets
- To evaluate quality through determination of pellet's parameters such as moisture content, ash content, calorific value, C-H-N content, content of volatile matter, mechanical durability and content of heavy metals.

4. Methodology

4.1 Methodology of literature review

The tool for the for elaboration of theoretical part of the present thesis – including literature review, available sources and literature of primarily foreign authors of scientific articles, was the web search engine and books were used. The scientific articles were obtained from scientific databases, mainly from Scopus, Science Direct and Web of Science, and also from web search engine Google Scholar. The articles were searched based on a combination of keywords: rice straw, solid, biofuels, standards, pellets, pressing process, ash melting behaviour, calcium additive, and biofuels quality. The scientific articles used in present thesis were published in journals including for example: Biomass and Bioenergy, Renewable and Sustainable Energy Reviews, Fuel, Fuel Processing Technology and Bioresource Technology.

4.2 Methodology of practical research

Methodology of the practical research was based on quantitative as well as qualitative research methods and included the following parts:

4.2.1 Material

In this study, pellets made of biomass material rice straw (*Oryza sativa*) were produced and used for research purposes. The rice straw is an appropriate feeding material due to the huge amount of postharvest residues secured every year. Because of that, it is also possible to secure a raw material supply (Suramaythangkoor and Gheewala, 2011; Yoon et al., 2012).

The biomass for research purposes was obtained from Cambodia. It was collected from Kampong Chhnang Province during winter 2015/2016. The Initial moisture content (IMC) of raw material was 8%. *Oryza Sativa* is further described in chapter 2.1 Rice and rice straw.

Part of the samples was produced with addition of calcium carbonate ($CaCO_3$) as a commercially available additive. $CaCO_3$ was used in powder form and it was added in 1%; 3% and 5%.

4.2.2 Grinding of the material for pelletizing

The feeding material was grinded twice. The first part of the grinding was performed at Research Institute of Agricultural Engineering (RIAE). The raw rice straw was grinded by the RS 650 hammer mill with the screen hole diameter of 15 mm, manufactured by the Czech company KOVO NOVÁK; input 7.5 kW.

The second grinding was realized at the Faculty of Engineering laboratory (FE) at the Czech University of Life Sciences Prague (CULS). The grinded rice straw was ground by the 9FQ-40C hammer mill (manufactured by the Pest Control Corporation company; input 5.5 kW) with the screen size 6 mm wide.

4.2.3 Pelletizing

The ground material was subsequently pressed to the form of solid fuel pellets. The pellets were processed at the RIAE Prague. At the RIAE the ground material of rice straw with and without additives was pressed by the MGL 200 pelleting machine (show Figure 7), manufactured by the Czech company KOVO NOVÁK, with the die hole diameter of 6 mm, which roughly corresponds to the diameter of the produced pellets.

The last modification of the material before granulation is moisturizing (or steaming). It includes the process of wetting the surface. However, the depth of the material remains unaffected. This moisture is subsequently introduced by a dosing device.

Figure 7 Pelletizer (left), feeding material and pellets (right)

Source: Author, 2016

Two types of pellets were produced. The first type was produced without any additives. The second type was produced with calcium carbonate. This additive was mixed in three different ratios – 1%; 3%; and 5% (99:1; 97:3; 95:5 – straw:additive). Totally four pellet samples were created.

Addition of calcium additive

Two additives calcium carbonate ($CaCO_3$) and calcium hydroxide (Ca (OH) 2) were chosen according to the available literature (Bostrom et al., 2009; Hutla and Jevič 2011; Wang et al., 2012; Schmitt and Kaltschmitt, 2013; Wang et al., 2016; Niu et al., 2016a).

Calcium carbonate was selected based on its beneficial properties related to ash melting behaviour. As was mentioned, rice straw contains high amount of ash, which can lead to sintering during the combustion process (Ewida et al., 2006; Bejlek and Sladký, 2012). Hutla and Jevič (2011) state that this can be influenced by the addition of additives such as kaolin, limestone, lime dolomite, burnt dolomite and ofit. Due to this research it was decided to add a calcium based additive - calcium hydroxide and calcium carbonate for the reason that higher melting points of calcium rich phases contribute to low ash sintering degrees (Wang et al., 2012).

The ratio of additives was selected based on the maximum allowed amount of additives (according to EN ISO 16559) which is 5%. Symmetrical distribution of 1%, 3% and 5% for the mixture with feeding material was suggested.

4.2.4 Preparation of the analytic sample from the material

The preparation of the analytic sample[7] from the material took place at the Faculty of Tropical AgriSciences laboratory at CULS. Dry above-ground plant biomass of rice straw was ground by Retsch Grindomix GM 100 Grinding knife mill (Figure 8) which ensured completely homogenous size lower than 1 mm (according to standard EN 14780). The material was ground to screen. No other components were added to the ground biomass.

Figure 8 Retsch Grindomix GM 100 Grinding knife mill

Source: Author, 2016

4.2.5 Determination of biomass moisture content

In this work the moisture content of ground material was measured according to the EN 14774-3 (2010) standards using the oven drying method at the Faculty of Tropical AgriSciences (FTA) laboratory at CULS.

---

[7] Analytic sample was prepared for determination of rice straw properties according to relevant standards.

The analytic sample (around 1 g) was put into two weighed glass dishes and then together weighed again. All weighings of materials were performed on the KERN digital laboratory scale (model ABJ 120-4NM) on Figure 9 with readout around 0.01 g. Next, the weighed samples were placed into the MEMMERT oven (model UFE 500) with samples and dried out at a constant temperature (105 ± 2) °C until the weight stopped changing (see below Figure 9) After the drying process, the uncovered dishes were covered by lids and then were removed from the oven, cooled in a desiccator for about 15 minutes until they reached room temperature after which they were reweighed. The formula to calculate moisture content is the following:

$$MC = \frac{(m_2 - m_3)}{(m_2 - m_1)} \times 100\ (\%)$$

where: MC - moisture content (%)

m_1 - mass of empty dish plus lid (g)

m_2 - mass of the dish plus lid plus sample before drying (g)

m_3 - mass of the dish plus lid plus sample after drying (g)

Figure 9 KERN Laboratory scale (model ABJ 120-4NM) and MEMMERT oven (model UFE 500) with samples

Source: Author, 2016

The result was reported as the mean of duplicate determinations.

4.2.6 Determination of moisture content - rice pellets

The EN 14774-2 standard was followed: dishes were weighed empty and then with the sample (minimum weight 300 grams; KERN scale was used - model ABJ 120-4NM, shown on Figure 9). The dishes with samples were placed into the oven on Figure 9 at a controlled temperature (105 ± 2) °C. The material was dried until the weight stopped changing. Constancy in mass is defined as a change not exceeding 0.2% of the total loss in mass after first weighing during a period of 60 min. The formula is the following:

$$M_{ar} = \frac{(m_2 - m_3) + m_4}{(m_2 - m_1) + m_4} \times 100$$

where: M_{ar} - moisture content in biofuels (%)

m_1 - mass of empty dish (g)

m_2 - mass of dish and sample before drying (g)

m_3 - mass of dish and sample after drying (g)

m_4 - mass of the moisture associated with the packing (g)

The result was reported as the mean of duplicate determinations to the nearest 0,1 %.

4.2.7 Determination of the content of volatile matter

The determination of the content of volatile matter was measured according to standard EN 15148 (2010) at the RIAE. The samples were dried and prepared according to EN 14774-3 (2010) standards using the oven drying method at laboratory of the Faculty of Tropical AgriSciences (FTA) at CULS (described above). The empty ceramic dishes with lid were put to the furnace (Figure 10) for 7 minutes while temperature obtained (900 ± 10) °C. Then the dishes were cooled to room temperature and put to the desiccator. Then, the dishes with samples (around 1 g) were weighted a put again to the furnace ELSKLO (model MF5) in cooled stand (Figure 10) for 7 minutes at temperature (900 ± 10) °C. After that were again cooled, put in desiccator and weighted. The content of volatile matter was calculated according to follow formula:

$$V_d = \left[\frac{100(m_2 - m_3)}{(m_2 - m_1)} - M_{ad}\right] \times \left(\frac{100}{100 - M_{ad}}\right)$$

where: V_d - Volatile matter (%)

m_1 - mass of empty dish and lid (g)

m_2 - mass of dish with sample and lid (g), before heating

m_3 - mass of dish with sample and lid (g), after heating

M_{ad} - MC (analysed according to standard EN 14774-3)

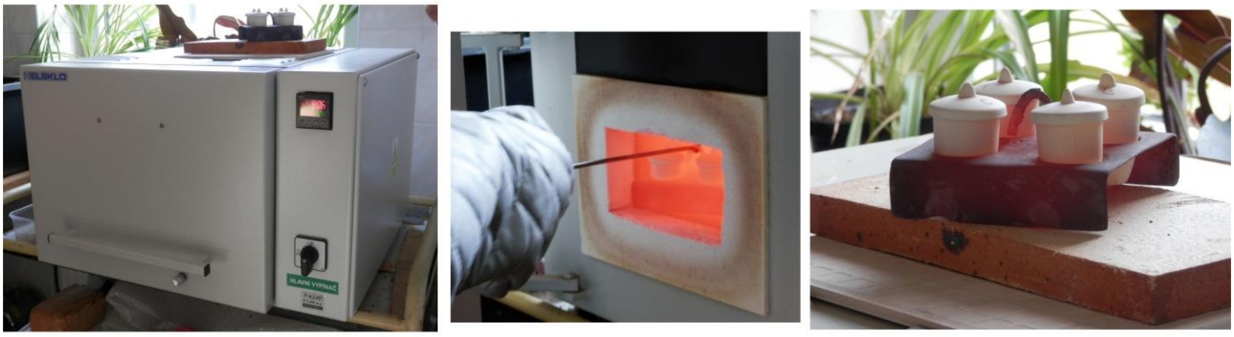

Figure 10 Determination of the content of volatile matter and laboratory equipment

Source: Author, 2016

The result was reported as the mean of duplicate determinations.

4.2.8 Determination of total content of carbon, hydrogen and nitrogen - Instrumental method

In order to determine carbon (C), hydrogen (H) and nitrogen (N) content it was used instrumental method according to the EN 15 104 standard was carried out at Institute of Agricultural Engineering. In order to determine the total content of these elements a sample of known mass is burnt in oxygen under such conditions as to convert it into ash and gaseous products of combustion analysed by gas analysis instrument. It was used LECO model CHN628 series which shows Figure 11.

During the calibration of the apparatus were established a calibration function for the measurement in accordance with the manufacturer's instructions. Weight of the samples was as near as possible to 0.1 grams; samples were put in aluminium foils and then placed into the equipment (Figure 11). Dry analytic samples were used for measurements.

The total content of the above mentioned elements, as analysed, shall be recorded as a percentage by mass as the mean of duplicate determinations.

Figure 11 Leco (model CHN628) and preparation of samples (on the right side)

Source: Author, 2016

4.2.9 Determination of calorific value

Determination of gross and net calorific value of rice straw was performed according to the standard EN 14918 standard. The IKA C6000 global standards oxygen bomb calorimeter operates according to all bomb calorimeter standards (Figure 12).

The measurements were conducted in a stainless steel high pressure vessel - bomb (on the right in Figure 12). Experimental dried samples of known weight around 1 g were burnt in oxygen-present atmosphere in the bomb which was placed in the calorimeter. The gross calorific value was calculated automatically by the calorimeter, after writing down required information (mass of samples). Net calorific value (Q_{net}) was calculated according to following formula:

$$Q_{net} = Q - 24.42 \times (w + 8.94 \times H^{a})$$

where: Q_{net} - net calorific value ($J.g^{-1}$)

Q_{gr} - gross calorific value ($J.g^{-1}$)

24.42 - coefficient corresponding to 1% of the water from the sample at 25°C

w - water content in the sample (%)

8.94 - coefficient for conversion of hydrogen to the water

H^a - hydrogen content in the sample[8] (%)

Figure 12 Calorimeter IKA C 6000 (left) and laboratory equipment (right)

Source: Author, 2016

Calorific value determines the energy value (Garcia-Maraver and Pérez-Jiménez, 2015) and it is the most important parameter to characterize combustibility of a substance (Liu et al., 2014).

4.2.10 Determination of mechanical durability

Mechanical durability of the produced pellets was tested according to EN 15210-1 using testing equipment at RIAE. In order to determine mechanical durability a standardly prescribed rotating steel cylindrical abrasion drum was used Figure 13.

---

[8] The value of hydrogen content in biomass (%) was counted according to chapter above.

The working procedure: first of all a sample had to be prepared. The sample portion of 1 kg to 1.5 kg of pellets was hand-shaken in circular movements (5-10 moves) on a sieve of 40 cm diameter with holes of 3.15 mm diameter.

The weighed amounts of pellets were retained on the sieve and calculate the initial amount of particles passing through the sieve in the sample portion in weight % was calculated.

Samples of each rice straw pellets type were weighed to reach the total mass of 2 kg (± 0.1 kg). Two testing samples of pellets were weighed (500 ± 10) g and the rest was followed to determination of MC (EN 14774-2). The samples in tumble were at (50 ± 2) rpm for 500 rotations. After that the samples were removed, sieved and weighed again. The mechanical durability was then calculated according to the formula**:**

$$D_U = \frac{m_A}{m_E} \times 100$$

where: D_U - mechanical durability (%)

m_A - mass of pre-sieved pellets before the tumbling treatment (g)

m_E - mass of sieved pellets after the tumbling (g)

Figure 13 Pellet Tester (left) and sieve with holes diameter of 3.15 mm (right)

Source: Author, 2016

The result was calculated to two decimal places and the mean result was rounded to the nearest 0,1 % for reporting.

4.2.11 Determination of total content of heavy metals

Determination of the total content of selected elements (Co, Ni, Cu, Zn, As, Cd, Hg, Pb) was determined according to Šindelářová et al. (2015) at the Interfaculty Centre of Environmental Sciences at CULS Prague.

Rice straw was freeze-dried and homogenized. The rice straw samples were decomposed in a microwave-assisted wet digestion system which focused on microwave heating (Discover SPD-Plus, CEM Inc., USA). Aliquot (~0.3 g of dry matter, in three replicates) samples were weighed in a quartz-glass digestion vessel (35 mL volume) to which 6.0 ml of concentrated nitric acid (Analytika Ltd.) was added. The mixture of biomass and nitric acid was heated at a maximum power of 300 W and temperature of 180 °C. The maximum pressure was determined to 21 bar per 12 minutes. After cooling, the solution was quantitatively transferred to plastic polyethylen tubes, filled to 30 mL with MilliQ water (purified water for laboratory purposes) and kept at laboratoty temperature until the measurement.

Element contents (Co, Ni, Cu, Zn, As, Cd, Hg, Pb) in the digests were measured by inductively coupled plasma mass spectrometry (according to ICP-MS, Agilent 7700x, Agilent Technologies Inc.). Method used no access gas mode or a collision cell mode to reduce potential interferencies for As. The experimental conditions for experiment were as follows: Sample depth of 8 mm, RF power of 1550 V, plasma flow of 15.0 L min^{-1}, auxiliary flow of 0.9 $L.min^{-1}$, He collision cell flow of 7.2 $L.min^{-1}$, to comply with internal standards Ge and Lu were used. The auto-sampler ASX-500, a 3-channel peristaltic pump, and a MicroMist nebulizer equipped the ICP-MS (Šindelářová et al., 2015). Units were detected as µg kg-1 in dry weight.

4.2.12 Determination of ash content

According to EN 14775 (2010) standard the ash content is determined by the calculation of the weight of the residue after combustion of the sample in air at a controlled temperature (550 ± 10) °C, under defined conditions at laboratory of the Faculty of Tropical AgriSciences (FTA) at CULS.

Analysis of ash content was performed on analytic dry sample. The procedure was following: the empty inert ceramic dishes were heated up to 550 °C during at least 60 min, after the dishes were taken from the furnace and cool down. Then, the dishes were put in an empty desiccator (Figure 14) and cool down to room temperature prior to the determination of its mass. Then, it was added minimum sample mass of around 1 g of analytic sample and it was used laboratory scale KERN (on Figure 9). The mass of the all dishes and the samples were measured before and after drying. The dishes with samples were put in the cold muffle furnace (Figure 14) and heated uniformly until 250 °C for 30 minutes, and then this temperature was kept for 60 min. After it the temperature was increased uniformly until constant temperature of 550 °C during 30 min and kept at this temperature for 120 min more. Formula to calculate determination of ash content for dried sample is following:

$$A_d = \frac{m_3 - m_1}{m_2 - m_1} \times 100$$

where: A_d - ash content (%)

m_1 - mass of empty dish (g)

m_2 - mass of the dish plus sample before drying (g)

m_3 - mass of the dish plus ash (g)

Figure 14 Muffle furnace and desiccator

Source: Author, 2016

The result was reported as the mean of duplicate determinations.

4.2.13 Determination of ash melting behaviour

Based on the results of ash content, the melting behaviour of ash was analysed. Documentation of ash melting behaviour followed Technical Specification (CEN/TS) which was approved by CEN - CEN/TS 15370-1. The working procedure used on the test samples of ash was prepared according to the method specified in EN 14775. The ash samples were mixed with additives ($CaCO_3$; $Ca(OH)_2$) with ratio of 1%, 3% and 5% from each additive and one pure sample (without additives) was used for comparison.

The furnace was set to raise the temperature to 550 °C at a uniform rate of 10 $°C.min^{-1}$. After that, a small test specimen (minimum of 2 samples of each) from ash, where observed during slow heating to maximum temperature of furnace. The muffle furnace (Figure 15) has limited by maximum temperature of 1,341 °C. To produce specimens (cylinder of height 3 mm to 5 mm and with diameter equal to the height) a hand press with spring pressure compression was used.

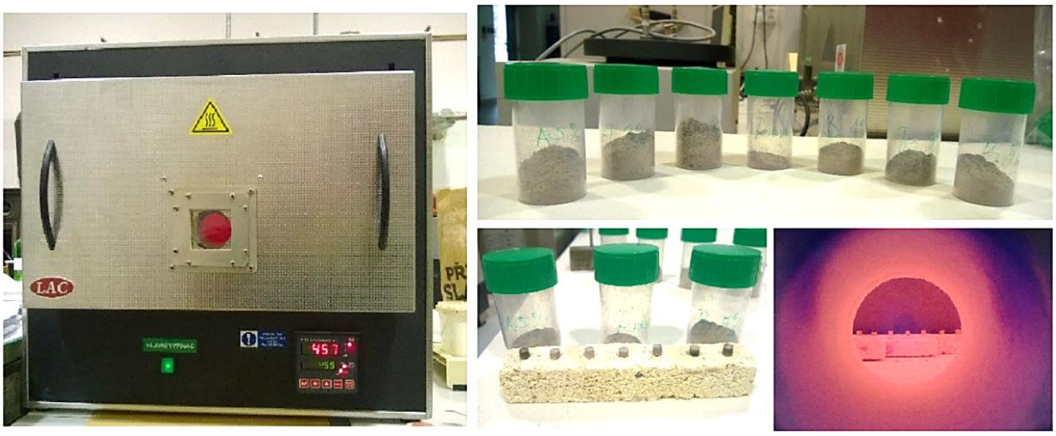

Figure 15 LAC LH 06/13 and ash samples

Source: Author, 2016

The assessment of the test was evaluated according to Figure 16 Phases in the ash melting process started measured at 550 °C (original shape) and the characteristic temperatures were determined based on the profiles of the test specimen.

The results of ash melting behaviour analysis were crucial for the selection of additives used for pellet production in the framework of present theses.

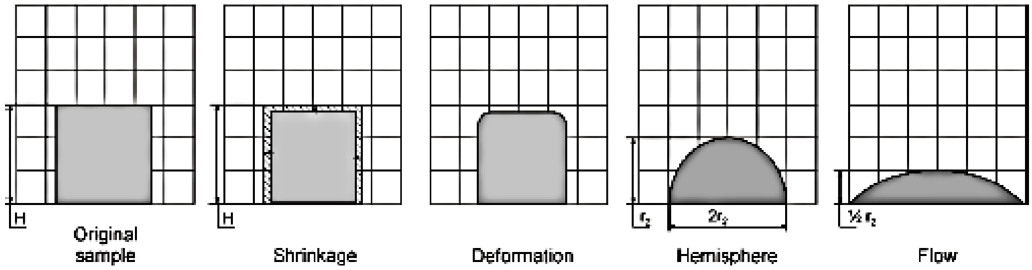

Figure 16 Phases in the ash melting process started measured at 550 °C (original shape)

Source: CEN/TS 15370-1, 2006

4.2.14 Data processing

The obtained data was compared with the current EN and ISO technical standards and evaluated according to them. The experimental results were processed via MS Excel and the results were tabulated and/or plotted. After proper processing of the results and subsequent discussion, conclusions and recommendations were formulated. The final results took into account the limits of repeatability according to relevant standards.

5. Results and discussion

This chapter provides the findings from the practical research according to the objectives of this thesis and compares it with the relevant findings of other authors. Firstly, results of input parameters of raw material, moisture content highly affects densification behaviour during the densification process, is presented, and followed by others results of chemical and mechanical properties of raw material and produced pellets.

5.1 Evaluation of moisture content of rice straw biomass and rice straw pellets

5.1.1 Moisture content of raw material

According to the EN 14774-2 standard (2010) 8.09% MC of pure rice straw was counted. According to technical standards for solid biofuels (EN ISO 17225-1, 2015) MC of quality solid biofuels should not exceed 15%. Yu et al. (2015) claim a rice straw MC of 13.40% which is a relatively higher number compared to the present thesis. However, it has to be taken into account that MC depends on harvesting conditions/area, the season and the storying conditions. The comparison of rice straw MC and other material are presented in Figure 17.

Chen et al. (2009) generally note a MC in the range of 10 – 15% for biomass as higher percentages lead to problems in firing and excessive energy which is required for drying. Kers *et al.* (2010) identified the optimal MC to the wider interval 10–18%. According to study of Ishii and Furuichi (2014) was identified the optimal IMC of rice straw before pelletization between 13-20% which leads to pellet MC of 11.7% (IMC of feeding material 13.1%); 12.7 (used IMC 17%); and 14.1 (used IMC 18.8%).

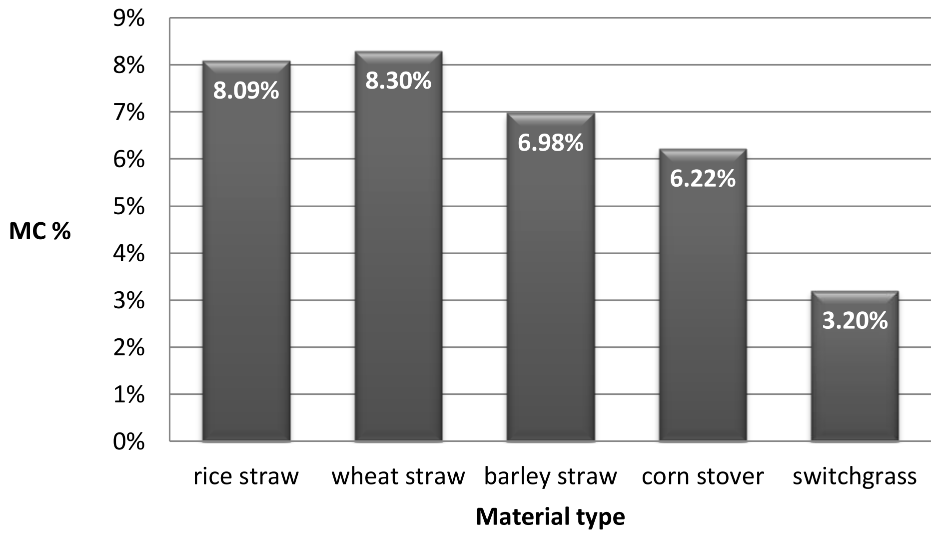

Figure 17 Moisture content of biomass materials

Notice: Comparison of measured moisture content of rice straw
with results of Mani et al. (2006).

It can be concluded that generally biomass samples before pelletization should not exceed 15% of MC. As the results have shown, the rice straw under examination here belongs to the generally recommended and standard set boundary.

5.1.2 Moisture content of rice straw pellet

According to the 14774-2 standard rice straw pellets MC of 13.03% was detected. This result is corresponding with study of Ishii and Furuichi (2014). For producing pellets it was used MC 8.09% with addition of water which increased IMC. 8% IMC was determined as too low and pellets would not be compact enough.

Ishii and Furuichi (2014) also used rice straw material for the production of pellets with the IMC of 8%. Subsequently, MC was also increased during the pelletization process to 13.1% as the IMC of feeding material 11.7% did not have enough water for pellet forming (Ishii and Furuichi, 2014). Conversely, Kott (2009) states that material which is entering the granulation process should have its moisture stabilized at 10-12%. Drier material requires careful handling, but the result is pellets of high quality. Conversely, high moisture content of rice straw pellets (IMC of feeding material of 25%) might have low calorific value, because Q_{net} decreased with an increase in the initial moisture content. Moreover, the high moisture content of rice straw pellets can be broken during the natural drying process when stored (Ishii and Furuichi, 2014). Any further increase in MC beyond the optimal range would reduce the inter-particle forces; an even higher MC causes swelling and disintegration of the pellets (Said et al., 2015). Kott (2009) also claims that moister material (18%) will reduce the long term quality of the final product, i.e. it will begin to crumble even if it is initially "firmer".

There is also a system with repeated granulation, in which the material is granulated for a long time, dried, screened and again granulated until the input material riches a moisture content of 30% and is able to produce pellets of the output moisture content of about 14% (Kott, 2009).

MC of pellets with the addition of CaCO3 in the ratio 99:1; 97:3; and 95:5 (rice straw to CaCO3) was also confirmed; it is shown in Figure 18. It can be seen that the MC of pellets with additives is lower.

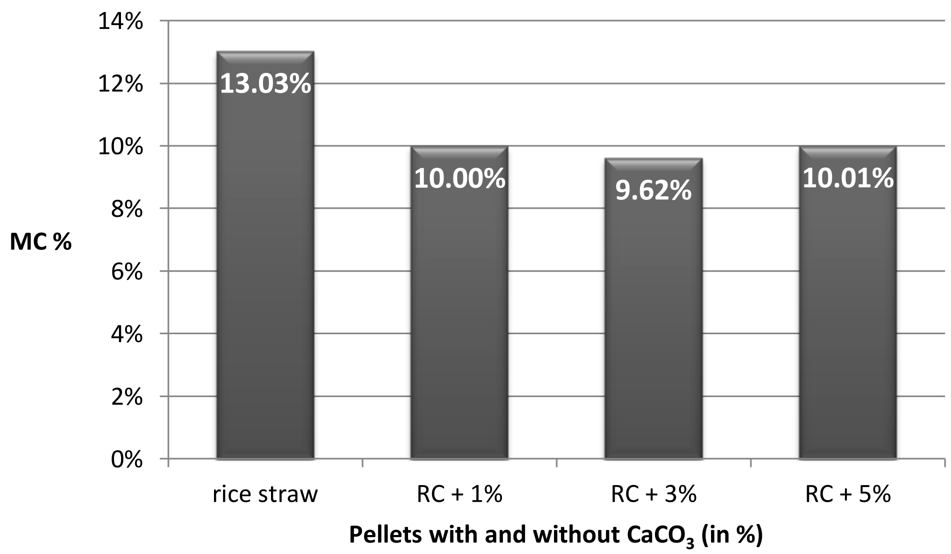

Figure 18 Moisture content of pellets

Presence of water or other liquids, during pelletization results in interfacial forces and capillary pressure increases particle bonding (Tumuluru, 2011b). Garcia-Maraver and Pérez-Jiménez (2015) state that it helps as a binding agent. On the other hand, it is also important as a critical MC for the safe storage of biomass which should not exceed 15% (Kaliyan, 2008).

5.2 Evaluation of the content of volatile matter

Determining the content of volatile matter was investigated on the basis of the EN 15148 (2010) standard with the result of 70.24%. It consists mainly of the combustibles - CxHy CO, H2 (Werther et al., 2000; Toman, 2011). The volatile portion is measured by a loss in ignition (case of Ishii and Furuichi, 2014 at 600 °C). The ash content is determined by heating (case of Ishii and Furuichi, 2014 at 815 °C).

Jenkins et al. (1998) in Lim et al. (2012) claim a slightly lower value for rice straw volatile matter - 65.47%, for rice husk an even lower value – 63.52%. Very similar results claim Yu et al. (2015) – 67.21% for rice straw. Nevertheless, compared with the volatile matter of wood (46.7%) the result are almost twice as high, with coal (34.0%) even more (Werther et al., 2000). Generally, agricultural residues are characterized by high contents of volatile matter (Werther et al., 2000) which is also proved by the results of rice straw as residue. Among other crops, wheat straw has a volatile matter of 76.4 % (Bridgeman et al., 2008) or 68.72%, corn stover 71.53% (Niu et al., 2016b). Table 4 shows to basic overview.

Table 4 Comparison volatile matter content of others authors and of different material

Material	VM	References
rice straw	70.24%	Author (2016)
rice straw	67.21%	Yu et al. (2015)
rice straw	65.47%	Jenkins et al. (1998) in Lim et al. (2012)
rice husk	63.52%	Jenkins et al. (1998) in Lim et al. (2012)
wheat straw	76.4 %	Bridgeman et al. (2008)
wood	46.7%	Werther et al. (2000)
coal	34.0%	Werther et al. (2000)

Due to the high contents of volatile matter as well as the need to operate at temperatures below the melting points of ash (more described in chapter 5.8 Evaluation of ash melting behaviour), high concentration of ash as well as unburnt pollutants may be expected in the flue gas (Werther et al., 2000; Toman, 2011).

However, according to Werther et al. (2000) it is possible to control these pollutants by the application of staged combustion.

The disadvantage is that high content of volatile matter indicates that the material is easier to ignite and to burn, which leads to the presupposition that combustion will happen very quickly (compared to coal) and will be difficult to control (Werther et al., 2000).

Werther et al. (2000) also claim that must be care allowed for achieve complete combustion of the volatiles to ensure higher combustion efficiency. Influencing factor is moisture content which increase the devolatilization time (Werther et al., 2000).

5.3 Evaluation of total content of carbon, hydrogen and nitrogen

The total content of C-H-N was analysed based on the EN 15104 standard. The results are presented in Table 5, along with the results of other authors. The content of nitrogen is within the limit according to the EN ISO 17225-6 standard. The results of the different types of material are similar to each other, in case of carbon and nitrogen even to the results of Jenkins et al. (1998) in Lim et al. (2012) and to the investigation recorded by Niu et al. (2016b). The results correspond with the statement of Werther et al. (2000) that nitrogen content is relatively low for agricultural residues. Hence, low emissions of NOx and N2O may be expected. According to Fernández et al. (2012) it was found that biomass has the disadvantage of carbon composition being much lower than that of coal (a lower gross calorific value) when compared with traditional fuels (fossil fuels).

Table 5 C-H-N analysis and comparison with literature

Material	C	H	N	Reference
Rice straw (RS)	41.37%	5.10%	0.68%	Author (2016)
RC + 1% $CaCO_3$	41.21%	5.13%	0.65%	Author (2016)
RC + 3% $CaCO_3$	41.31%	5.14%	0.63%	Author (2016)
RC + 5% $CaCO_3$	40.04%	4.93%	0.64%	Author (2016)
RS	38.24%	5.20%	0.87%	Jenkins et al. (1998) in Lim et al. (2012)
RS	40.65%	5.35%	0.85%	Niu et al. (2016b)
Wheat straw	47.3%	6.8%	0.8%	Bridgeman et al. (2008)
Barley straw	44.5%	5.8%	1.9%	Satpathy et al. (2014)

It can be concluded that the addition of $CaCO_3$ does not affect the composition of C-H-N significantly. Anyway, the carbon and hydrogen content is smaller in the case of the CaCO3 amount of 5%. This could be a drawback, because the increase of carbon also increases the calorific value (Fernández et al., 2012).

5.4 Evaluation of calorific value

5.4.1 Gross calorific value

The identification of gross calorific value was realized according to the calorimeter method. The gross calorific value of dry basis rice straw was calculated as 16,401.5 J.g-1. The results all of measurements were recorded in Table 6 including of investigation others authors where rice straw is also compared with others straw biomass. According to Straka (2010) and Ishii and Furuichi (2014) with increasing MC decreases calorific value.

Table 6 Gross Calorific Value and comparison with literature

Material	Qgr $J.g^{-1}$	References
Rice straw (RC)	16,401.5	Author (2016)
RC + 1% CaCO3	15,085.5	Author (2016)
RC + 3% CaCO3	15,199.0	Author (2016)
RC + 5% CaCO3	14,844.0	Author (2016)
RC	< 15,500	Liu et al. (2014)
RC	15,090	Jenkins et al. (1998) in Lim et al. (2012)
Wheat straw	18,900	Bridgeman et al. (2008)
Wheat straw	17,800	Satpathy et al. (2014)
Barley straw	17,700	Satpathy et al. (2014)

The typical Q_{gross} of agricultural residue ranges between 15,000 $J.g^{-1}$ and 17,000 $J.g^{-1}$. The Q_{gross} influences the ash content and extractive content of biomass (Lim et al., 2012). Table 6 shows that shows that the results of the gross calorific value of rice straw in the present research are higher than those published by other authors. In comparison with other cereal straw the presented value is lower

5.4.2 Net calorific value

Net calorific value was calculated according to EN 14918 standard and hydrogen content was substituted according to the results of total content of carbon, hydrogen and nitrogen (standard EN 15104) described in chapter above. Dry basis Q_{net} were calculated for:

- Rice straw – 15,288.1 J.g^{-1}
- RC + 1% $CaCO_3$ –13,956.6 J.g^{-1}
- RC + 3% $CaCO_3$ –14,076.9 J.g^{-1}
- RC + 5% $CaCO_3$ –13,767.7 J.g^{-1}

All of the measurements have been evaluated consistently with the EN ISO 17225-6 standard. The values higher than 14,500 J.g-1 are in accordance with this standard. Unfortunately, three out of four samples did not exceed the mentioned value (involved in all samples with additives). The comparison of gross and net calorific value is presented in Figure 19. Zhang et al. (2015) claim lower Qnet (14,790 J.g-1) than the present paper arrived at. Ishii and Furuichi (2014) claim Qnet in the range of 10,100 – 12,600 J.g-1 for pellets made of rice straw. The range depends on the MC of pellets. A Qnet of 17,000 J.g-1 is generally presented for straw pellets (Teixeira et al., 2012). According to Tumuluru et al. (2011b) there is another factor which affects the pellet calorific value – density. With higher density increases the calorific value.

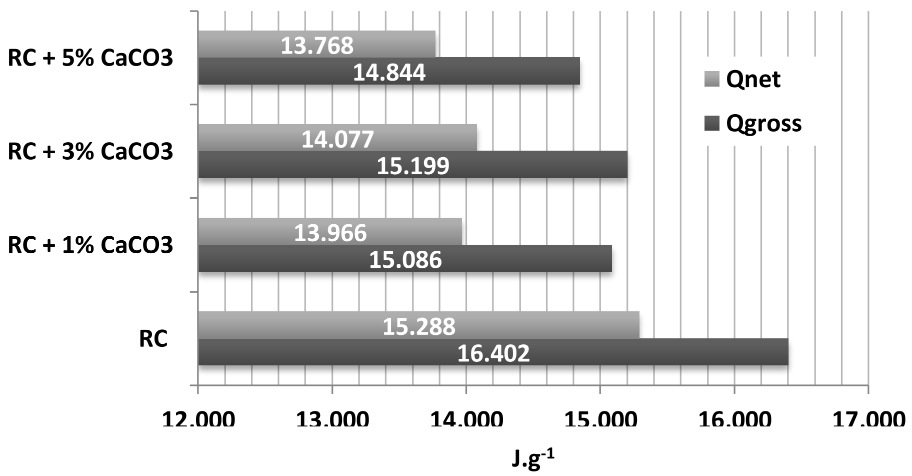

Figure 19 Gross and net calorific value – rice straw pellets

For each pellet type tests for the analysis of calorific value (gross/net) were conducted. The results are shown in Figure 19. . As can be observed, lower results are present in types with additives than without them. It can therefore be concluded that a mixture with additives leads to lower calorific value .

5.5 Evaluation of mechanical durability

Mechanical durability of all pellet kinds was tested according to the EN 15210-1 standard. Four types pellets were tested. The lowest result monitored in pellets was when additives were added in the amount of 5% – 95.04%. Conversely, the greatest durability - 96.12% was achieved with the addition of 3% of calcium carbonate. The graphic comparison of the feedstock materials of pellets can be seen in Figure 20 where the mean resulting values of all measurements are also shown. High durability means high quality, it is therefore one of the most important factors. Dust emission is avoided (Said et al., 2015).

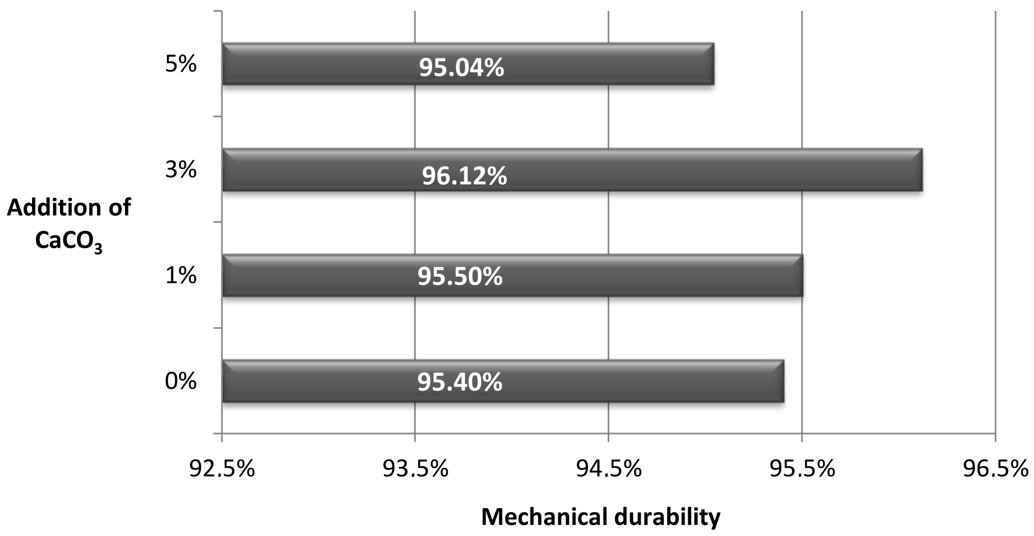

Figure 20 Mechanical durability of rice straw pellets with and without calcium carbonate additives

Liu et al. (2014) investigated rice straw pellets when mixed with bamboo. They stated that rice straw improves the durability of bamboo pellets. The best result was with the ratio of bamboo and rice straw being 2:3 (99.03%). In the case of ratio 1:4 the value of little under 99% was observed (Liu et al., 2014). The highest rice straw pellet quality, with 99.31% durability, was found in the study of Said et al. (2015) with 2% of starch, 17% of IMC and die size 8/32 mm.

In general, the factors affecting the durability of biomass products which underwent densification (Ishii and Furuichi, 2014; Tulumuru et al., 2011b; Kaliyan and Morey, 2009) are biomass constituents (starch, protein, fiber, fat[9]/oil, Lignin and extractives and others), binders or additives; particle size and distribution; forming temperature including preheating; densification equipment variables (forming temperature, die dimension, die speed, etc.); and MC.

Conversely, Theerarattananoon et al. (2011) found that for wheat straw pellets and corn stover, MC reduced the durability of corn stover and wheat straw pellets from higher value than 14%.

According to the EN 15210-1 standard the amount of particles passing through the sieve was counted in weight % separated from the sample before the establishment of mechanical durability. The sample portions in weight for all kinds of pellets were:

- 1.70% for pure rice straw pellets (MC 13.03%)
- 0.41% in the case of 1% additive (MC 10.00%)
- 0.36% in the case of 3% additive (MC 9.62%)
- 0.65% in the case of 5% additive (MC 10.01%)

The highest results were again found for pellets with 3% additive ratio. Conversely, 1.70% for pure rice straw pellets is the highest value. Ishii and Furuichi (2014) concluded that the amount of particles passing with lower MC tended to be of lower number than the amount of particles passing with higher MC. To sum up, the passing of particles in 1.70% is caused by the highest amount of MC in final products.

Generally, highest durability is present in wood material such as red maple 98.8%, tupelo 98.4%, or yellow poplar 99.0% (Kaliyan and Morey, 2009). For non-wood

[9] Too much high fat content will result in low durability (Tumuluru et al., 2011b).

material, such as sorghum stalk pellet Theerarattananoon et al. (2011) state the durability between 85.7 – 93.5%, for wheat straw pellet even 95.8 – 98.3%.

Durability is important to determine the standard for storage and transportation purposes and it is the main parameter in describing the physical quality defined as the ability of densified biofuels to remain intact when handled (Ishii and Furuichi, 2014; Temmerman, 2006). In conclusion, the greatest mechanical durability of rice pellets was achieved in the case of 3% calcium carbonate ratio and was the only one correspondent to the EN ISO 17225-6 standard (durability higher than 96%). The lowest value belongs to pellets with 5% calcium carbonate; in general, all of the measured durability values are high (above 95%). Thus, could be concluded that the additive amount of 5% may be too much for producing durable pellets.

5.6 Evaluation of total contents of heavy metals in rice biomass

Rice straw was analysed and the results presented in Table 7. According to the EN ISO 17225-6 standard the results were within the allowed extent with the exception of cobalt which is not specified in the EN ISO 17225-6 standard. The results were compared with the results of Latare et al. (2014), who evaluated rice and wheat straw and arrived at higher values with the exception of zinc (there a lower value was reached). Moreover, it is obvious that cadmium value exceeds the standard limits in the case of Latare et al. (2014). The differences of values may be explained by the dissimilar area of the studied biomass. Latare et al. (2014) used Oryza sativa, developed at the Indian Agricultural Research Institute in New Delhi. Oryza sativa from Kampong Chhnang Province, Cambodia was used in the present study.

Table 7 Contents of heavy metals in rice straw and comparison with literature

Content of selected elements in rice straw ($mg.kg^{-1}$)		EN ISO 17225-6 ($mg.kg^{-1}$)	Latare et al. (2014) Rice straw ($mg.kg^{-1}$)	Latare et al. (2014) Wheat straw ($mg.kg^{-1}$)
Ni	**1.426**	≤ 10	3.67	3.43
Cu	**1.151**	≤ 20	3.52	16.13
Zn	**29.962**	≤ 100	22.48	25.62
As	**0.878**	≤ 1	-	-
Cd	**0.114**	≤ 0.5	0.86	1.27
Hg	**0.010**	≤ 0.1	-	-
Pb	**0.310**	≤ 10	0.56	not detectable
Co	**0.251**	not specified	-	-

5.7 Evaluation of ash content

5.7.1 Evaluation of rice straw ash content

According to the EN 14775 (2010) standard AC for sample rice straw was calculated with the result of 16.11%. Straw biomass can contain up to 8% of ash (Hansen et al., 2009). In the case of rice straw, Liu et al. (2014) found that the inorganic ash content of rice straw pellets was 15.94%. Jenkins et al. (1998) in Lim et al. (2012) claim 18.67% of ash content in rice straw and the lowest content of rice straw is presented by Yu et al. (2015) - 13.13%. Anyway Niu et al. (2016b) stated that rice straw has higher AC than other biomass material (e.g. corn stover, wheat straw, cotton stalk, rape straw, etc) but also claim lower value of AC – 11.99% ± 2.20. Summarization of the previous mentioned ash contents is presented in Table 8.

Table 8 Ash content of rice straw and comparing with others authors

Reference	**AC**
Author (2016)	16.11%
Liu et al. (2014)	15.94%
Jenkins et al. (1998) in Lim et al. (2012)	18.67%
Yu et al. (2015)	13.13%

AC is an important property of solid biofuels because higher ash content means lower heating value and a greater risk of sintering (Garcia-Maraver and Pérez-Jiménez,

2015) which is corresponds with the results from Chapter 5.4 Evaluation of calorific value. It is based on inorganic material content expressed in percentage. The results for rice straw pellets (including the mixture with bamboo) shows

Figure 6. The inorganic ash of biomass pellets depends on the composition, mainly the composition of ash-forming elements. These elements are mainly mineral components such as Na, K, Si, Fe, Mg, Al, Na, Ca, Zn and Ti too (Liu et al., 2014), for more information see Table 9. Apart from this, high alkali content (Na and K) and presence of phosphorous in feedstock can decrease the melting temperature of ash (Lim et al., 2012). A specific form of influencing the decrease in gross energy and the increase of ash could be any soil contamination of the feedstock (Cherney and Verma, 2013). Chen et al. (2009) state ash content and composition greatly affect the tendency to slagging behaviour. They also noticed that agricultural residues often comprise contain alkaline earth metals.

Table 9 Ash-forming elements of rice straw pellets:

Ash-forming elements (mg.kg^{-1})	K	Ca	Si	Mg	Na	Fe	Al	Zn	Ti
	11,234.3	2,407.38	2,321.88	1,136.92	718.27	187.81	51.23	45.43	7.2

Source: Liu et al., 2014.

Comparison of rice straw AC with others materials:

According to Andert (2010) the content of ash in bent grass (*agrostis*) in the dry matter is 1.92%. On the other hand, it must be noted that the chemical composition of the ash in bent grass causes the formation of sintered pieces of stalks. These are on its surface covered with plastic ash, which is melted and acts as mutual bonding of the ash particles. At the same time, it also restricts access to the rest of the combustion air to carbon from the organic matter. This was caused by a higher content of combustible substances in the ash under the grate (also concerns bent grass and mixtures thereof). This leads to the slagging of boilers.

Andert (2010) claims that corn straw has AC in dry matter of 14%. When burning cornstalks with fuel, it was proved that there is a tendency to sintering in a lesser degree of the ash content. Compared to wood matter, however, it was necessary to attend to the boiler twice a day to collect the ashes from it.

The rye straw studied by Wang et al. (2016) has also shown a high AC and contains large amounts of the elements K, Si, Ca and P. Wang et al. (2012) state that the AC for rye straw is 4.9% (3.1% for husk), lower data when compared to raw wheat straw - 6.3% (Bridgeman et al., 2008) as well as barley straw – 8.1% (Satpathy et al., 2014).

Wood chips and firewood have the lowest ash content of all - 0.5-3.0 % (Hansen et al., 2009).

5.7.2 Evaluation of ash content of rice straw with additives

Figure 21 below shows the increase of AC when $CaCO_3$ and $Ca(OH)_2$ was added to the rice straw. As was mentioned above, the initial AC for pure rice straw is 16.11%. It is evident that by increasing the amount of additives the AC also increases. The results do not fulfil the EN ISO 17225-6 technical standards because all of the samples exceeded the AC of 10%. According to Liu et al. (2014) the rice straw pellets showed major problems in terms of its high content of ash. Lower AC was monitored for $Ca(OH)_2$ which had lower impact on the ash melting behaviour (further described in the chapter below). Due to the fact that the main aim of the research was to improve ash melting behaviour.

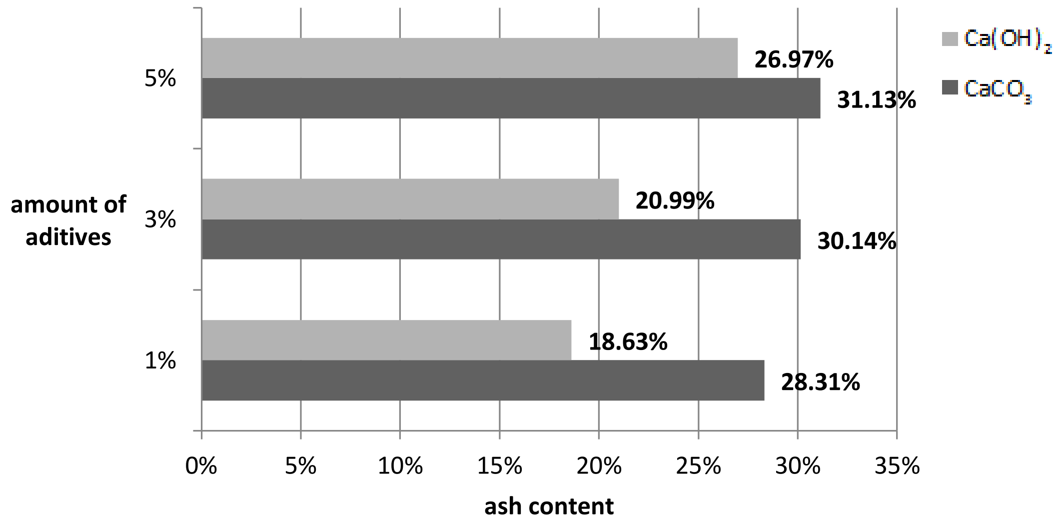

Figure 21 Ash content of samples with additives

$CaCO_3$ contains mainly calcium oxide and carbonate (Wang et al., 2016); more about its composition is presented in Table 10. Within the addition of $CaCO_3$ addition, CaO (mainly originated from a surplus of $CaCO_3$) was observed as the main crystalline phase in barley husk ash caused by the decomposition into CaO and CO_2 (Wang et al., 2012). Important is also the content of potassium because it decrease the ash melting point which also causes slagging and even fouling (Garcia-Maraver and Pérez-Jiménez, 2015). In comparison to straw the content of potassium in wood chips is approximately 10 times lower (Hansen et al., 2009).

Table 10 Chemical composition of $CaCO_3$ ash

Chemical composition of the ash (wt %)	SiO_2	K_2O	Al_2O_3	CaO	Na_2O	MgO	Fe_2O_3	SO_3
$CaCO_3$[1]	0.2	0.02	0.80	95.12	0.22	2.99	0.52	0.05
$CaCO_3$[2]	-	-	-	99.10	-	0.03	-	0.02

Source: Wang et al. (2012)[1]; Wang et al. (2016)[2]

5.8 Evaluation of ash melting behaviour

Evaluation of ash melting behaviour (shrinkage, deformation, hemisphere and flow) was realized according to CEN/TS 15370-1 technical specification. This method is based on observation shown in Figure 22. Seven types of samples were investigated, these are also shown Figure 22 – from left to middle ashes containing CaCO3 were observed (in three different ratios), in the middle rice straw ash without any additives, and from middle to right ashes with Ca(OH)2 were observed (again in three different ratios). This research was limited by the maximum reached temperature of 1,341 °C of the employed muffle furnace and by the location of the heater (which is situated on the left and right side of the samples). Thus, samples of ratios of 5% of Ca(OH)2 and 5% of CaCO3 may be influenced by higher temperature.

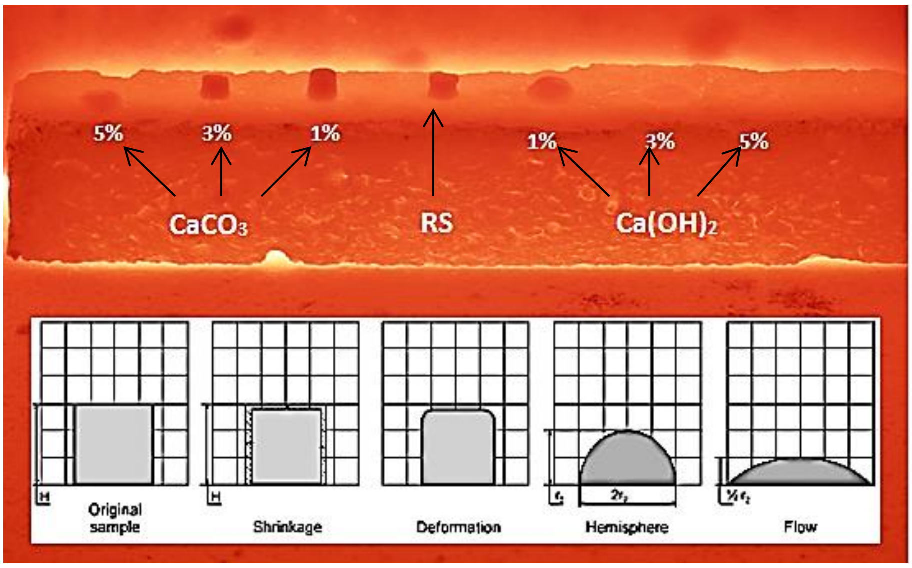

Figure 22 Evaluation of ash melting behaviour

Source: Author, 2016; CEN/TS 15370-1, 2006.

The results are presented in Figure 23. The samples with 1% of $Ca(OH)_2$, pure rice straw or samples with 1% and 3% of $CaCO_3$ have slag formation over 1,341 °C. The poorest results are recorded for ashes with 5% and 3% of $Ca(OH)_2$. This fact led to the decision about choice of additive for production pellets made of rice straw.

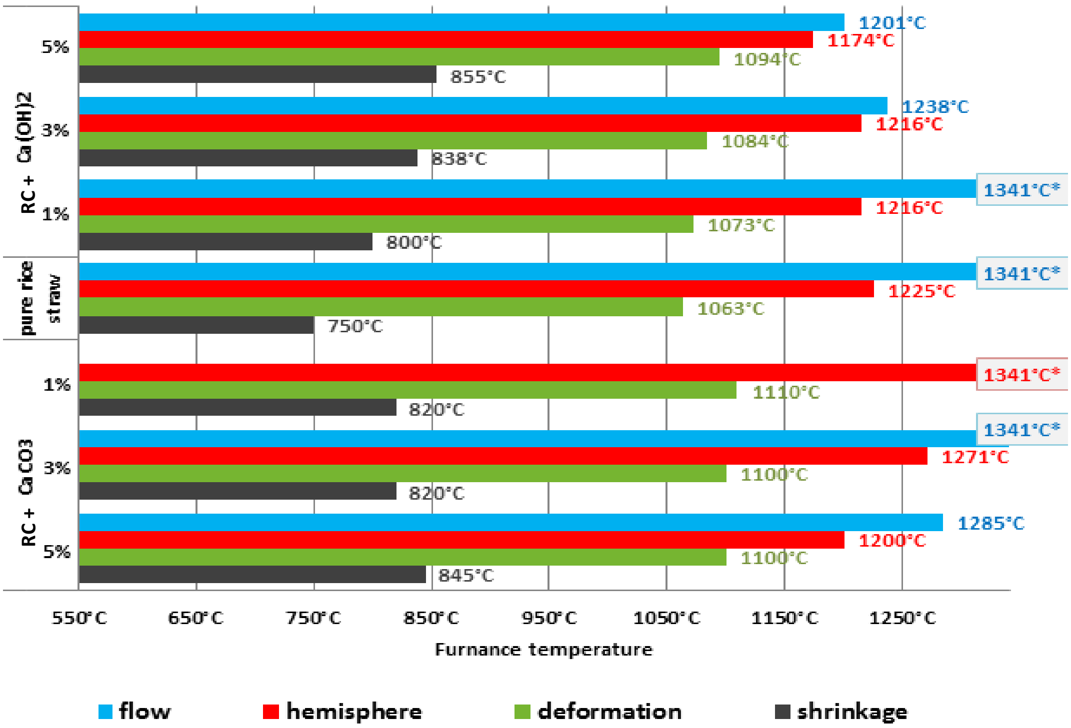

Figure 23 Resulted temperature of ash melting behaviour

* Note: The highlighted temperatures are not the final temperatures of the process but the maximum allowed temperature of the muffle furnace. The flow temperature for sample RS + 1% of CaCO3 could not be investigated due to the limited temperature of the muffle furnace.

Schmitt and Kaltschmitt (2013) proved that calcium hydroxide helps the enhancement of the ash melting temperature[10]. On the other hand, the present research showed the enhancing impact of calcium hydroxide just in certain stages of ash melting behaviour – shrinkage and deformation (compare with pure rice straw - Figure 23).

According to Niu et al. (2016a) besides lime (CaO, $Ca(OH)_2$) and calcite ($CaCO_3$) are utilized as additives kaolin and feldspars with the expectation to improve ash-related problems during biomass combustion. CaO, $Ca(OH)_2$ and ($CaCO_3$) significantly reduce slag formation during biomass combustion (Steenari et al., 2009 and Lindstrom

[10] On the other hand at the same time potassium release is increased, thus leading to higher emissions of inorganic components.

et al., 2008 in Niu et al., 2016a). Wang et al. (2016) used three additives: kaolin, calcium carbonate and Ca-sludge waste. $CaCO_3$ proved to be superior to the others in terms of mitigating the sintering degree of rye straw ash and its addition contributed to the reduction of ash melts. It was stated there that $CaCO_3$ may hinder the aggregation of ash melts and further formation of large ash slag. Moreover, Niu et al., (2016a) state that $CaCO_3$ is more effective than kaolin in reducing molten slagging, which decreases by two-thirds and one-half, respectively. On the other hand, the best anti-slagging effect is achieved when both lime and kaolin are used as additives together; lime alone provides almost the same effect (Steenari et al., 2009 in Niu et al., 2016a).

According to this research $CaCO_3$ reached higher results than $Ca(OH)_2$ (Figure 22 and Figure 23). Also, Wang et al. (2012) proved that $CaCO_3$ addition can reduce slagging and formation of ash melts during biomass pellet combustion even with the addition of a small amount. Furthermore, sintering of barley straw ash was significantly depressed with the addition of $CaCO_3$ (also in powder form). The results were compared to others researches in Table 11.

Table 11 Comparison of ash melting behaviour with others materials

Material	Shrinkage	Deformation	Hemisphere	Flow	Reference
Rice straw (RC)	750°C	1,063°C	1,225°C	>1,341 °C	Author (2016)
RC + 1% Ca(OH)2	800°C	1,073°C	1,216°C	>1,341 °C	Author (2016)
RC + 3% Ca(OH)2	838°C	1,084°C	1,216°C	1,238°C	Author (2016)
RC + 5% Ca(OH)2	855°C	1,094°C	1,174°C	1,201°C	Author (2016)
RC + 1% CaCO3	820°C	1,110°C	>1,341 °C	>1,341 °C	Author (2016)
RC + 3% CaCO3	820°C	1,100°C	1,271°C	>1,341 °C	Author (2016)
RC + 5% CaCO3	845°C	1,100°C	1,200°C	1,285°C	Author (2016)
Rye straw	840°C	990°C	1,040°C	1,100°C	Wang et al. (2016)
Rye straw + CaCO3	990°C	1,210°C	1,380°C	1,350°C	Wang et al. (2016)
Straw pellets	819°C	1,014°C	1,167°C	1,238°C	Teixeira et al. (2012)

The low melting point of the ash causes slagging and leads to corrosion which ultimately leads to boiler damaging (Garcia-Maraver and Pérez-Jiménez, 2015). To sum up, the greatest result of ash melting behaviour was monitored for ashes containing calcium carbonate.

Limitation of the present research: limited temperature of the muffle furnace (maximum attainable temperature of 1,341 °C) could probably affect the ash melting behaviour.

6. Conclusion

Currently, the production of high-quality pellets which abound with satisfactory chemical, mechanical and physical properties is strongly desired. Unlike coals and conventional fuels, there are physical and chemical properties of agricultural residues which complicate their processing and combustion, such as high moisture content, low melting point of the ash and high content of volatile matter. Because of the high content of volatile matter it is recommended to keep temperatures in the combustion furnace below the ash melting behaviour. Based on the evaluation of research and measurements conducted with relevant theoretical background, the following conclusions were formulated.

Commercially available additives Ca(OH)2 and CaCO3 were tested in terms of their abilities to abate the sintering of the rice straw ash. Generally, the samples with CaCO3 (1% and 3%) have better properties of ash melting behaviour than pure rice straw ash. The lowest results were recorded for ash containing Ca(OH)2 (primarily of 5% and 3%). This led to the fact that calcium carbonate was chosen as more suitable additive for the production of rice straw pellets.

The pellets were evaluated according to the EN ISO 17225-6 standards for non-wood pellet; moisture content and total contents of heavy metal were within the stated standard amounts as well as C-H-N content. The durability test just have complied pellets with 3% of CaCO3. The calorific value meets the standard requirements only in the case of samples without additives. The decrease in calorific value probably correlates with the increase of ash content and with the amount of additives (Garcia-Maraver and Pérez-Jiménez, 2015). None of the samples meet ash content requirements, which was changed with the addition of additives when ash content rapidly increased. Potentially, ash originating from biomass combustion may be used as a fertilizer thanks to its rich composition of Mg and Ca. Conversely, it is partially limited in application due to its lack of N and soluble P (Tumuluru et al., 2011a). Other uses of biomass ash also exist - in building processes (limited to bottom ash types) or as raw material for the production of building materials (Tumuluru et al., 2011a). Based on these findings, the set hypothesis “biopellets produced of rice straw feature some negative properties related to combustion processes, which can be eliminated by the use of appropriate additives” was partially verified. In the case of rice straw pellets with calcium carbonate the ash melting behaviour is truly higher than of the other pellet types when produced under the same conditions. The highest temperature was found for calcium carbonate in the amount of 1%. Finally, recommendations for future research are presented below.

6.1 Recommendations for further research

It was certified that mixing types of biomass were helpful to improving the properties of pellets (Liu et al., 2014). Previous studies have been performed to determine the fuel quality and mixture rice straw with bamboo. Thus, further research may focus on of utilization of other waste materials in mixtures with rice biomass (Bejlek and Sladký, 2012). It is recommended to continue in examining impacts of additives. The further research also may focus on improving calorific value as well as decreasing ash content. Thus, further research on the ash is highly recommended, since, as was stated, it may be potentially used as fertilizer which may *"close whole rice process cycle*", which will be without residues as well as unusable by-products[11].

[11] Development of biomass combustion power generation is growing rapidly and that is related with ash as by-product which has become an intractable problem throughout the world. The worldwide output of biomass ash per year is comparable with coal ash with an annual production of 780 million tons, is approximately 476 million (Vassilev et al., 2013).

7. References

Andert D. 2010. Zkušenosti ze spalování alternativních peletek. Available at http://biom.cz/cz/odborne-clanky/zkusenosti-ze-spalovani-alternativnich-peletek: Accessed 2015-12-18.

BEC. 2011. What is biomass? Available at http://www.biomassenergycentre.org.uk/portal/page?_pageid=76,15049&_dad=portal&_schema=PORTAL: Accessed 2015-02-04.

Bejlek J, Sladký V. 2012. Available at http://zemedelec.cz/zpracovani-slamy-na-topne-pelety-2/: Accessed 2011-12-11.

Bostrom D, Grimm A, Boman C, Bjornbom E, Ohman. 2009. Influence of Kaolin and Calcite Additives on Ash Transformations in Small-Scale Combustion of Oat. ENERGY & FUELS 23: 5184-5190.

Bridgeman TG, Jones JM, Shield I, Williams PT. 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 87: 844-856.

Bryol C. 2009. Vytápění peletami v českých zemích. Available at http://biom.cz/cz/odborne-clanky/vytapeni-peletami-v-ceskych-zemich: Accessed 2015-12-19.

Buranov AU, Mazza G. 2008. Lignin in straw of herbaceous crops. Industrial crops and products 28: 237–259.

CEN/TS 15370-1. 2007. Solid biofuels. Method for the determination of ash melting behaviour. Characteristic temperatures method. London. BSI. 14p.

Chao-Lung H, Anh-Tuan BL, Chun-Tsun C. 2011. Effect of rice husk ash on the strength and durability characteristics of concrete. Construction and Building Materials 25: 3768–3772.

Chen L, Xing L, Han L. 2009. Renewable energy from agro-residues in China: Solid biofuels and biomass briquetting technology. Renewable and Sustainable Energy Reviews 13: 2689 - 2695.

Cherney JH, Verma JK. 2013. Grass pellet Quality Index: A tool to evaluate suitability of grass pellets for small scale combustion systems. Applied Energy 103: 679–684.

Chou C-S, Lin S-H, Peng C-C, Lu W-C. 2009a. The optimum conditions for preparing solid fuel briquette of rice straw by a piston-mold process using Taguchi method. Fuel Processing Technology 90: 1041–1046.

Chou C-S, Lin S-H, Lu W-C. 2009b. Preparation and characterization of solid biomass fuel made from rice straw and rice bran. Fuel Processing Technology 90: 980–987.

Demirbas MF, Balat M, Balat H. 2011. Biowastes to biofuels. Energy Conversion and Management 52: 1815–1828.

EN 14774-2. 2010. Solid biofuels. Determination of moisture content. Oven dry method. Total moisture. Simplified method. London. BSI. 10p.

EN 14774-3. 2010. Solid biofuels - Determination of moisture content - Oven dry method - Part 3: Moisture in general analysis sample. London. BSI. 10p.

EN 14775. 2010. Solid biofuels. Determination of ash content. London. BSI. 12p.

EN 14780. 2011. Solid biofuels — Sample preparation. London. BSI. 28p.

EN 14918. 2010. Solid biofuels. Determination of calorific value. London. BSI. 64p.

EN 15104. 2011. Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods. London. BSI. 18p.

EN 15148. 2010.Solid biofuels. Determination of the content of volatile matter. London. BSI. 16p.

EN 15210-1. 2010. Solid biofuels - Determination of mechanical durability of pellets and briquettes - Part 1: Pellets. London. BSI. 14p.

EN ISO 16559. 2014. Solid biofuels. Terminology, definitions and descriptions. London. BSI. 44p.

EN 17225-1. 2015. Solid biofuels. Fuel specifications and classes. General requirements. London. BSI. 68p.

EN ISO 17225-6. 2014. Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets. London. BSI. 18p.

Estrellan CR, Iino F. 2010. Toxic emissions from open burning. Chemosphere 80: 193–207.

Ewida KT. El-Salmawy H. Atta NN. Mahmoud MM. 2006. A sustainable approach to the recycling of rice straw through pelletization and controlled burning. Clean Technologies and Environmental Policy 8: 188–197.

FAO. 2013. Production - Crops. Available at http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor: Accessed 2015-12-10.

FAO. 2015. FAOSTAT: Production – Crops. Available at http://faostat3.fao.org/browse/Q/QC/E: Accessed 2015-11-13.

Fasina OO. 2007. Physical properties of peanut hull pellets. Bioresource Technology 99: 1259–1266.

Fernández RG, García CP, Lavín AG, Bueno de las Heras JL. 2012. Study of main combustion characteristics for biomass fuels used in boilers. Fuel Processing Technology 103:16-26.

Gadde B, Christoph Menke C, Wassmann R. 2009. Rice straw as a renewable energy source in India, Thailand, and the Philippines: Overall potential and limitations for energy contribution and greenhouse gas mitigation. Biomass and Bioenergy 33: 1532–1546.

Garcia-Maraver A, Pérez-Jiménez JA. 2015. Biomass pelletization: standards and production. Southampton: WIT Press. 194p.

Gilbe C, Öhman M, Lindström E, Boström D, Backman R, Samuelsson R, Burvall J. 2008. Slagging Characteristics during Residential Combustion of Biomass Pellets. Energy Fuels 22: 3536–3543.

Hansen MT, Jein AR, Hayes S, Bateman P. 2009. English Handbook for Wood Pellet Combustion - Pellet Atlas. Available at http://pelletsatlas.info/wp-content/uploads/2015/09/Handbook_English_disclaimer.pdf: Accessed 2015-12-12.

Hiloidhari M, Das D, Baruah DC. 2014. Bioenergy potential from crop residue biomass in India. Renewable and Sustainable Energy Reviews 32: 504–512.

Hoover AN, Tumuluru JS, Teymouri F, Moore J, Gresham G. 2014. Effect of pelleting process variables on physical properties and sugar yields of ammonia fiber expansion pretreated corn stover. Bioresource Technology 164: 128–135.

Hutla P, Jevič P. 2011. Vlastnosti topných briket z kombinovaných rostlinných materiálů. AGRITECH SCIENCE 11: 1-5.

International Energy Agency (IEA). 2015. Topics. Available at http://www.iea.org/topics/: Accessed 2015-12-01.

Ishii K, Furuichi T. 2014. Influence of moisture content, particle size and forming temperature on productivity and quality of rice straw pellets. Waste Management 34: 2621–2626.

Islam AKMS, Ahiduzzaman M. 2012. Biomass Energy: Sustainable Solution for Greenhouse Gas Emission. The 4th International Meeting of Advances in Thermofluids. Melaka, Malaysia: American Institute of Physic, p23-32.

Kaliyan N. 2008. Densification of biomass [PhD]. Minneapolis: University of Minnesota, 409p.

Kaliyan N, Morey RV. 2009. Factors affecting strength and durability of densified biomass products. Biomass and Bioenergy 33: 337–359.

Kers J, Kulu P, Aruniit A, Laurmaa V, Križan P, Šoos L, Kask Ü. 2010. Determination of physical, chemical and burning characteristics of polymeric waste material briquettes. Estonian Journal of Engineering 16: 307–316.

Khush GS. 1997. Origin, dispersal, cultivation and variation of rice. Plant Molecular Biology 35: 25-34.

Kott T. 2009. Výroba pelet z biomasy – technické a ekonomické aspekty. Energie 21 6: 9.

Lal R. 2005. World crop residues production and implications of its use as a biofuel. Environment International 31: 575–584.

Latare AM, Kumar O, Singh SK, Gupta A. 2014. Direct and residual effect of sewage sludge on yield, heavy metals content and soil fertility under rice–wheat system. Ecological Engineering 69: 17–24.

Leeweonjoon. 2012. A Comparative Study on Fuel Characteristic and Combustion Behaviour of Biomass Fuel Types. JOURNAL OF KOREA SOCIETY OF WASTE MANAGEMENT 29: 421-430.

Lim JS, Manan ZA, Alwi SRW, Hashim H. 2012. A review on utilization of biomass from rice industry as a source of renewable energy. Renewable and Sustainable Energy Reviews 16: 3089-3094.

Liu Z, Liu X, Fei Z, Jiang Z, Cai Z, Yu Y. 2013. The properties of pellets from mixing bamboo and rice straw. Renewable Energy 55: 1-5.

Mani S, Tabil LG, Sokhansanj S. 2006. Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. Biomass and Bioenergy 30: 648–654.

Matsumura Y, Minowa T, Yamamoto H. 2005. Amount, availability, and potential use of rice straw (agricultural residue) biomass as an energy resource in Japan. Biomass and Bioenergy 29: 347–354.

McKendry P. 2002. Energy production from biomass (part 1): overview of biomass. Bioresource Technology 83: 37-46.

Missagia B, Guerrero C, Narra S, Sun Y, Ay P, Krautz HJ. 2011. Physicomechanical Properties of Rice Husk Pellets for Energy Generation. ENERGY & FUELS 25: 5786-5790.

Moldenhauer KAK, Gibbons JH. 2003. Rice Morphology and Development. In: Smith CW, Dilday RH editors. Rice: origin, history, technology, and production. Hoboken: John Wiley & Sons, p103-128.

Moskalík J, Baláš M, Lisý M, Bogdálek J. 2008. Tavení popele z bioamasy. Energie z biomasy 9:1-6.

New Energy Foundation. 2011. Japanese projects for bioethanol production from rice straw. Available at https://www.asiabiomass.jp/english/topics/1101_02.html: Accessed 2016-01-01.

Niu Y, Tan H. Hui S. 2016a. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Progress in Energy and Combustion Science 52: 1–61.

Niu W, Han L, Liu X, Huang G, Chen L, Xiao W, Yang Z. 2016b. Twenty-two compositional characterizations and theoretical energy potentials of extensively diversified China's crop residues. Energy 100: 238–250.

Natural Resources Defense Council (NRDC). 2015. Renewable Energy for America: Overview. Available at http://www.nrdc.org/energy/renewables/default.asp: Accessed 2015-10-30.

Okasha F, Zaater G, El-Emam S, Awad M, Zeidan E. 2014. Co-combustion of biomass and gaseous fuel in a novel configuration of fluidized bed: Thermal characteristics. Energy Conversion and Management 84: 488–496.

Okasha F. 2007. Staged combustion of rice straw in a fluidized bed. Experimental Thermal and Fluid Science Volume 32, Issue 1: 52–59p.

Prasertsan P, Sajjakulnukit B. 2006. Biomass and biogas energy in Thailand: potential, opportunity and barriers. Renewable Energy 31: 599–610.

Ray S, Kim K. 2014. The pollution status of sulfur dioxide in major urban areas of Korea between 1989 and 2010. Atmospheric Research 147-148: 101-110.

Ren MN, Cui ZY, Li X, Qu YX, Zhang LH. 2012. The Influence of Industry Analysis Value to Combustion Characteristics for Pellet Fuel. Advanced Materials Research 446-449: 2934-2940.

Sadehgi A. 2012. Thermal Conductivity of Feed Pellets. JOURNAL OF AGRICULTURAL SCIENCE AND TECHNOLOGY 14: 975-984.

Said N, El-Shatoury SA, Díaz LF, Zamorano M. 2013. Quantitative appraisal of biomass resources and their energy potential in Egypt. Renewable and Sustainable Energ y Reviews 24: 84-91.

Said N, Abdel daiem MM, García-Maraver A, Zamorano M. 2015. Influence of densification parameters on quality properties of rice straw pellets. Fuel Processing Technology 138: 56-64.

Satpathy SK, Tabil LG, Meda V, Naik SN, Prasad R. 2014. Torrefaction of wheat and barley straw after microwave heating. Fuel 124: 269–278.

Schmitt VEM, Kaltschmitt M. 2013. Effect of straw proportion and Ca- and Al-containing additives on ash composition and sintering of wood–straw pellets. Fuel 109: 551–558.

Silalertruksa T, Gheewala SH. 2013. A comparative LCA of rice straw utilization for fuels and fertilizer in Thailand. Bioresource Technology 150: 412–419.

Solid Standards. 2011. Solid biofuels related standards. Available at http://www.Solid Standards.eu/standardisation/standards-list.html: Accessed 2015-29-10.

Stelte W, Holm JK, Sanadi AR, Barsberg S, Ahrenfeldt J, Henriksen UB. 2011. A study of bonding and failure mechanisms in fuel pellets from different biomass resources. Biomass and Bioenergy 35: 910–918.

Straka F. 2010. Alternativní energetické zdroje a měrné emise CO2. Available at http://biom.cz/cz/odborne-clanky/alternativni-energeticke-zdroje-a-merne-emise-co2: Accesed 04-10-2016.

Šindelářová K, Száková J, Tremlová J, Mestek O, Praus L, Kaňa A, Najmanová J, Tlustoš P. 2015. The response of broccoli (Brassica oleracea convar. italica) varieties on foliar application of selenium: uptake, translocation, and speciation. Food Additives & Contaminants: Part A 32: 2027-2038.

Teixeira P, Lopes H, Gulyurtlu I, Lapa N, Abelha P. 2012. Evaluation of slagging and fouling tendency during biomass co-firing with coal in a fluidized bed. Biomass and Bioenergy 39: 192–203.

Temmerman MI, Rabier F, Jensen PD, Hartmann H, Böhm T. 2006. Comparative study of durability test methods for pellets and briquettes. Biomass and Bioenergy 30: 964–972.

Theerarattananoon K, Xu F, Wilson J, Ballard R, Mckinney L, Staggenborg S, Vadlani .P, Pei ZJ, Wang D. 2011. Physical properties of pellets made from sorghum stalk, corn stover, wheat straw, and big bluestem. Industrial Crops and Products 33: 325–332.

Toman Z. 2011. Mechanismus a podmínky dokonalého spalování biomasy. Available at http://biom.cz/cz/odborne-clanky/mechanismus-a-podminky-dokonaleho-spalovani-biomasy: Accessed 2016-04-01.

Tumuluru JS, Wright CT, Kenny KL, Hess JR. 2010. A Review on Biomass Densification Technology for Energy Application. Idaho: Idaho National Laboratory. 96p.

Tumuluru JS, Sokhansanj S, Wright CT, Boardman RD, Yancey NA. 2011a. A Review on Biomass Classification and Composition, Co-Firing Issues and Pretreatment Methods. ASABE International Meeting, Paper No. 1110458, Idaho: Idaho National Laboratory. 32p.

Tumuluru JS, Wright CT, Hess JR, Kenny KL. 2011b. A review of biomass densification system to develop uniform feedstock commodities for bioenergy application. Biofuels, Bioproducts and Biorefining 5: 683–707.

United Nations. 2015. Sustainable Development Goals. Available at http://www.un.org/sustainabledevelopment/sustainable-development-goals: Accessed 2015-10-30.

Vassilev SV, Baxter D, Andersen LK, Vassileva CG. 2013. An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification. Fuel 105: 40-76.

Wang L, Skjevrak G, Hustad JE, Grønli M, Skreiberg Ø. 2012. Effects of additives on barley straw and husk ashes sintering characteristics. Energy Procedia 20: 30-39.

Wang L, Skreiberg Ø, Becidan M, Li H. 2016. Investigation of rye straw ash sintering characteristics and the effect of additives. Applied Energy 162: 1195–1204.

Welfle A, Gilbert P, Thornley P. 2014. Increasing biomass resource availability through supply chain analysis. Biomass and bioenergy, 70 (2014): 249-266.

Werther J, Saenger M, Hartge E-U, Ogada T, Siagi Z. 2000. Combustion of agricultural residues. Progress in Energy and Combustion Science 26: 1-27.

World Meteorological Organization. 2015. Greenhouse Gas Concentrations Hit Yet Another Record. Available at https://www.wmo.int/media/content/greenhouse-gas-concentrations-hit-yet-another-record: Accessed 2015-11-09.

Yoon SJ, Son Y-I, Kim Y-K, Lee J-G. 2012. Gasification and power generation characteristics of rice husk and rice husk pellet using a downdraft fixed-bed gasifier. Renewable Energy 42: 163–167.

Yu Z, Fang S, Lin Y, Liao Y, Ma X. 2015. Investigation of Rice Straw Combustion by Using Thermogravimetric Analysis. Energy Procedia 75: 144–149.

Zhang Y, Chen X, Gu Y, Zhou X. 2015. A physicochemical method for increasing methane production from rice straw: Extrusion combined with alkali pretreatment. Applied Energy 160: 39–48.

Zhang Q, Zhou D, Fang X. 2014. Analysis on the policies of biomass power generation in China. Renewable and Sustainable Energy Reviews 32: 926-935.