EXPERIMENTAL STUDY ON THE IMPACT OF PROCESS PARAMETERS ON ENERGY AND ASH YIELD OF BIO COAL PRODUCED WITH HYDROTHERMAL CARBONIZATION (HTC)

Markus Ulbrich¹*, Robert Schwarz¹, Hartmut Spliethoff¹, Matthias Gaderer¹

¹Institute for Energy Systems, Technical University of Munich, Boltzmannstr. 15, 85748 Garching, Germany *Corresponding author; Email: Markus.Ulbrich@tum.de

ABSTRACT: Depleting fossil resources require changes in the current energy mix towards renewable sources. Hence, upgrading processes such as torrefaction and hydrothermal carbonization (HTC) play an important role to increase biomass energy density and to convert biomass into a homogeneous coal product.

This study focuses on the influence of temperature, residence time and feed concentration on the energy and ash yield of the process. Experiments have been carried out in a temperature and pressure controlled batch reactor using beech wood and rice shells to determine the influence of temperature, residence time and feedstock concentration on the solid bio coal.

Experiments have shown that higher temperature increases carbon content and therefore the heating value of the coal. However, due to increasing mass loss with higher temperature the energy yield of the coal is affected negatively. Increasing residence time leads to increasing heating value and increasing energy yield. Feedstock concentration has no effect on coal properties but increases mass yield and hence the energy yield of the process. Ash yield has been found to increase with increasing concentration due to a decreased mass loss.

Keywords: biochar; biomass; energy; yield;

1 INTRODUCTION

With the growing need of utilizing biomass feed stocks for power generation the interest in biomass upgrading processes has been renewed in the past few years. Due to the huge diversity of biomass properties processes to convert these feed stocks into valuable uniform fuels are of vital importance for unlocking the energy potential of these sources to combustion and gasification processes.

Hydrothermal Carbonization (HTC) is a process found by Bergius et al. [1] to convert lignocellulose matter into a lignite coal product in the presence of liquid water at temperatures in the temperature range from 180° C - 300° C which has been subject to recent studies but is still in an early development stage. For a commercial implementation of the process energy and ash balances have to be considered to find optimal process parameters for an efficient plant operation.

Many recent studies focus on the general feasibility of the hydrothermal carbonization for different biomass side products and general trends of the influence of reaction parameters [2,3,4] However the influence of process parameters on the energy and ash yield of the hydrothermal carbonization process is still missing a comprehensive picture. Most studies performed the reaction in a broad parameter range with too few points to actually get an exact picture of the respective trends.

This study focuses on the influence of the vital reaction parameters, temperature, concentration and residence time and their impact and sensitivity on the resulting coal product.

2 EXPERIMENTAL

2.1 Experimental Methods

Experiments are conducted in a Parr 4560 stirred mini batch reactor with a volume of 600 mL designed for a temperature range up to 350°C and a pressure range up

to 200 bar. Temperature is controlled with three heating sleeves with a power of 700 W each and an Eurotherm 3508 controller. The system is pressurized with argon (4.6 purity) from Riessner Gas and pressure is controlled with a Swagelok KPB series backpressure controller. The experimental setup is shown in figure 1. The biomass used for the experiments was rice husk obtained from agricultural residues. Proximate and ultimate analysis for the biomass is shown in table I

Table I: Biomass Properties

	Rice Husk
Proximate Analysis	
Ash Content (%) (dry)	11,79
Humidity (%)	
Volatile Matter (%) (dry)	81,40
LHV (MJ/kg) (dry)	16,47
Ultimate (%) (dry)	
С	45,31
Н	5,79
0	64,48
Ν	0,46
S	0,17

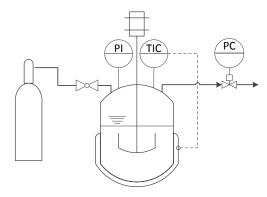


Figure 1: Parr 4560 reaction system

The rice husks were milled to a mean diameter of 0.5 mm and brought into the reactor with deionized water. The reactor was pressurized with Argon to 70 bar and the reactor was heated to the designated temperature with a heating rate of 20 K/min to 95% of the designated temperature and with 10 K/min to the final temperature to prevent oversteering of the controller. After the reaction the product was filtered, washed with deionized water, dried at 110°C at room atmosphere and stored 24h under room atmosphere for resaturation with humidity.

2.2 Characterization Methods

Humidity is analyzed according to CEN/TS 14774 [6] with a humidity analyzer IR35 from Denver Instruments. Ash content is analyzed according to CEN/TS 14775 [7]. Heating value is obtained with a Parr 1351 bomb according to DIN 5499 [8].

From these values the relative energy change x_i [-] is calculated from the fraction of the LHV H_i (MJ/kg) divided by the original LHV $H_{i,0}$ [MJ/kg] according to formula 1:

$$x_i = \frac{H_i}{H_{i,0}} \tag{1}$$

Mass yield Y[%] is calculated from the mass of the solid product m_i (dry basis) divided by the original sample mass $m_{i,0}$ (dry basis)

$$Y_i = \frac{m_i}{m_{i,0}} \cdot 100\%$$

From these values the Energy Yield EY_i [%] can be obtained from the product of the fraction of the heating values and the mass yield:

(2)

$$EY_i = \frac{H_i \cdot m_i}{H_{i,0} \cdot m_{i,0}} \cdot 100\%$$
(3)

Similar to the energy yield the ash yield AY is calculated from the product of the fraction of the ash contents of the treated sample a_i [%] (dry basis) and the original sample $a_{i,0}$ [%] (dry basis) and the mass yield:

$$AY_{i} = \frac{H_{i} \cdot m_{i}}{H_{i,0} \cdot m_{i,0}} \cdot 100\%$$
(4)

3 RESULTS AND DISCUSSION

3.1 Temperature

Energy and ash yield have been investigated for a temperature range of $160^{\circ}C - 260^{\circ}C$ with a biomass concentration of 10g/100ml and a residence time of 3 h. The temperature was increased in $10^{\circ}C$ steps for each experiment and 5°C in the temperature range from $220^{\circ}C - 250^{\circ}C$ for a better resolution of the sensitive range.

Increasing temperature has been found to have only a small influence on the energy and ash yield which is shown in figure 2. For the tested combination of concentration and residence time the energy yield remains constant with a fluctuation around 75 % over the tested temperature range, exhibiting a slight maximum at 220°C with 79 %. The values obtained from the samples were found to fluctuate for similar temperatures since the yield of the experiments is strongly influenced by inhomogeneities of the biomass.

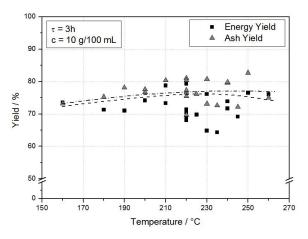


Figure 2: Energy and ash yield over temperature of HTC treated rice husks

The constant progression of the energy yield with temperature can be seen in detail by a comparison of the relative energy change (REnC) and the mass yield of the samples which is shown in figure 3.

The relative energy change increases with a higher reaction temperature from 1.00 at 160°C to 1.63 at 260°C. The progression shows a pronounced incline in the temperature range from 210°C to 250°C suggesting the beginning of hydrothermal decomposition of cellulose as it is reported by Reza et.al.[3]. Simultaneously the mass yield decreases with temperature exhibiting a sensitive behavior in the 210°C – 250°C temperature range also indicating the decomposition and dissolution of cellulose and removal of oxygen from the biomass [5]. Similar findings have been reported by Liu et. Al. who also found a decreasing yield and increasing energy content for eucalyptus leaves at 30 min. residence time with increasing temperature [2]. Regarding the used definition of the energy yield (see formula 3) the two described trends compensate thus leading to a constant energy yield.

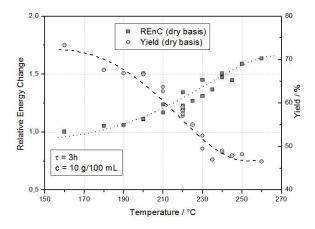


Figure 3: Relative energy change and mass yield over temperature of HTC treated rice husks

A similar trend can be found for the ash yield which remains constant over the observed temperature range. The ash of rice husks mostly contains silicon (75.93 %, own unpublished results) which is insoluble in water so that the absolute ash content and therefore the ash yield remains constant.

3.2. Residence time

The influence of residence time on the energy and ash yield has been tested from 0 h (directly after heating the reactor) to 18 h at 220°C and a concentration of 10g/100ml which is illustrated in figure 4.

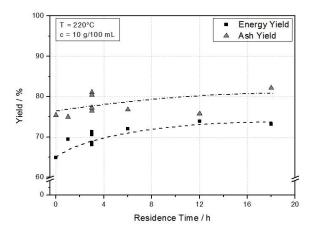


Figure 4: Energy and ash yield over residence time of HTC treated rice husks

Residence time shows a slight influence on the energy yield. With increasing residence time energy yield increases from 64.8 % to 73.2 % at 18 h with a steeper incline in the range from 0 h to 6 h and a subsequent asymptotic trend. The tested samples exhibit higher energy densification with longer residence time and a mass loss which can be seen in figure 5.

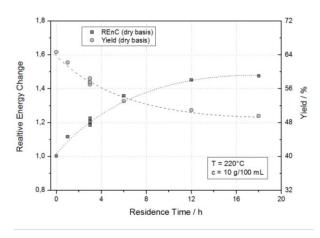


Figure 5: Relative energy change and mass yield over residence time of HTC treated rice husks

Similar to the influence of temperature (see figure 3) energy densification is increased from 1,00 at 0 h to 1.35 at 18 h and simultaneously mass yield is decreased 64.7 % to 49.6 % from 0 h to 18 h, respectively. With increasing residence time the carbonization progresses with oxygen removal and dissolution of biomass compounds accounting for the mass loss [5]. However the progress of energy densification at low residence time is steeper than the mass loss so that the energy yield is influenced positively by residence times shorter than 6 h.

Ash yield is not affected by residence time. The high silicon content in the ash cannot be dissolved in the process water. However at 0 h residence time the ash yield is 75.4 % indicating that the dissolution of the light soluble components of the ash is completed at this point.

3.3 Biomass concentration

Samples have been tested with increasing biomass concentration at 220°C and 3 h with biomass concentrations from 6,67 g/100ml to 40 g/100ml for the influence on energy and ash yield which is shown in figure 6

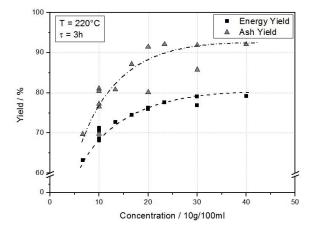


Figure 6: Energy and ash yield over biomass concentration of HTC treated rice husks

An increase in concentration is found to have strong effect on the energy yield. The energy yield is increased from 63.2 % at 6,67 g/100ml to 79.2 % at 40 g/100ml with a steep incline in the concentration range from

6,67 g/100ml to 13,33 g/100ml. Energy densification and mass yield, which are displayed in figure 7 reveal that increase in concentration does not affect the energy densification but significantly increases the mass yield. Hence, the energy yield is affected positively by biomass concentration.

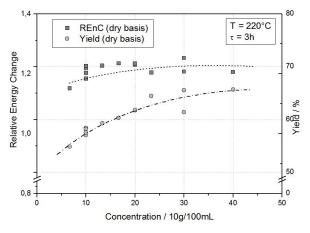


Figure 7: Relative energy change and mass yield over biomass concentration for HTC treated rice husks

With progressing carbonization, biomass is hydrothermally decomposed and dissolved in the process water [5]. With increasing biomass concentration the results hint to a dissolution process which is slowed down by a saturation of the process water with dissolved biomass compounds and thus increased mass yield at equal residence times and temperatures. However the progress of carbonization is not effected since the energy densification remains unchanged.

The same effect can be observed for the ash yield which is increased from 69,7 % to 77,6 % for biomass concentrations of 6,67 g/100ml and 40 g/100ml, respectively. For higher concentrations the ash content in the coal is slightly increased, the mass yield is increased and hence, the ash yield is also increased.

4 CONCLUSION

The results from this parameter study show that the energy yield is only influenced significantly by biomass concentration with an increasing mass yield and constant energy densification. Temperature and residence time affect energy densification positively but the higher energy densification is compensated by a mass loss caused by oxygen removal from the fuel solid body and dissolution of biomass components in the process water. Ash yield is also only affected by concentration preventing biomass and ash compounds from dissolving due to saturation of the process water. For temperature and residence time the absolute ash content remains constant and therefore the ash yield is not affected by these parameters. However, light soluble compounds can be removed during the process for the whole tested parameter range with a maximum ash recovery for rice husks of 77.6 %. For process design energy and ash yield have to be considered especially for an increased concentration which offers a higher coal yield but also increases the ash recovery. Regarding the energy density of the received coals high temperatures and residence times are favorable which lower the overall coal yield but due to the constant energy yield the mass loss points to a loss of mainly low energy compounds of the biomass.

5 REFERENCES

[1] F.Bergius, Naturwissenschaften Vol.16 (1928), pag. 1-10.

[2] Z.Liu, Fuel, Vol 103 (2013), pag. 943-949

[3] M.T. Reza, Biomass and Bioenergy, Vol 49 (2013), pag. 86-94.

[4] L. Xiao, Bioresource Technology Vol. 118 (2012) pag. 619 – 623.

[5] D. Knezevic, Hydrothermal Conversion of Biomass, University of Twente, 2009

[6] CEN/TS 14774 Solid biofuels, Methods of determination of moisture content, November 2004

[7] CEN/TS 14775 Solid biofuels, Determination of ash content, April 2010

[8] DIN 5499, Brennwert und Heizwert, January 1972