THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

A pilot-scale biomass pyrolytic poly-generation plant performance study and self-sufficiency assessment

Citation for published version:

Cong, H, Zhao, L, Masek, O, Yao, Z, Meng, H, Huo, L, Ma, T & Hu, E 2019, 'A pilot-scale biomass pyrolytic poly-generation plant performance study and self-sufficiency assessment', *Bioresource technology*, vol. 273, pp. 439-445. <https://doi.org/10.1016/j.biortech.2018.10.084>

Digital Object Identifier (DOI):

[10.1016/j.biortech.2018.10.084](https://doi.org/10.1016/j.biortech.2018.10.084)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Bioresource technology

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

A pilot-scale biomass pyrolytic poly-generation plant performance study and self-sufficiency assessment

Hongbin Cong^{a,c}, Lixin Zhao^{a,c}, Ondřej Mašek^b, Zonglu Yao^{a,c}, Haibo Meng^{a,c}, Lili Huo^{a,c}, Teng Ma^{a,c}, Erfeng Hu^{a,c}

a Center of Energy and Environmental Protection, Chinese Academy of Agricultural Engineering, Beijing, China 100125; *b* University of Edinburgh, School of Geosciences, UK Biochar Research Centre, King's Buildings, Edinburgh, EH93FF, UK; *c* Key Laboratory of Energy Resource Utilization from Agriculture Residue, Ministry of Agriculture, Beijing, China 100125

HIGHLIGHTS

- Pilot-scale plant with rotary kiln for biomass pyrolytic poly-generation was used.
- Pyrolysis gas yield increased with increasing pyrolysis temperature (550-650 °C).
- Pyrolysis gas rich in H₂, CH₄, other alkanes, and olefins; LHV >17.10 MJ/m³.
- Energy balance assessment showed 74.8% energy conversion efficiency.
- Surplus of pyrolysis gas increased as pyrolysis temperatures increased 550-650 °C.

ABSTRACT: This work studied the influence of pyrolysis temperature on the energy and mass balance of pyrolysis of rice husk (RH), cotton stalk (CS) and fruit branch(FB) in a pilot-scale biomass pyrolytic poly-generation plant.

The paper presents energy balance and self-sufficiency assessment of pilot-scale pyrolysis plant processing different types of biomass. The results also include characterization of the pyrolysis products. The volatile matter varied from 6.5-25.8% at different temperatures for the three feed stocks, which can be used as indexes for the degree of carbonization of biochar. The yield of pyrolysis gases enriched with H₂, CH₄ and other alkanes, and olefins increased significantly with increasing pyrolysis temperature from 550-650 °C. With a lower heating value >17.1 MJ/m³, an energy self-sufficient system is possible using only the pyrolysis gas. Biomass pyrolytic poly-generation technology offers a promising means of converting abundant agricultural residues into energy and added-value products.

Keywords: Slow pyrolysis, Poly-generation, Pilot plant, Energy self-sufficient, Performance

1. Introduction

Pyrolytic poly-generation is a promising approach in the thermochemical conversion of biomass in which biomass is thermally decomposed in an oxygen-depleted environment into three fractions, i.e., biochar, pyrolysis gas, and liquid fractions (Chen et al., 2016; Cong et al., 2015; Chen et al., 2012, 2014a; Yang et al., 2016). Among the converted products, biochar has attracted much attention due to its

numerous applications (e.g., slow release fertilizer, soil remediation, carbon sequestration, and high quality fuels) addressing a number of challenges in sustainable food production, environmental contamination, and climate change mitigation ([Gómez et al., 2016](#); [Laird et al., 2010](#); [Barrow, 2012](#); [EBC, 2013](#)). Meanwhile, pyrolysis gas is a clean fuel that can be used for heating and cooking applications. Since no gasification medium is required in the pyrolysis process, the heating value of pyrolysis gas is quite high ([Aysu et al., 2014](#)), especially when its heating value and tar content is improved ([Nguyen et al., 2013](#)). The liquid fractions can be used as a fuel or as a source of chemicals such as phenols and organic acids ([Ning et al., 2013](#)). Biomass pyrolytic poly-generation technology offers a promising means of converting abundant agricultural residues into high-value products, so it can further promote the comprehensive utilization of agricultural waste and provide additional value.

Compared to batch processing, continuous biomass pyrolysis technology has many advantages, such as high productivity, convenient process control, and consistent product quality; therefore, it has been the primary focus of applied research and technology development. Rotary kiln reactors in particular appear to be advantageous for solid treatments ([Kern et al., 2012](#)), due to their ability to process different types of biomass with minimum pre-treatment, making them appropriate for biochar production on large scales ([De et al., 2016](#)). Despite a large number of studies on the topic of biomass pyrolysis and biochar production, ([Chen et al., \(2017a\)](#); [Zhang et al., 2018](#); [Yang et al., 2016](#) ; [Mei et al., 2016](#); [Crombie et al., 2014](#); [Klinar et al.,](#)

2016; Mašek, et al, 2018), there are still considerable gaps in knowledge with regard to the slow pyrolysis of different biomasses in continuous pilot-scale biomass pyrolytic poly-generation plants using kiln reactors, which limits industrialization.

The primary objective of this study was therefore to investigate the influence of peak pyrolysis temperature (550, 600, and 650 °C), which was shown to be one of the key process parameters (Zhao et al., 2013), on the pyrolysis performance of several agricultural wastes: rice husks (RH), cotton stalks (CS), and fruit branches (FB) in a pilot-scale biomass pyrolytic poly-generation plant. Moreover, a characterization of the pyrolysis products and an assessment of product yields and energy balance was performed, and the potential energy self-sufficiency of the process reusing the gas and liquid fractions was estimated. Such data are essential for design of industrial biomass pyrolysis and biochar production plants.

2. Materials and methods

2.1 Characterization of the feedstock

The pyrolysis feedstock (RH, CS, and FB) used in this study were collected from Tonghe (Heilongjiang Province), Hengshui (Hebei Province), and Xingtai (Hebei Province) in China. These materials are produced in large quantities as agricultural waste, especially in North China, representing waste with physicochemical properties that have been underutilized as a resource for conversion into high-value products. Table 1 presents characteristics of the feed stocks. Before pyrolysis, the feed stocks were naturally air-dried and CS, FB were crushed to lengths of 6-10 mm using a

Jingxing9ZT-0.4 chaff cutter (made in China). The heating values were measured using a LECO AC-300 analyzer following an adiabatic method according to UNE 32006. The ultimate analysis (CHNS) was performed using a Vario ELIII Elemental Analyzer according to ASTM 5373 and ASTM 4239, while the O content was obtained by subtraction. The proximate analysis was carried out according to ASTM 3302, UNE 3219, and UNE 32004 for the total moisture, volatile matter, and ash, respectively.

Table 1: Characteristics of the feed stocks:rice husks (RH), cotton stalks (CS), and fruit branches (FB).

Feedstocks		RH	CS	FB
Particle size [mm]		original	6-10	6-10
Bulk density [$\text{kg}\cdot\text{m}^{-3}$]		116	182	221
LHV [$\text{MJ}\cdot\text{kg}^{-1}$]		14.65	17.58	18.75
Proximate analysis [wt%, ad]	Moisture	7.62	6.78	6.61
	Volatile	60.61	66.54	71.28
	Ash	17.82	3.97	2.84
	Fixed carbon	13.95	22.71	19.27
Ultimate analysis [wt%, daf]	C	49.81	45.58	47.28
	H	6.18	6.14	5.73
	O*	43.56	46.60	46.40
	N	0.44	1.62	0.59

S	0.00	0.05	0.00
O/C molar			
ratio	0.66	0.77	0.74
H/C molar			
ratio	1.49	1.62	1.45

ad: air dry basis; daf: dry and ash free basis;

^a LHV: lower heating value; ^b Calculated by difference.

2.2 Pilot-scale biomass pyrolytic poly-generation system

The continuous pyrolysis poly-generation technology consists of three main parts: continuous pyrolysis, gas-liquid separation, and reactor heating. Continuous pyrolysis is a multistage process that effectively converts biomass into product through sealed feeding, uniform transport of material in the reactor, thermal decomposition, solid-gas separation, insulation, carbonization, and biochar cooling. Gas-liquid separation includes dust removal, multi-stage condensation, and purification. The multi-stage condensation system is composed of three condensers with condensing temperatures in the range of 200-250, 80-90, and 5-15 °C. The liquids from the second and third condensers were obtained by separators, which roughly separated vinegar-like fractions and bio-oils. The bio-oils were reused as fuels for the reactor heating, and the pyrolysis gas was also used in part for heating the pyrolysis system.

Fig. 1 Schematic diagram of pilot system of biomass continuous pyrolytic poly-generation using the rotary kiln. (1) conveyor, (2) screw feeder, (3) carbonization equipment, (4) hot air furnace, (5) cooling charging unit, (6) explosion-proof device, (7) metal flame arrester, (8) dust collector, (9) primary condenser, (10) secondary condenser, (11) third condenser, (12) scrubber, (13) roots blower, (14) water seal flame arrester. S1-S7 represent temperature sensors 1-7.

Fig.1 shows a schematic diagram of the continuous pyrolysis poly-generation system used in this work, which was developed by the Center of Energy and Environmental Protection and UK Biochar Research Centre. The pyrolyzer is a horizontal rotary kiln that consists of a SUS316L tube with an inner diameter of 500 mm and a length of 5200 mm. Movement of the material in the rotary kiln relies on double-spiral blades. The rotating speed of the pyrolyzer kiln is adjustable, allowing the residence time of the solid product to be changed (Cong et al., 2017). The pyrolyzer was heated by a gas burner and an oil burner, which reused pyrolysis gas and oil, respectively. Biomass enters the reaction chamber of the continuous pyrolysis system at a constant rate of 40-60 kg/h by adjusting the speed of a screw sealed

feeder. With rotation of the continuous pyrolysis reaction kiln, the materials are slowly transported along the length of the reactor, gradually undergoing drying, volatilization, and initial carbonization. The pyrolysis gas and biochar were then separated after the rotary kiln section. The biochar fell into the thermal insulation device with an oxygen-depleted environment for 30-40 minutes of further carbonization, then the biochar was appropriately cooled and discharged in batches. The pyrolysis gas flowed into the purification system composed of dust removal, multi-stage condensation, and spraying, and was then finally stored in a high-pressure gas storage. The pyrolysis gas compressor was controlled using a real-time control loop to maintain slightly positive pressure in the reaction chamber.

2.3 Setting of process parameters

The pyrolysis behavior of biomass depends on several factors, including the type and properties of the biomass, the selected equipment, and the pyrolysis conditions (Gómez et al., 2016). Continuous pyrolysis conditions include pyrolysis temperature, material residence time, and feeding rate. The heating rate is another important factor that is affected by the above factors, and as such cannot be controlled independently from the other parameters (Cong et al, 2018; Wan 2013). Slow pyrolysis has a wide range of working conditions using moderate temperatures (up to 600 °C) to produce biochar (Basu, 2010; Cong et al, 2017). The process settings used in this study were defined based on an extensive set of preliminary experiments; working temperatures set at 550 ,600, and 650 °C; and a residence time of 30 min, with the aim to assess

product yields and the energy balance. To reduce systematic errors for product yields resulting from e.g., feed or transport fluctuations, the duration of each experiment was set to 4.0 h under stable running conditions, over which the yield was averaged. The quantity of raw material processed and biochar produced were both directly weighed using a digital weight scale (accuracy 10g) during each test. After the system started running, the pyrolysis gas was sampled once every 30 minutes.

The samples of rice husk char (RHC) with pyrolysis temperatures of 550, 600, and 650 °C (RHC 550, RHC 600, and RHC 650, respectively) were studied. Similarly, cotton stalk char (CSC) marked as CSC 550, CSC 600, and CSC 650; and fruit branch char (FBC) as FBC 550, FBC 600, and FBC 650, under the corresponding pyrolysis temperatures (550, 600, and 650 °C, respectively) were also compared.

2.4 Product Analysis

The gas products were analyzed using a HP 5890 gas chromatograph (HP-Agilent, Santa Clara, CA, USA) with three separation columns and two detectors. A HP-AL/S semi capillary column (50 m long $\times$ 0.35 mm inner diameter) using helium as the carrier gas and a flame ionization detector (FID) was used to analyze the hydrocarbons (C_xH_y). A 5 Å molecular exclusion column was employed (1.83 m long $\times$ 3.175 mm outer diameter) with a mesh size of 60/80 to separate H_2 , O_2 , N_2 , CH_4 , and CO using helium as the carrier gas and a thermal conductivity detector (TCD). The CO_2 concentration was determined with a Chromosorb 102 packed column (1.83

m long $\times$ 3.175 mm outer diameter) with a mesh size of 80/100, while using helium as the carrier gas; a TCD was used for this measurement. Once the composition of the gas was quantified, the heating value and density were estimated according to UNE-EN ISO 6976. The liquid fractions were fed into brown sample bottles separately and then stored at -18 °C for future analysis. The water content was determined using a Swiss Metrohm KFT 870 Karl Fischer titration system, according to standard ASTM E203. The heating value was determined according to ASTM 240-09. The obtained biochar was characterized using the methods of ultimate analysis, heating value, and proximate analysis for feedstock analysis.

Product yields of bio-oil and biochar were reported on an as received basis. Biochar yield was calculated by determining the mass gained with the biochar container. Each piece from the three bio-oil storage tanks was calculated before and after the experiments. The data on status, such as from the gas-flow indicator and pressure sensor of the gas storage, were recorded to quantify the pyrolysis gas the using Clapeyron equation. The ratios of biochar yield, pyrolysis gas, and pyrolysis liquid were determined from the known amounts of collected products and from the known amount of biomass fed to the reactor.

3. Results and discussion

3.1 Biochar and pyrolysis gas properties

3.1.1 Biochar properties

The proximate analysis results for RHC, CSC, and FBC on dry basis are shown in

Fig. 2. It can be seen that as expected, with increasing pyrolysis temperature the degree of devolatilization increased and as a result the concentration of fixed carbon and ash in biochar increased. The lower heating value of RHC varied greatly from CSC and FBC due to its high ash content (> 40%), which was related to the much higher ash content of the RH compared to the CS and FB. The ash content is an important quality index when biochars are intended for fuel (McKendry,2002), and is likely also quite important when the biochars are used for fertilizers, due to the presence of P and K in some ashes.

Volatile matter is closely related to pyrolysis temperatures, with content from 17.79-26.80% at 550 °C, 13.49-18.95% at 600 °C, and 6.95-11.33% at 650 °C (Fig. 4) for the three feed stocks, these ranges could be used as an index to establish the degree of biochar carbonization (Gómez et al, 2016; Volpe et al., 2017; Crombie. et al., 2013; Li et al, 1999). The volatilization, pyrolysis, and carbonization of RH in the continuous reactor were faster than those of CS and FB, which might be related to its lower lignin and higher volatile contents (Burhenne et al,2013). The RHC could be used to improve soil properties(Xie et al, 2017), and would be less suitable as a fuel, due to the high ash content associated with it. On the other hand CSC and FBC could be used as either soil amendment or as fuels for rural clean heating, due to their lower heating value ranging from 24.89 to 27.82 MJ/kg (Sugumaran et al.,2010).

Fig. 2 Characterization of the rice husk char (RHC), cotton stalk char (CSC), and fruit branch char (FBC) at the three pyrolytic temperatures.

The Van Krevelen diagram shown in Fig. 3 can be used for the initial biochar evaluation as a soil amendment and as a fuel. The molar H/C_{org} and O/C_{org} ratios could provide some information regarding biochar stability (Crombie. et al., 2013) and fuel properties (Van, 1950), in which C_{org} represented organic carbon atom. The molar H/C_{org} and O/C_{org} ratios of the three biochars all decrease with increasing pyrolysis temperature while the properties of biochar approach those of coal (Wu et al., 2012). The H/C_{org} ratio is correlated with the degree of thermochemical conversion and with fused aromatic ring structures formed in the process. The upper H/C_{org} limit of 0.7 has been proposed as a threshold for biochar capable of storing carbon (IBI, 2014).

The RH, CS, and FB before pyrolysis are well outside the delimited area, so that they are easy to degrade in soil. The molar O/C_{org} ratio describes the stability of

biochar. The oxygen content can drive chemical reactions and thus degradation potential (Spokas, 2010). The low molar O/C_{org} ratios generate a product with stable carbon. The ratios below 0.2 are typically the most stable, with an estimated half-life exceeding 1000 years; ratios between 0.2 to 0.6 could have intermediate half-lives varying from 100 to 1000 years (Spokas, 2010). The O/C_{org} of RHC, CSC, and FBC are between 0.2 to 0.6, therefore, quite long half-lives are expected, suggesting that these would be helpful for carbon sequestration as a response to climate change.

Fig. 3 Van Krevelen diagram of biomass and biochar produced at pyrolysis temperatures of 550, 600 and 650 °C.

3.1.2 Pyrolysis gas properties

Pyrolysis gas is considered a clean energy source due to its renewable origin.

Fig.4 shows the pyrolysis gas composition obtained by pyrolysis of RH, CS, and FB at the three different pyrolysis temperatures. The main gases generated by slow pyrolysis were CO , CO_2 , light hydrocarbons, and H_2 . While H_2 and CH_4 consistently

increased with increasing temperature, the C₂-C₆ hydrocarbons increased from 550 °C to 600 °C, then decreased from 600 °C to 650 °C. This is likely due to the partial cracking of C₃-C₆ hydrocarbons at the higher pyrolysis temperatures (Taghvaei et al.,2013). For the three feedstocks, the highest LHV of gases was achieved at the pyrolysis temperature of ~600 °C.

Air retained between feedstock particles provided N₂ while O₂ mainly arose from air leaking into the system from the discharge of biochar despite a slightly positive pressure environment in the reactor. The overall tendency was for contents of the N₂ and O₂ to decrease with increasing pyrolysis temperature, as a result of the increasing volume of pyrolysis gases. The LHV of the pyrolysis gas varied from 17.10-19.57 MJ/Nm³ for RH, 18.01-20.19 MJ/Nm³ for CS, and 18.42-18.90 MJ/Nm³ for FB.

Fig. 4 Gas composition (V/V%) from the pyrolysis of rise husks (RH), cotton stalks (CS) and fruit branches (FB) versus different temperatures.

3.2 Product yields and energy balance assessment

3.2.1 Mass distribution of pyrolysis products

The mass distribution of different fractions produced by slow pyrolysis typically changes depending on residence time, particle size, and pyrolysis temperature. In order to remove any variability associated with the residence time and particle size,

the mean residence time was pre-set as 30 min based on preliminary tests and previous studies ([Cong et al, 2018](#)) and the particles of comparable size were used, as introduced in *Section 2.1*.

Table 2 shows the variation of the pyrolysis product yields at different pyrolysis temperatures. As reported by other researchers, higher temperatures clearly increased the volatile fraction during slow pyrolysis ([Rezaei et al., 2014](#); [Crombie et al., 2014](#); [Crombie et al., 2015](#)). The pyrolysis gas yields varied from 29.7-31.8 % at 550°C, 33.5-35.6 % at 600°C, and 35.8-37.7% at 650°C. Meanwhile, the biochar yields decreased at higher temperature, similar to the liquid fraction. These behaviors can be attributed to an increase in devolatilization of organic material and secondary cracking reactions of condensable vapors at higher temperatures ([Basu, 2010](#)).

All three feedstocks yielded relatively high yields of biochar. This is attributed to the relatively high lignin content in FB and CS, as presence of lignin promotes char formation more than cellulose or hemicellulose (Watkins et al., 2015; ([Stefanidis et al., 2014](#))). The biochar yields of RH was high due to its high ash content. The pyrolysis liquids were completely recovered from the multistage condenser and spray tower, and the percentage of vinegar-like fraction and bio-oil phases was measured. The bio-oils accounted for ~14%-17% of the total liquid mass. The LHVs of bio-oil were ~24.3 to 28.7 MJ/kg under different reaction conditions.

Table 2: Product yields in the pyrolysis process for rice husk (RH), cotton straw (CS), and fruit branch (FB) biomass at three temperatures.

Feedstocks	Pyrolysis temperature/°C	Yields(wt%)		
		Biochar	Pyrolysis gas	Liquid
Rice husk	550	36.70	31.80	31.50
	600	34.80	34.50	30.70
	650	32.90	36.80	30.30
Cotton stalk	550	35.60	30.50	33.90
	600	32.10	35.40	32.50
	650	31.00	37.70	31.30
Fruit branch	550	37.50	29.70	32.80
	600	33.30	35.60	31.10
	650	32.20	37.10	30.70

3.2.2 Energy balance

The energy balance assessment mainly considers the input energy and output energy of the pyrolysis process. The input energy contains feedstock energy and heating energy, and the output energy is composed of product energy and energy losses. The heating energy for the pyrolysis process depends on several factors, such as energy losses, pyrolysis temperature, type of feedstock, and residence time. The process energy balance can be expressed as shown in eq. 1

$$Q_{in} = Q_{out}$$

or

$$Q_{feedstock} + Q_{heating} = Q_{bc} + Q_{sg} + Q_{pl} + Q_{dh} \quad (1)$$

where all values are in units of MJ and $Q_{feedstock}$ is chemical energy of the feedstock; $Q_{heating}$ is the external heating energy; Q_{bc} , Q_{sg} , and Q_{pl} are the chemical energies of the products for biochar, pyrolysis gas, and oil, respectively; Q_{dh} is dissipating heat, including dissipating heat from products (sensible heat) and equipment; and Q_{in} and Q_{out} are input and output energies of the system, respectively.

Considering cotton stalks at 600 °C for example, the feedstock and product energy as well as the heat parameter values are shown in Fig. 5. Note that all data were calculated based on 1 kg of cotton stalks. The biochar energy (Q_{bc}), pyrolysis gas energy (Q_{sg}), and bio-oil energy (Q_{pl}) were 8.61, 6.62, and 1.13 MJ, respectively. The heating energy calculated by the reused quantity of the oil and pyrolysis gas was 4.31 MJ. Dissipating heating (Q_{dh}) calculated according to eq 1 was ~5.34 MJ.

Energy conversion efficiency (η) was employed to evaluate energy transformation in the pyrolysis system, defined as the ratio of useful output energy to input energy (Gómez et al, 2016). This is described in eq 2

$$\eta = \frac{Q_{bc} + Q_{sg} + Q_{pl}}{Q_{feedstock} + Q_{heating}} \quad (2)$$

where the abbreviations are as indicated for eq. 1. The energy conversion efficiency according to data in Fig. 5 indicates that 74.8% of the total energy input can be

transferred into the products, which was similar to that observed by other researchers (Gómez et al, 2016; Yang et al, 2016). Under these conditions, a surplus of pyrolysis gas (51.9%) was not used for the self-sufficient system that reused all oil and part of the pyrolysis gas.

Fig. 5 Sankey diagram of system energy balance with cotton stalk as feedstock and pyrolysis temperature of 600 °C. All values are in units of MJ, and $Q_{\text{feedstock}}$, Q_{bc} , Q_{sg} , and Q_{pl} , are chemical energy of the feedstock, the biochar, the pyrolysis gas, and the oil, respectively while Q_{heating} , and Q_{dh} ; are the external heating energy and dissipating heat respectively.

3.3 Assessment of a self-sufficient system

3.3.1 Running assessment

Fig.6 shows the temperature profiles in different parts of the kiln during kiln operation with cotton stalks as the feedstock, which corresponds to the schematic diagram of system energy balance in Fig. 5. The temperature sensors 1-7 were installed in the heating chamber from front to back as shown in Fig.1. The process could be divided into four stages: pyrolysis gas preheating, oil heating, reused pyrolysis gas heating, and shutting down. The pre-stored pyrolysis gas was used to

warm the system, but the heating-up rate was quite slow due to a small gas burner (Cong et al, 2017). After the system was pre-warmed, the heating system switched to an oil burner and the temperature rise accelerated.

At this stage, the range control method was adopted for the target temperature, so the temperature curves fluctuated rather drastically. After the temperature reached a set value and the system produced pyrolysis gas normally, the heating system switched to the pyrolysis gas burner again, and sensor 4 was used for the temperature-control, achieving a very steady operation. Meanwhile, the surplus of pyrolysis gas in storage increased consistently, indicating that a self-sufficient system even with only pyrolysis gas was undoubtedly feasible, which was in agreement with the energy balance assessment. The last stage was shutting down, steep temperature declined.

Fig. 6 Running curves during kiln operation with cotton stalk as feedstock and pyrolysis temperature of 600 °C.

3.3.2 Biomass decomposition and flue gas emission

In order to better understand the decomposition process in the rotary kiln reactor, the properties of pyrolysis gas during the entire operation were analyzed. As shown in

At the beginning of the operation (30 min), the main gas component was N₂ (up to 45 vol%), but the pyrolysis gas gradually replaced the original air in the reaction chamber as the system was running, so N₂ quickly decreased and the LHV of pyrolysis gas increased accordingly. Approximately 2.5 h after the experiment started, the LHV of pyrolysis gas samples increased to 17.1-21.1 MJ/Nm³. These values were rather stable with little fluctuation mainly caused by air flowing into the system in short periods during char discharge. The pyrolysis gas meets the CNS (Chinese national standard) requirement of fuel for urban residents (GB 50028-2006). Thus, the surplus pyrolysis gas could conceivably be moved to a gas storage facility for local residential use.

The pyrolysis gas variable components affected the conventional burning systems with specific air requirements. The bio-oils had a high water content(>10%w/w) and extremely complex components that also hindered its direct use in conventional burners. Nevertheless, the bio-oil and partial pyrolysis gas were introduced to an improved burner in the pilot-scale plant. According to test reports on the pilot-scale biomass pyrolytic poly-generation plant by a third-party agency, the NO_x (78.6 mg/m³), SO₂ (0 mg/m³), CO (0 mg/m³), and particulate matter (2.4 mg/m³) emission in the flue gas from the heating system met the minimum CNS requirements of “Emission standards of air pollutants for heating boilers(GB13271-2014)”.

3.3.3 Assessment of a self-sufficient system

The pyrolysis temperature was deemed to be important to achieve a self-sufficient

system, and too low pyrolysis temperatures cannot provide pyrolysis gas with sufficient energy to support the heating system (Crombie et al., 2014 Cong et al., 2018). Table 2 shows the required energy for each test calculated by reused pyrolysis gas for the heating system, the available energy in pyrolysis gas and oil, as well as the possibility of a self-sufficient system. A self-sufficient system would be possible only by reusing the pyrolysis gas. The surplus of the pyrolysis gas increased significantly as pyrolysis temperature increased, varying from 24.51-32.23 % for RH, 25.78-35.34 % for CS, and 24.70-39.78% for FB. When all oil and partial pyrolysis gas were reused, the pyrolysis gas surplus increased, varying from 44.13-47.96 % for RH, 51.04-51.96% for CS, and 48.00-56.51% for FB. The fluctuation in the range became smaller because bio-oil yields decreased significantly with increasing temperature.

With an appropriate pre-treatment (drying, crushing, etc.) of common agricultural and forestry residues during the pyrolysis process, a self-sufficient system would be able to sustain the process in energy terms. In addition, surplus energy could be recovered and used to increase the energy conversion efficiency. For instance, sensible heat in the flue gases from the pyrolysis heating system could be used to dry the feedstock or used for torrefaction pretreatment.

Table 2

Preliminary assessment of a self-sufficient system from the gas and liquid fraction of the pyrolysis process for RH, CS, and FB at three temperatures.

Feedstoc	Pyrolysis	Heating energy	Energy of	Energy of bio-	Energy of	Pyrolysis gas
----------	-----------	----------------	-----------	----------------	-----------	---------------

ks	temperature/°	MJ/kg(feedstoc	pyrolysis gas	oil	biochar	surplus of self-	
	C	k)	MJ/kg(feedstoc	MJ/kg(feedstoc	MJ/kg(feedstoc	sufficient system	
			k)	k)	k)	Using Using oil and only part pyrolysi pyrolysi s gas s gas	
	550	4.25	5.63	1.32	6.88	24.51%	47.96%
Rice husk	600	4.42	6.41	0.99	6.41	31.05%	46.49%
	650	4.73	6.98	0.83	6.28	32.23%	44.13%
Cotton	550	3.81	5.13	1.30	9.36	25.78%	51.04%
stalk	600	4.31	6.62	1.13	8.61	34.89%	51.96%
	650	4.58	7.05	1.09	8.31	35.34%	50.47%
Fruit	550	3.97	5.28	1.23	10.08	24.70%	48.00%
branch	600	4.11	6.76	1.17	9.16	38.20%	56.51%
	650	4.36	7.24	1.03	8.74	39.78%	54.01%

4. Conclusions

The influence of temperature on pyrolysis performance and self-sufficiency for a pilot-scale biomass pyrolytic poly-generation plant was assessed. Volatile matter can be used as an index for degree of carbonization of biochar. Pyrolysis gas enriched with H₂, CH₄ and other alkanes, and olefins increased with increasing temperatures

(550-650 °C). The pyrolysis poly-generation system can be energy self-sufficient even using only pyrolysis gas. Energy conversion efficiency of the pyrolytic poly-generation plant was 74.8%. This study showed the potential of pyrolysis poly-generation systems to effectively and cleanly convert abundant agricultural residues into energy and added-value products.

Acknowledgements

The financial support from the Introduction of China Agriculture Research System (No.CARS-02) and International Advanced Agricultural Science and Technology Program (No.2016-X55) are greatly acknowledged. The study also benefitted from the technical support of the Key Laboratory of Energy Resource Utilization from Agriculture Residue, Ministry of Agriculture, China

References

1. Aysu, T., Küçük, M.M., 2014. Biomass pyrolysis in a fixed-bed reactor: effects of pyrolysis parameters on product yields and characterization of products. *Energy* 64, 1002-1025.
2. Barrow, C.J., 2012. Biochar: potential for countering land degradation and for improving agriculture. *Appl. Geogr.* 34, 21-28.
3. Basu, P., 2010. *Pyrolysis and Torrefaction in Biomass Gasification and*

Pyrolysis: Practical Design, vol. 5. Academic Press, Elsevier, UK, 65-164.

4. Burhenne, L., Messmer, J., Aicher, T., Laborie, M.-P., 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *J. Anal. Appl. Pyrolysis* 101, 177-184.
5. Chen, D., Li, Y., Cen, K., Luo, M., Li, H., Lu, B., 2016. Pyrolysis polygeneration of poplar wood: Effect of heating rate and pyrolysis temperature. *Bioresour. Technol.* 218, 780-788.
6. Chen, X., Chen, Y., Yang, H., Chen, W., Wang, X., Chen, H., 2017a. Fast pyrolysis of cotton stalk biomass using calcium oxide. *Bioresour. Technol.* 233, 15-20.
7. Chen, Y., Yang, H., Wang, X., Zhang, S., Chen, H., 2012. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: influence of temperature. *Bioresour. Technol.* 107, 411-418.
8. Chen, Y., Yang, H., Yang, Q., Hao, H., Zhu, B., Chen, H., 2014a. Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation. *Bioresour. Technol.* 156, 70-77.

9. Cong, H., Mašek, O., Zhao, L., Yao, Z., Meng, H., Hu, E., Ma, T., 2018. Slow pyrolysis performance and energy balance of corn stover in continuous pyrolysis-based poly-generation systems. *Energy Fuels* 32, 3743-3750.
10. Cong, H., Yao, Z., Zhao, L., Jia, J., Lan, S., 2017. Development of carbon, gas and oil poly-generation pilot system based on biomass continuous pyrolysis. *Trans. Chinese Soc. Agric. Eng.* 33, 173-179.
11. Cong, H., Zhao, L., Yao, Z., Meng, H., Li, M., 2015. Research status of biomass carbonization technical equipment and its development proposals in China. *China Agric. Univ.* 20, 21-26.
12. Crombie, K., Mašek, O., 2014. Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions. *Bioresour. Technol.* 162, 148-156.
13. Crombie, K., Mašek, O., Sohi, S. P., Brownsort, P., Cross, A., 2013. The effect of pyrolysis conditions on biochar stability as determined by three methods. *Glob Change Biol Bioenergy.* 5(2), 122-131.

14. Crombie, K., Mašek, O., 2015. Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. *Glob Change Biol Bioenergy*, 7(2), 349-361.
15. De Conto, D., Silvestre, W.P., Baldasso, C., Godinho, M., 2016. Performance of rotary kiln reactor for the elephant grass pyrolysis. *Bioresour. Technol.* 218, 153-160.
16. EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.european-biochar.org/en/download>. Version 6.5E of 30th August 2018, DOI: 10.13140/RG.2.1.4658.7043
17. , N., Rosas, J.G., Cara, J., Martínez, O., Albuquerque, J.A., Sánchez, M.E., 2016. Slow pyrolysis of relevant biomasses in the Mediterranean basin. Part 1. Effect of temperature on process performance on a pilot scale. *J. Cleaner Prod.* 120, 181-190.
18. IBI, 2014. International Biochar Initiative, Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, Version 2.0 (27 October 2014); International Biochar Initiative (IBI). Available online:<http://www.biochar->

international.org/sites/default/files/IBI_BiocharStandardsV2.0_final.pdf

(accessed 06.11.14.).

19. Kern, S., Halwachs, M., Kampichler, G., Pfeifer, C., Pröll, T., Hofbauer, H.,
2012. Rotary kiln pyrolysis of straw and fermentation residues in a 3MW pilot
plant - Influence of pyrolysis temperature on pyrolysis product performance. J.
Anal. Appl. Pyrolysis 97, 1-10.
20. Klinar, D., 2016. Universal model of slow pyrolysis technology producing
biochar and heat from standard biomass needed for the techno-economic
assessment. Bioresour. Technol. 206, 112-120.
21. Laird, D.A., Fleming, P., Dedrick, D.D., Horton, R., Wang, B., Karlen, D.L.,
2010. Impact of biochar amendments on the quality of a typical Midwestern
agricultural soil. Geoderma 158, 443-449.
22. Li, A.M., Li, X.D., Li, S.Q., Ren, Y., Chi, Y., Yan, J.H., Cen, K.F., 1999.
Pyrolysis of solid waste in a rotary kiln: influence of final pyrolysis
temperature on the pyrolysis products. J. Anal. Appl. Pyrolysis 50, 149-162.
23. Mašek, O., Buss, W. , Audrey R-P, Lowe, W., Peters, C., Brownsort P., 2018.

- Consistency of biochar properties over time and production scales: a characterisation of standard materials. *J. Anal. Appl. Pyrolysis*.
24. McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. *Bioresour. Technol.* 83, 37-46.
25. Mei, Y., Liu, R., Wu, W., Zhang, L., 2016. Effect of hot vapor filter temperature on mass yield, energy balance, and properties of products of the fast pyrolysis of pine sawdust. *Energy Fuels* 30, 10458-10469.
26. Nguyen, T.L.T, Hermansen, J.E., Nielsen, R.G., 2013. Environmental assessment of gasification technology for biomass conversion to energy in comparison with other alternatives: the case of wheat straw. *J. Cleaner Prod.* 53, 138-148.
27. Ning, S.-K., Hung, M.-C., Chang, Y.-H., Wan, H.-P., Lee, H.-T., Shih, R.-F., 2013. Benefit assessment of cost, energy, and environment for biomass pyrolysis oil. *J. Cleaner Prod.* 59, 141-149.
28. Rezaei, P.S., Shafaghat, H., Daud, W.M.A.W., 2014. Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived

- from biomass pyrolysis: A review. Appl. Catal. A 469, 490-511.
29. Spokas, K.A., 2010. Review of the stability of biochar in soils: Predictability of O/C molar ratios. Carbon Manage. 1, 289-303.
30. Stefanidis, S.D., Kalogiannis, K.G., Iliopoulou, E.F., Michailof, C.M., Pilavachi, P.A., Lappas, A.A., 2014. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. J. Anal. Appl. Pyrolysis 105, 143-150.
31. Sugumaran., P., Seshadri., S., 2010. Booklet on biomass charcoal briquetting: Technology for alternative energy based income generation in rural areas. Shri AMM Murugappa Chettiar Research Centre. Taramani, Chennai – 600113.
http://www.amm-merc.org/publications/biomasscharcoalbriquetting_english.pdf.
32. Taghvaei, H., Jahanmiri, A., Rahimpour, M.R., Shirazi, M.M., Hooshmand, N., 2013. Hydrogen production through plasma cracking of hydrocarbons: Effect of carrier gas and hydrocarbon type. Chem. Eng. J. 226, 384-392.
33. Van Krevelen D.W., 1950. Graphical-statistical method for the study of

- structure and reaction processes of coal. *Fuel* 29, 269-284.
34. Volpe, M., Fiori, L., 2017. From olive waste to solid biofuel through hydrothermal carbonisation: The role of temperature and solid load on secondary char formation and hydrochar energy properties. *J. Anal. Appl. Pyrolysis*. 124, 63-72.
35. Wan, Y., Zhang, K., Dong, Z., Hu, J., 2013. Distribution is a major factor affecting bioaccumulation of decabrominated diphenyl ether: Chinese sturgeon (*Acipenser sinensis*) as an example. *Environ. Sci. Technol.* 47, 2279-2286.
36. Watkins, D., Nuruddin, M., Hosur, M., Tcherbi- Narteh, A., Jeelani, S., 2015. Extraction and characterization of lignin from different biomass resources. *J. Mater. Res. Technol.* 4, 26-32.
37. Wu, K.-T., Tsai, C.-J., Chen, C.-S., Chen, H.-W., 2012. The characteristics of torrefied microalgae. *Appl. Energy* 100, 52-57.
38. Xie, Y., Zhang, L., Zhi, H., Sun, M., Yingchao, L. I., & Shen, G., 2017. The passivation of pb,as,cr,cd and the effects of paddy after applying biochar

- combined with fertilizer. *Journal of Fudan University*. 56(2), 228-232.
39. Yang, H., Liu, B., Chen, Y., Chen, W., Yang, Q., Chen, H., 2016. Application of biomass pyrolytic polygeneration technology using retort reactors. *Bioresour. Technol.* 200, 64-71.
40. Zhang, X., Che, Q., Cui, X., Wei, Z., Zhang, X., Chen, Y., Wang, X., Chen, H., 2018. Application of biomass pyrolytic polygeneration by a moving bed: Characteristics of products and energy efficiency analysis. *Bioresour. Technol.* 254, 130-138.
41. Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. *Journal of Hazard. Mater.* 256-257(1), 1-9.