IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

Virginia Mallow as an energy crop - current status and energy perspectives

To cite this article: S Szwaja *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **214** 012078

View the article online for updates and enhancements.

This content was downloaded from IP address 180.117.128.145 on 10/10/2019 at 01:43

Virginia Mallow as an energy crop - current status and energy perspectives

S Szwaja[1,*], A Magdziarz[2], M Zajemska[1], A Poskart[1], D Musiał[1]

[1] Czestochowa University of Technology, Armii Krajowej 21 Av., 42-201 Czestochowa, Poland
[2] AGH University of Science and Technology, Mickiewicza 30 Av., 30-059 Krakow, Poland

E-mail: szwaja@imc.pcz.czest.pl

Abstract. Currently, the energy crops are designed as promising renewable energy source. The most popular are Miscanthus Giganteus, willow and Virginia mallow. They are well known as plans, but use as a fuel in energy production still needs more investigations. It results from some disadvantages such as biological degradation, low bulk density and low energy density of Virginia mallow. That is why, pre-treatment processes are required to enhance combustible properties. Thus, this paper demonstrates the current state and energy perspectives of Virginia mallow which can be one of the most promising energy crops in Poland. The study of Virginia mallow focuses on combustion characteristics of torrefied biomass using both experiments and modelling. This energy crop was torrefied using TGA apparatus. The studied biomass was characterized in terms of its ultimate and proximate analysis. After the torrefaction process of Virginia mallow, improvements in energy properties were observed. The impact of torrefaction was confirmed by enhancing fuels properties (higher carbon content, and HHV, lower moisture content, lower ratio O/C). The Chemkin calculations showed changes in composition of the main evolved gaseous products.

1. Introduction

Biomass is still the most promising alternative energy source which can replace fossil fuels for greener energy generation. Biomass is considered as renewable fuel because it is reproducible whereas fossil fuels do not, that is why it is named a “carbon neutral” fuel. Biomass used as a fuel covers a wide range of materials. There are mainly wood, straws, agriculture residues, organic wastes, as well as sewage sludge [1-3]. The following three kinds of fuels can be produced from biomass: gaseous (e.g. biogas, syngas, torgas, producer gas), liquid (e.g. alcohols, biodiesel, biooil) and solid (charcoal and torrefied biomass). Besides a great energy potential, biomass has some disadvantages influencing on combustion process. The most important are: relatively high moisture content, ease of biological degradation, nonhomogeneous chemical structure, bulky and inconvenient form, and additionally the problems with handling, storing and transportation [4]. These features of biomass require the necessity of conversion raw biomass to reduce mentioned disadvantages enhancing its properties. This can be achieved through pre-treatment processes. Several pre-treatment methods can be applied to improve biomass properties: dewatering, drying, torrefaction, hydrothermal carbonization, and slow pyrolysis [5]. As was reported by Wilk and Magdziarz [4,5] the pre-treatment processes not only improve carbonization of biomass (higher HHV and energy density, a lower O/C ration and moisture content)

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

but also the obtained material is easier to grind and is hydrophobic that lead it to be to be a more friendly fuel for thermal processes.

In the recent years, in Poland, the interest of energy crops is still growing. The most popular are Miscanthus, Virginia mallow, willow and oilseed rape. The main properties that should characterize plants used for energy purposes are as follows: large annual growth with little or no fertilizer needs, disease and pest resistance, low requirements for growing, and the ability to mechanize field work on plantation and biomass harvesting. Additionally, the important parameter is high energy yields per unit of area [6].

Virginia mallow is a plant which is attracting attention as potential energy crop. Virginia mallow came from the United States to Poland in the 1950s [7]. In the studies of Borkowska and Molas [7, 8] the cultivation of Virginia plant was presented. They studied the influence of seed dressing on height of biomass' yields, achieving significant increase in biomass yields and production in energy per hectare. Virginia mallow is lignocellulosic biomass consisting of varied structural compounds. The detail composition and structural investigations were presented by Damm et al. [9]. The structure of plant is important factor that determines lignocellulose recalcitrance and significantly influences on treatment processes (torrefaction, fermentation, biogas production). Siaudinis et al. [10] showed that Virginia mallow can be used as a solid biofuel because the main parameters of this plant satisfy the requirements for solid biofuels. Moreover, the study of hydrothermal depolymerization of Virginia mallow by using the microwave radiation as a potential method for substrate pre-treatment before the process of methane fermentation, was reported by Zieliński et al. [11]. Figure 1 presents the possible paths of Virginia mallow conversion. Additionally, it should be mention that Virginia mallow is energy crop with wide range potential plant, which can be used as a renewable energy source, fertilizer in agriculture, substrate in paper industry as well as cattle feed. Unfortunately, all these applications needs more investigations.

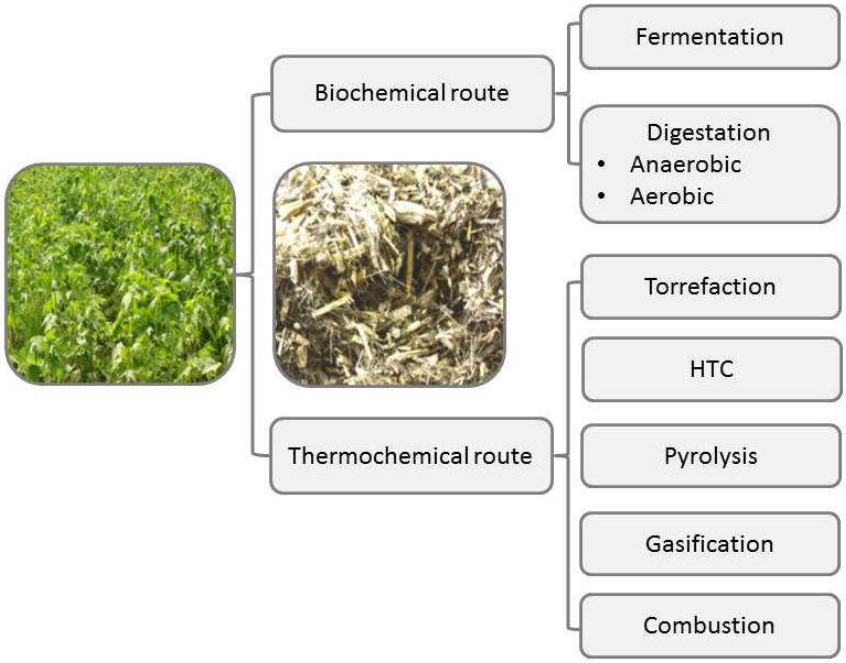


Figure 1. Possible routes of Virginia mallow conversion.

Taking into account the current state about Virginia mallow, in this study the main objective was to investigate the torrefaction process of Virginia mallow supported by Chemkin calculations to enable a better understanding of this process. Thus, proximate and ultimate analysis of raw and torrefied

Virginia mallow was investigated. Authors believe that energy application of Virginia mallow is important and novel because this topic still needs investigations.

2. Material and methods

Viginia mallow was used in the experiments in this study. The proximate analysis of raw and torrefied Viginia mallow were performed according to European Standards (M, moisture content - EN 15934:2012; A, ash content –EN 15403:2011; VM, volatile matter – EN 15402:2011 methods). Elemental Analyser Truespec CHN Leco was used to determine the carbon, hydrogen and nitrogen contents. Simultaneous determination of C, H and N is based on the Dumas method of combustion, also referred to as the method of high-temperature combustion in oxygen. High temperature (950°C) in combination with the flow of pure oxygen results in a rapid and efficient burning of the fuel analyzed.

The thermal conversion of raw Viginia mallow in air and argon atmospheres, respectively, was studied by thermogravimetric analyser using (Netzsch STA 449 F3 Jupiter). The samples were heated in alumina crucibles from ambient temperature up to 700°C at a constant heating rate 10°C/min. The gas flow was 40 ml/min.

The main focus was torrefaction process of Virginia mallow. It was performed using thermal analysis. The raw biomass was heated from ambient temperature to 300°C at a constant heating rate 10°C/min and at a 40 ml/min flow of argon, and next isothermally heated through 1 hour. The thermogravimetric results were presented in the form of TG, DTG and DSC curves. The TG curves reflect the instantaneous weight percentage of the tested fuels in contrast to the initial weight. The DTG curves (weight loss rate) were calculated ($dm/dt = f(t)$, where m – mass sample, t - time). DSC curves presents thermal effects (endo- and exothermic). The TG/DTG/DSC curves were used in order to assess the thermal characteristics of the fuel samples. TGA technique allows to obtain the information about the thermal effects and when thermal processes start and end [12].

Additionally, the numerical calculations of flue gas composition during the torrefation process was carried out using the CHEMKIN-PRO software. CHEMKIN is a product of Reaction Design, which evolved from its origin as a Sandia National Laboratory combustion code Chemkin II. Currently, CHEMKIN is commercial-quality software which enables the simulation of complex chemical reactions for modelling and surface phase chemistry. CHEMKIN-PRO is specifically designed for large chemical simulation applications requiring complex mechanisms. For the calculations the chemical mechanism involving 53 chemical elements and compounds, and 325 chemical reactions were implemented. Chemical mechanism was developed based on a database of the University of Leeds and Department-in of Chemistry, Materials, and Chemical Engineering in Milano and on the basis of the mechanism developed by the Gas Research Institute, University of California (GRI-Mech, version 3.0) and Lawrence Livermore National Laboratory [13, 14].The input file of kinetics data contained elements and compounds as well as a set of reactions enabling calculation of the rate constant of reactions given by the Arrhenius equation. The Perfectly Stirred Reactor (PSR), where combustion takes place in the chamber with ideal mix reagents, was used for calculations. The boundary conditions were as follows: chemical composition of raw and torrefied biomass (Table 1), mass loss based on TGA results, average mass loss of the fuel during time period: 0.000000024 do 0.0000021 g/s, temperature of reactor 300°C, atmosphere: argon, fluxes of argon in the reactor: constant and equal to 40 ml/min, residence time: 1 h.

3. Results and Discussion

In this study, the effect of torrefaction at 300°C through 1 hour on Virginia mallow properties was analysed. Additionally, the authors have focused on numerical calculations of gaseous compounds generated during torrefaction process. The results of proximate and ultimate analysis of raw and torrefied Virginia Mallow are given in the Table 1.

The most important parameter in torrefaction process is moisture content. After undergoing torrefaction, it was observed the significant reduction of moisture, from 5.14% up to 1.75%, whereas ash content had increased more than two times.

Torrefied Virginia mallow characterises higher carbon content and higher HHV (up to 67%). Carbon content had increased c.a. 70%. Consequently, the hydrogen content was decreased. The impact of torrefation process on properties of raw biomass is also well seen by H/C and O/C ratios. The hydrogen and oxygen contents of torrefied biomass decreased resulting in decreased H/C and O/C ratios from 1.62 to 0.80, and 0.69 to 0.28 respectively. The decreased of H/C and O/C confirms the advantage of torrefaction process giving product with high carbon content and calorific value, and less moisture content, which can be named hydrophobic material.

Table 1. Proximate and ultimate analysis of raw and torrefied Virginia Mallow (content of M-moisture, VM – volatile matter, A – ash, C – carbon, H – hydrogen, N – nitrogen, HHV – higher heating value).

	Proximate analysis			Ultimate analysis			
Sample	M, %	VM, %	A, %	C, %	H, %	N, %	HHV, MJ
Raw biomass	5.14	84.04	1.71	48.41	6.55	0.44	15.985
Torrefied biomass	1.75	54.00	4.50	68.79	4.62	0.76	23.745

Figures 2 and 3 show the mass change (TG curve), derivative thermogravimetric (DTG curve) and thermal effects (DSC curve) up to 700°C in air and argon atmospheres, respectively. The combustion process of raw Virginia mallow resulted in a mass loss of c.a. 95% at 700°C. The loss of moisture content was observed in the first step of the process up to 150°C. The main thermal degradation took place in the temperature range 220 – 480°C, where the combustion process was. This process had gone into two stages, what was observed in the form of two peaks at DTG (313.2 °C and 398.72 °C) where the rate of the reactions was the highest. Moreover, two exothermic peaks were observed, too confirming combustion process. This main step is connected with degradation of basic organic compounds (e.g. hemicellulose, cellulose, and lignin). Mass loss occurred due to release of gaseous products of combustion. At 700°C c.a. 5% of residue was obtained, what confirmed the low ash content of Virginia mallow. The thermogravimetric analysis allowed to analysis how the combustion process of Virginia mallow took place, and it was observed that this biomass has good reactivity and the combustion process was ended c.a. 500°C.

Comparing the thermal degradation in air (N_2/O_2) and argon (Ar), it was observed quite different character of TG, DTG and DSC curves. Itindicates that thermal processes took place in other mechanisms. The most important differences are observed in the second stage. It could be noticed that there was one main DTG peak, furthermore there were no evident endo- and exothermic effects. It could be assumed that one fuzzy exothermic peak was observed in studied temperature range. The residual matter was c.a. 30% at 700°C.

Figure 4 presents isothermally heating of Virginia mallow 300°C through 1 hour in argon atmosphere to study the torrefaction process. Based on TG curve it could be observed that torrefaction, with significant mass loss, had place in the first 20 min. With the increase of residence time slightly mass loss was observed. It could suggest that in the case of Virginia mallow the 0.5 hour of torrefaction residence time could be enough.

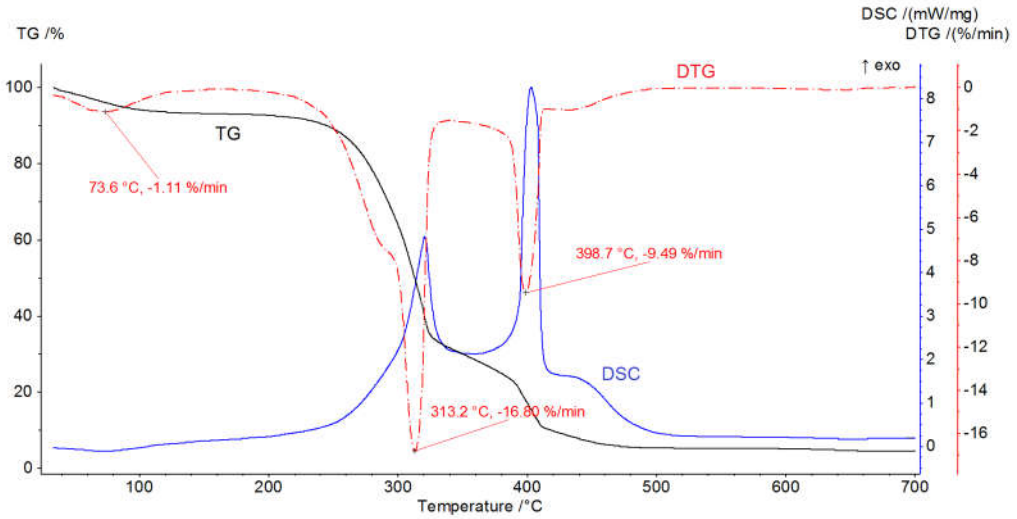


Figure 2. TG, DTG and DSC curves for raw Virginia mallow (B) at 10°C/min heating rate in air atmosphere.

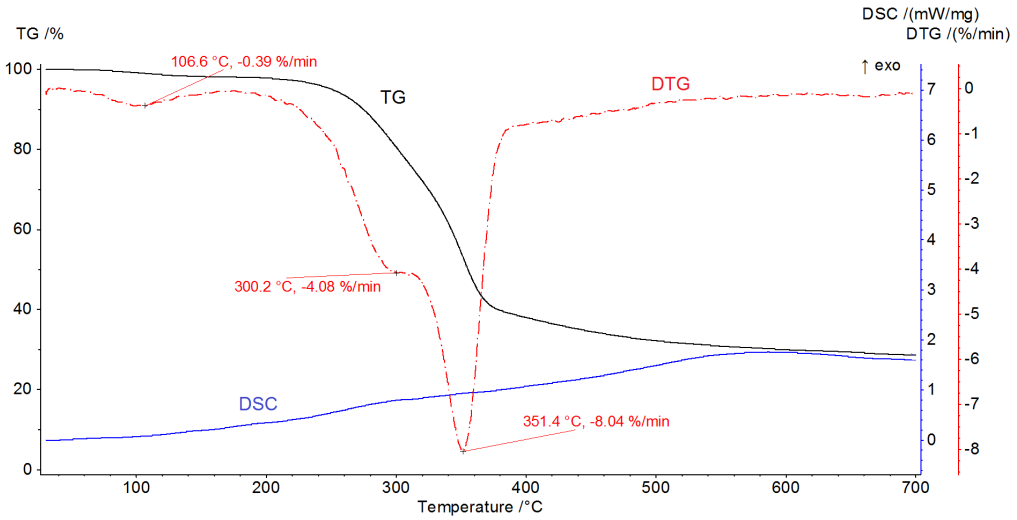


Figure 3. TG, DTG and DSC curves for raw Virginia mallow (B) at 10°C/min heating rate in argon atmosphere.

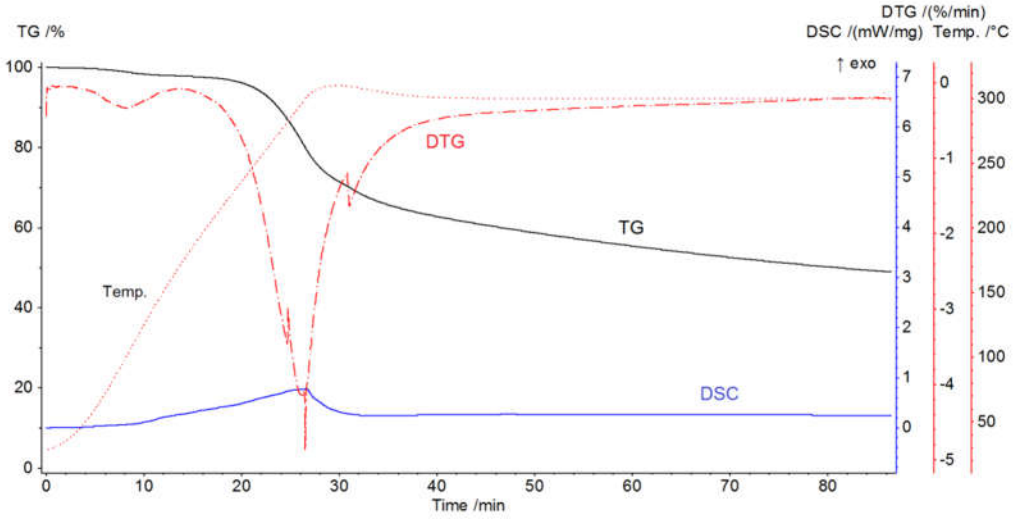


Figure 4. TG, DTG and DSC curves for raw Virginia mallow (B) at isothermally heated at 300°C through 1 h.

The torrefaction is connected with the release of gaseous compounds during process. Chemkin allowed to calculate these compounds based on TGA experimental results (Figure 4). The Figure 5 presents a comparison of H_2, H_2O CO, and CO_2 mole fractions as a function of temperature. The main emissions of H_2, H_2O CO, and CO_2 were observed up to 40 min, what was connected with the decomposition of structural compound during the torrefaction. In this range of time the highest emission was observed for H_2 and CO. They could be the products of decomposition of organic compounds. With the increase of time, the CO_2 and H_2O mole fractions had not changed, whereas the changes in mole fraction of CO and H_2 were detected up to 70 min. Additionally, the emissions of organic compounds such as CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6, CH_2CO, C_2H_5OH, CH_3COOH were determined. Generally it could be assumed that they were generated within first 40 min of torrefaction process. But, it should be highlighted that the mole fractions of these compounds were in the range 10^{-5} to 10^{-8}. The Table 2 presents the detail mole fraction (average value up to 40 min) of the most important organic compounds.

Table 2. Average value of mole fractions of gaseous species generated during the torrefaction process of Viginia mallow.

Gas phase	Mole fraction	Gas phase	Mole fraction
CH_2O	$2.97 \cdot 10^{-4}$	C_2H_4	$2.00 \cdot 10^{-5}$
CH_4	$6.64 \cdot 10^{-8}$	CH_3COOH	$1.30 \cdot 10^{-15}$
C_2H_2	$1.71 \cdot 10^{-4}$	CH_3OH	$1.09 \cdot 10^{-4}$
C_2H_6	$3.87 \cdot 10^{-5}$	C_2H_5OH	$1.18 \cdot 10^{-4}$
C_3H_8	$1.75 \cdot 10^{-5}$	C_3H_6	$4.70 \cdot 10^{-6}$
C_6H_6	$8.66 \cdot 10^{-7}$	C_6H_5OH	$6.40 \cdot 10^{-7}$

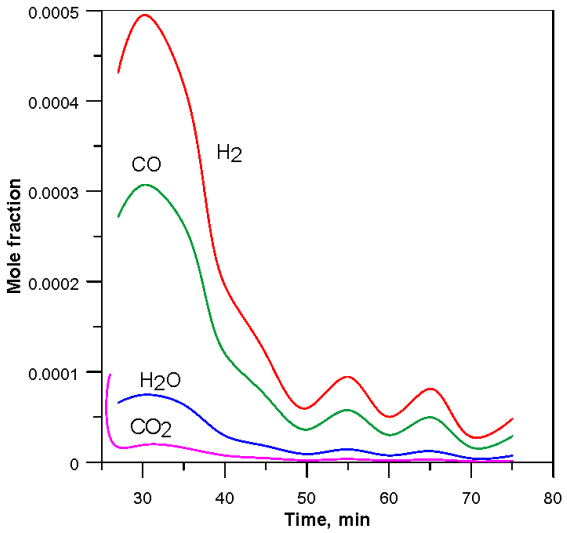


Figure 5. Mole fractions of gaseous species as a function of time generated during the torrefaction of Virginia mallow.

4. Conclusions

This paper aimed to present Virginia mallow as an energy crop, which could be considered as alternative renewable energy source. As found, the physical and chemical properties of Virginia mallow provide satisfactory prospects for its energetic utilization. Additionally, the torrefation process improving combustion properties of Virginia mallow is possible to conduct. The torrefaction process was done and it was confirmed the enhancing fuels properties such as higher carbon content and HHV, lower moisture contentand lower ratio O/C. Based on the Chemkin calculations, changes in the mole fractions of the main evolved products H_2, CO, CO_2, H_2O were observed. On the basis of TGA results of torrefaction process and Chemkin calculation one can assume that residence time of 0.5 h allows to obtain good carbonaceous product. From this point, there is no need to extend residence time over that one proposed, because it does not change significantly the properties of torrefied Virginia mallow. The presented investigations are promising studies but preliminary ones. Thus, they require more studies to better understand the torrefaction process of Virginia mallow.

Acknowledgements

This work was performed within the project entitled: "Dietary, Power and Economic Potential of Sida Hermaphrodita Cultivation on Fallow Land", realized within the frame of the BIOSTRATEG program; contract number: BIOSTRATEG1/270745/2/NCBR/2015 financed by the National Centre for Research and Development, Poland.

References

[1] Fernández R G, García C P, Lavín A G, de las Heras J L B, 2012, *Fuel Processing Technology* **10** 316–26.
[2] Khan A A, de Jong W, Jansens P J, Spliethoff H, 2009, *Fuel Processing Technology* **90** 21–50.
[3] Saidur R, Abdelaziz E A, Demibras A, Hossain M S, Mekhilef S, 2011, *Renewable and Sustainable Energy Reviews* **15** 2262–2289.
[4] Wilk M, Magdziarz A, Gajek M, Zajemska M, Jayaraman K, Gokalp I, 2017, *Bioresource Technology* **243** 304–314.
[5] Wilk M, Magdziarz A, 2017, *Energy* **140** 1292–1304.
[6] Fernando A L, Duarte M P, Almeida J, Boléo S, 2010, *Biofuels, Bioproducts and Biorefning* **4** (6) 594–604.

[7] Borkowska H, Molas R, 2012, *Biomass and Bioenergy* **36** 234-240.
[8] Borkowska H, Molas R, Kupczyk A, 2009, *Polish Journal of Environmental Studies* **18**(4) 563–568.
[9] Damm T, Pattathil S, Günl M, Jablonowski N D, O'Neill M, Grün K S, Grande P M, Leitner, U. Schurr W, Usadel B, Klose H, 2017, *Carbohydrate Polymers* **168** 94–102.
[10] Jasinskas G A, Sarauskis E, Steponavicius D, Karcauskiene D, Liaudanskiene I, 2015, *Energy* **93** 606–612.
[11] Zieliński M, Nowicka A, Dębowski M, 2017, *Energy Procedia* **105** 694 – 699.
[12] Magdziarz A, Wilk M, Straka R, 2017, *Journal of Thermal Analysis and Calorimetry* **127** 1339-1349.
[13] Corbetta M, Frassoldati A, Bennadji H, Smith K, Serapiglia M J, Gauthier G, Melkior T, Ranzi E, Fisher E M, 2014, *Energy & Fuels* **28** 3884–3898.
[14] Ranzi E, Corbetta M, Manenti F, Pierucci S, 2014, *Chemical Engineering Science* **110** 2–12.