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DI PERUGIA

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Sviluppo Sostenibile, Tutela dell'Ambiente
e della Salute Umana

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A Novel Lab-Scale Fixed-Bed Pyrolysis Reactor for Biofuel Production from Agro-Waste: Experimental Set-up and Preliminary Life Cycle Assessment Study

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Abstract: The present study reports the features and set-up of a novel lab-scale fixed bed pyrolysis reactor for the production of solid and liquid bio-fuels from waste biomass. The fixed bed reactor is tested by carrying out pyrolysis experiments using two different waste biomasses. Olive tree trimmings (OT) and olive pulp (OP), olive cultivation and olive mill industries residues respectively, are pyrolyzed, under nitrogen atmosphere, between 200 and 650 °C for a residence time of 0.5 h. The OT and OP pyrolysis chars were characterized in terms of mass yields, high calorific values (HHVs), proximate and elemental analysis. Char mass yields, on a dry basis (d.b.), decreased from 91 to 23 wt% and from 93 to 32 wt% for OT and OP respectively with increasing pyrolysis temperature. HHVs increased between 200 and 325 °C up to 27.71 and 31.42 MJ/kg for OT and OP respectively but start decreasing when further rising the pyrolysis temperature to 24.36 and 28.44 MJ/kg for OT and OP respectively at 650 °C. The novel pyrolysis system set-up shows to be an efficient and effective tool to test biomass pyrolysis at lab scale level and adapt to produce high energy dense bio-chars for solid fuel applications starting from waste biomass. A preliminary life cycle assessment (LCA) of the pyrolysis process is carried out for the two examined waste biomasses, for calculating the life-cycle environmental impacts for the production of 1 MJ of thermal energy by pyro-char combustion.

Keywords: Pyrolysis, fixed bed reactor, waste biomass, biofuel, life cycle assessment.

1. Main information

The increasing concern for the environmental impacts associated to the production of power and heat using fossil fuel sources has boosted, in the last years, the interest for developing new reliable technologies for increasing the production of energy from renewable and sustainable sources. The development of Photovoltaic and Eolic technologies and the large amount of PV and Eolic power installed in the last few years have contributed to reach the 2020 Italian renewable energy production targets. Nevertheless it is clear that PV, Eolic plants together with other not programmable renewable energy production technologies, cannot cover the new EU 2030 targets [1].

For what stated above the energy sector is now more and more driving its attention to energy conversion valorization of waste biomass. Residual biomass is globally available in large quantities and its energy exploitation could, on the one hand provide a fossil carbon neutral, more sustainable and programmable power and heat source and on the other hand, contribute to mitigate the problem of environmentally safe and economically sustainable treatment and disposal of organic waste. Unfortunately the direct use of waste biomass for the production of power and heat is severely hampered by its high moisture content, low energy density and perishability.

Thermochemical conversion of waste biomass as pyrolysis has been largely investigated in the last few years to produce higher energy density and stable solid and liquid biofuels, and/or as pretreatment for biomass gasification and production of activated carbons [2–5].

During pyrolysis, devolatilization of high oxygenated compound, produced by decomposition of the polymeric biomass frameworks, produces a stable and high energy dense solid material (bio-char) that could be used as solid biofuel and a liquid phase (bio-oil) that, when appropriately upgraded, could be used as liquid bio-fuel and/or as precursor for platform chemical compounds and bio-plastic. Several pyrolysis system set-ups have been since now described but most of them have shown to be not easily operated and/or presenting low conversion efficiency [6–8].

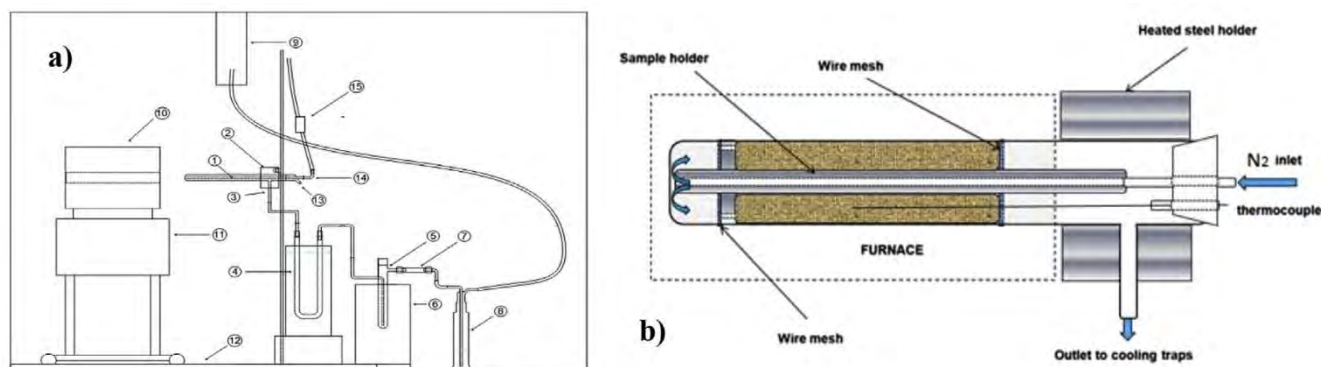
In this study we describe a novel, easily operated lab-scale pyrolysis system set up to test waste biomass pyrolysis reactivity at lab scale. The system allows to produce high homogeneous pyro-char samples by treating up to 10 g d.b. of biomass waste per batch. In order to assess the environmental impacts generated during the bio-char production process in a life cycle perspective, the Life Cycle Assessment methodology is applied according to the international standards of the ISO 14040 series.

2. Materials and Methods

2.1 Fixed bed pyrolysis system set-up

A horizontal fixed-bed type reactor, was purposely design to allow the flow of an inert gas carrier to sweep out the pyrolysis products during reaction. Figure 1 shows a schematic representation of the pyrolysis apparatus (figure 1a) and a schematic representation of the quartz 20 mm OD pyrolysis reactor assembly (figure 1b).

Figure 1a, b. a) Schematic representation of the fixed bed lab scale pyrolysis system; b) schematic representation of the quartz 20 mm OD pyrolysis reactor assembly



The fixed bed lab-scale pyrolysis system consists of a quartz cylindrical reactor 340 mm long and 20 mm internal diameter closed at one end and provided with a 29/32 mm open end. The reactor body is provided with a 8 mm diameter side-arm to drive the pyrolysis vapors and gases to the cooling traps.

A special quartz cap equipped with an 8 mm internal diameter inner tube allows the inert gas flow into the biomass sample during reaction. The quartz cap is equipped with a Rotulex™ fitting for gas inlet and a screw cap to insert a K-type thermocouple. The thermocouple is connected to a data logger to monitor and record the temperature.

Condensable vapors (tars) are formed along the reactor through the biomass bed and remain in gas phase until they leave the hot area and pass through a colder section. To avoid condensation of the vapors before reaching the cooling traps, the reactor system (1) is held by a purposely shaped aluminum heating jacket (2) which keeps a constant temperature of approximately 180 °C to prevent premature condensation of bio-oils.

Vapors and gases formed during the reaction exit the reactor through the side arm connected via a Rotulex™ joint to a gas pipe line directly connected to two traps.

The first trap is a U-shaped tube (4) immersed in a water/ethylene glycol and dry ice bath which allows it to reach a temperature of about -30 °C; the second trap is a glass finger (5) kept at -30 °C by a refrigerating system (6) (Isocal 2140B, Isotech, Colchester, VT, USA).

A glass fiber filter (7) is located downstream of the second trap to avoid the loss of bio-oil which has not condensed in the traps. A water bubbler (8), placed at the end of the system, is used to monitor the correct gas flow into the system. The uncondensed gases are then discharged into an exhaust hood (9).

The quartz reactor, (1) is heated up by an external furnace (Carbolite MTF 12/38/250) (10), that allows it to reach a maximum temperature of 1200 °C. The temperature, the ramp rate, and the residence time are easily set by the control panel of the furnace (11). The furnace is mounted on rails (12) which easily allow it to be slid back and forward, while the reactor is held in place by the heating aluminum jacket. Figure 1b shows the quartz reactor assembly comprising a 20 mm OD quartz tube and a metal 10 mm OD stainless steel tube equipped with an 19 mm steel disc welded at one end to work as biomass sample holder during the pyrolysis experiment.

2.2 Sample preparation, pyrolysis experiments procedure and material characterization

Pyrolysis runs are carried out using olive tree trimmings (OT) and olive pomace (OP), typical olive cultivation and olive mill industries residues. OT were collected fresh from years old trees (holder than 50 years) of the “Moresca” variety in the Enna province during the pruning season, between January and February, while olive pomace, still from the Moresca variety olives, was collected from mill farms of the “two phase decanter” type. After collection, biomass was milled using a knife mill, to a particle size lower than 1 mm, then sieved to select particle size range 425–850 μm portion.

Approximately 10.00 g of feedstock (OT or OP) was weighted to nearest of 0.01 g and loaded into the reactor, which was then closed hermetically. Pyrolysis experiments are carried out at 200, 250, 300, 325 400, 500 and 650 $^{\circ}\text{C}$, under nitrogen (Alphagas 1TM – airliquide) flowing at a rate of 1.5 L/min. Heating rate kept at 50 $^{\circ}\text{C}/\text{min}$, and constant reaction time at the peak temperature of 30 min. To ensure reliability of the data pyrolysis experiments are repeated at least three times and average values of the resulting data are reported. At the end of the reaction time the furnace is promptly slide out the reaction system disassembled and char recovered, weighted for mass yield calculations and stored in a desiccator prior of further analysis and characterizations.

Solid mass yields and energy properties of the pyrolysis products were determined and compared to the values of the raw materials. HHVs are determined through a Calorimeter model “Leco AC 500” following UNI EN 14918:2010 standard method. Solid mass Yields (SY), Energy Yield (EY) and Energy Densification ratio (ED) were calculated as follow (Eq. 1-3):

$$SY = \frac{W_c}{W_{raw}} \quad (1)$$

Where W_c and W_{raw} are respectively the weight of the obtained char, and the weight of the raw, both on a dry basis (d.b.).

$$EY = SY \frac{HHV_c}{HHV_{raw}} \quad (2)$$

where HHV_c and HHV_{raw} are respectively the high calorific values of the char and raw feedstock;

$$ED = \frac{EY}{SY} \quad (3)$$

Proximate analysis, for the determination of volatile matter (VM), ash (Ash) and fixed carbon (FC) carried out by thermo-gravimetric analysis using a “LECO TGA701” TGA instrument, following UNI EN 15148:2010 standard method. Ultimate analyses were done using an Elementar Macro Vario Cube analyzer for simultaneous CHNS determination.

2.3 The Life Cycle Assessment methodology

The LCA study is developed under the following assumptions, described per each LCA stage:

- Goal and scope definition, that includes a description of the product system in terms of system

boundaries (unit processes that are part of a product system), functional unit (quantified performance of a product system for use as a reference unit), impact categories and methodologies for the impact assessment, etc. In detail, the system boundaries are selected according to a “from cradle to gate” approach, thus from the raw materials supply to the bio-char production. The functional unit selected is 1 MJ of thermal energy that can be obtained by combustion of the char.

The energy and environmental indices chosen to assess the life cycle impacts of the functional unit investigated are: global warming potential (GWP), ozone depletion potential (ODP), human toxicity - cancer effects (HTc), human toxicity - non-cancer effects (HTn-c), particulate matter (PM), ionizing radiation - effect on human health (IRh), ionizing radiation - effect on ecosystem (IRE), photochemical ozone formation (POF), acidification (Ac), terrestrial eutrophication (TE), freshwater eutrophication (FE), marine eutrophication (ME), freshwater ecotoxicity (FET), land use (LU), mineral - fossil - renewable resources depletion (RD).

The environmental impact assessment is carried out by means of the ILCD 2011 Midpoint method.

- Life Cycle Inventory analysis, that involves data collection and calculation procedures to quantify resources consumption, air, water and soil emissions. In detail, the inputs of materials and energy sources and the outputs during the pyrolysis process are quantified, information on the biomass transport as well as data on some system components (materials and masses) are collected and elaborated.

- Life Cycle Impact Assessment and interpretation, aimed at calculating and analyzing the final results, expressed as potential environmental impacts, and drawing the conclusions of the LCA study. The final results are calculated for the two examined waste biomasses (OT and OP) and for three different temperatures of the pyrolysis phase (400 °C, 500 °C, 650 °C).

3. Results and discussions

3.1 Char mass yields and energy properties

Table 1 reports the OT and OP char mass yields at different pyrolysis temperatures and their energy properties in terms of HHV, EY and ED. As expected both OT and OP solid yields decrease with pyrolysis temperature due to the devolatilization of volatile oxygenated compounds. The solids mass yields reach the values of 26.4 and 33.3% d.b. for OT and OP respectively. HHVs show different trends, on the one hand HHV values increase both for OT and OP with temperature in the range 200-325 °C reaching the value of 27.71 and 31.42 MJ/kg respectively, on the other hand the HHV values decrease within the temperature range of 400-650 °C down to 24.26 and 28.44 MJ/kg for OT and OP respectively. This behavior can be explained looking at the data reported in table 2.

Table 1. Solid mass yields and high calorific values of OT and OP raw and pyro-char samples.

Sample	SY % (d.b.)	HHV MJ/kg	EY %	ED %	Sample	SY % (d.b.)	HHV MJ/kg	EY %	ED %
<i>OT raw</i>	-	19.81	-	-	<i>OP raw</i>	-	22.60	-	-
<i>CH-OT 200</i>	92.8	20.88	97.8	105.4	<i>CH-OP 200</i>	91.2	22.78	91.9	100.8

CH-OT 250	74.4	23.33	87.6	117.8	CH-OP 250	72.9	24.38	78.6	107.9
CH-OT 300	51.2	27.21	70.3	137.4	CH-OP 300	56.2	28.58	71.1	126.5
CH-OT 325	48.9	27.71	68.4	139.9	CH-OP 325	50.1	31.42	69.7	139.0
CH-OT 400	38.5	27.32	53.1	137.9	CH-OP 400	37.7	30.26	50.5	133.9
CH-OT 500	28.7	26.84	38.9	135.5	CH-OP 500	32.4	28.72	41.2	127.1
CH-OT 650	26.4	24.36	32.5	123.0	CH-OP 650	33.3	28.44	41.9	125.8

Table 2 reports the results of proximate and elemental analysis, where we can see that with increasing pyrolysis temperature volatile matter decrease and fixed carbon content increase in the chars testifying an increase in carbonization of the samples with temperature. The increase in carbonization with temperature is however, accompanied with an increase of ash content of the chars and at the most severe conditions (400-650 °C) also with an evident decrease in H element content. The decrease of hydrogen element together with the increase of minerals (ashes) in the most carbonized samples (400-650 °C) is responsible for their decrease in energy properties. Energy densification ratios of chars reach their maximum values at 325 °C. ($ED_{CH-OT\ 325} = 139.0\%$; $ED_{CH-OP\ 325} = 139.9\%$). Char produced at 325 °C show high heating values and ash content ($CH-OT_{ash325} = 8.2\%$ d.b. and $CH-OP_{ash325} = 6.8\%$ d.b.) compatible with their possible use biochar-coal co-fired power plants [9,10].

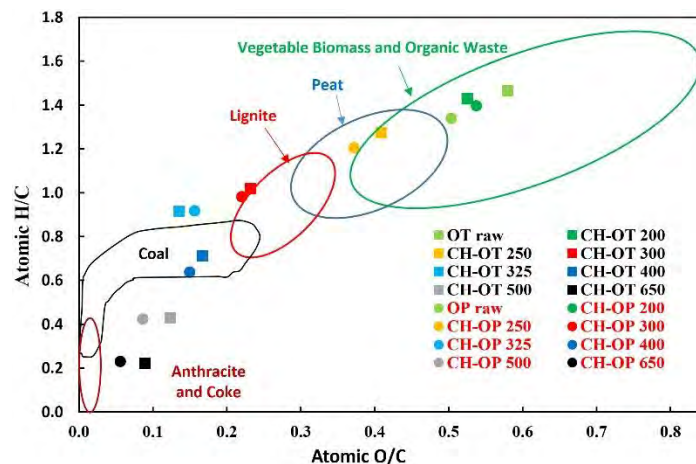
Table 2. Proximate and elemental analysis (d.b.) of OT and OP raw and pyrochar samples.

Sample	VM %	FC %	Ash %	C %	H %	N %	S %	O*
OT raw	80.1	15.5	4.4	49.27	6.06	2.09	0.16	38.02
CH-OT 200	78.4	16.8	4.8	51.61	6.19	1.12	0.19	36.07
CH-OT 250	73.4	21.9	4.7	56.71	6.06	1.48	0.19	30.83
CH-OT 300	65.4	29.8	4.8	66.71	5.71	1.97	0.23	20.59
CH-OT 325	58.0	33.8	8.2	71.16	5.48	2.24	0.11	12.85
CH-OT 400	39.7	49.4	10.9	67.98	4.07	1.78	0.17	15.08
CH-OT 500	28.8	57.5	13.7	70.44	2.54	1.58	0.19	11.53
CH-OT 650	21.9	63.0	15.1	73.07	1.36	1.60	0.22	8.67
OP raw	75.3	21.4	3.3	52.66	5.92	2.67	0.16	35.29
CH-OP 200	75.5	21.9	2.6	52.54	6.16	2.97	0.10	35.59
CH-OP 250	67.4	29.7	3.0	59.97	6.07	1.23	0.08	29.69
CH-OP 300	51.0	44.4	4.6	68.18	5.62	1.49	0.09	19.99
CH-OP 325	49.6	43.7	6.8	71.23	5.49	1.63	0.09	14.80
CH-OP 400	33.7	57.5	8.9	70.87	3.80	2.26	0.11	14.10
CH-OP 500	23.5	65.3	11.2	75.26	2.68	2.06	0.12	8.64
CH-OP 650	21.0	68.3	10.7	79.59	1.54	2.09	0.13	5.91

*calculated by difference $O = 100 - \text{ash} - C - H - N - S$

The van krevelen diagram (figure 2), obtained by plotting the H/C to O/C atomic ratios evidences the increased degree of carbonization of the OT and OP samples with the pyrolysis temperature. OT and OP chars obtained at temperatures equal or higher than 325 °C start behaving like mineral coal and coke.

Figure 2. Van krevelen diagram for OT and OP raw and char samples



3.2. Life Cycle Assessment of the Pyrolysis System

Table 3 shows the life-cycle environmental impacts of the functional unit, for OT and OP. The results point out that when a temperature of 400 °C is used for the pyrolysis process, the best life-cycle environmental performances are obtained for both the examined biomasses. Furthermore, a comparison of OT and OP reveals better performances for the second biomass.

Table 3. Life-cycle environmental impacts of OT and OP for three different temperatures of the pyrolysis process.

Impact category	OT 400	OT 500	OT 650	OP 400	OP 500	OP 650
<i>GWP (kg CO_{2eq})</i>	6.68E+00	6.97E+00	7.77E+00	6.13E+00	6.19E+00	6.27E+00
<i>ODP (kg CFC-11_{eq})</i>	3.17E-04	3.28E-04	3.60E-04	2.91E-04	2.91E-04	2.91E-04
<i>HTc (CTU_h)</i>	2.49E-06	2.59E-06	2.86E-06	2.28E-06	2.30E-06	2.31E-06
<i>HTn-c (CTU_h)</i>	6.52E-07	6.77E-07	7.48E-07	5.98E-07	6.01E-07	6.04E-07
<i>PM (kg PM_{2.5eq})</i>	3.46E-03	3.61E-03	4.02E-03	3.18E-03	3.21E-03	3.24E-03
<i>IRh (kBq U_{235eq})</i>	1.35E+00	1.41E+00	1.56E+00	1.24E+00	1.25E+00	1.26E+00
<i>IRe (CTU_e)</i>	3.49E-06	3.63E-06	4.03E-06	3.20E-06	3.22E-06	3.25E-06
<i>POF (kg NMVOC_{eq})</i>	1.71E-02	1.78E-02	1.98E-02	1.57E-02	1.58E-02	1.60E-02
<i>Ac (molc H_{+eq})</i>	6.38E-02	6.66E-02	7.43E-02	5.85E-02	5.92E-02	6.00E-02
<i>TE (molc N_{eq})</i>	1.84E-01	1.92E-01	2.15E-01	1.69E-01	1.71E-01	1.73E-01
<i>FE (kg P_{eq})</i>	3.13E-03	3.26E-03	3.61E-03	2.87E-03	2.89E-03	2.92E-03
<i>ME (kg N_{eq})</i>	6.79E-03	7.08E-03	7.88E-03	6.23E-03	6.29E-03	6.36E-03
<i>FET (CTU_e)</i>	1.46E+02	1.52E+02	1.69E+02	1.34E+02	1.35E+02	1.37E+02
<i>LU (kg C_{deficit})</i>	1.37E+01	1.43E+01	1.60E+01	1.26E+01	1.27E+01	1.29E+01
<i>RD (kg Sb_{eq})</i>	2.71E-04	2.81E-04	3.11E-04	2.49E-04	2.50E-04	2.51E-04

5. Conclusions

This study report the main features and preliminary experimental results of a novel fixed-bed lab-scale pyrolysis reactor, demonstrating its effectiveness and reliability for waste biomass pyrolysis test.

The system allows to produce and recover bio-char from biomass and bio-oils (tars) with the use of two cold traps. In this work preliminary results for the production of solid pyrolysis residue from two types of waste biomass are reported and their mass yields and energy properties reported. Recovery and characterization of pyrolysis bio-oils will be reported in a future study. The pyrolysis experiments carried out on two typical Sicilian regional waste biomass: olive tree trimmings (OT) and olive pulp (OP) demonstrate that it is possible to produce high energy dense solid biofuels at relatively low temperature in pyrolysis regime. Both OT and OP chars show best energy properties when reacted at 325 °C for 0.5 h of residence time. OT and OP chars produced at 325 °C show HHV of 27.7 and 31.4 MJ/kg and energy densification ratios of approximately 139 and 140% respectively, thus showing energy properties higher than those of the most common mineral coals used in power plants[10,11].

The Life cycle assessment study of the lab-scale fixed bed pyrolysis set-up presented in this study highlights that, for each examined biomass, 400 °C is the temperature that allows for obtaining the lower environmental impacts. Focusing on the comparison of the two biomasses, the best environmental performances are observed for OP.

The results of the LCA study are a “knowledge basis” to assess the real advantages arising from the bio-char production from waste biomasses and to identify eco-design strategies for improving the environmental performances of the pyrolysis process, in particular for the transition from lab-scale to pilot scale.

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References

1. European Commision A policy framework for climate and energy in the period. *Communication From the Commission To the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions* **2014**, 18.
2. Prins, M.J.; Ptasiński, K.J.; Janssen, F.J.J.G. Torrefaction of wood Part 1. Weight loss kinetics. *Journal of Analytical and Applied Pyrolysis* **2006**, 77, 28–34.
3. Prins, M.J.; Ptasiński, K.J.; Janssen, F.J.J.G. More efficient biomass gasification via torrefaction. *Energy* **2006**, 31, 3458–3470.
4. You, S.; Ok, Y.S.; Chen, S.S.; Tsang, D.C.W.; Kwon, E.E.; Lee, J.; Wang, C.H. A critical review on sustainable biochar system through gasification: Energy and environmental applications. *Bioresource Technology* **2017**, 246, 242–253.
5. Van Der Stelt, M.J.C.; Gerhauser, H.; Kiel, J.H.A.; Ptasiński, K.J. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy* **2011**, 35, 3748–3762.

6. Cousins, A.; Zhuo, Y.; George, A.; Paterson, N.; Dugwell, D.R.; Kandiyoti, R. Development of a bench-scale high-pressure fluidized bed reactor and its sequential modification for studying diverse aspects of pyrolysis and gasification of coal and biomass. *Energy & Fuels* **2008**, *22*, 2491–2503.
7. Dabai, F.; Paterson, N.; Millan, M.; Fennell, P.; Kandiyoti, R. Tar Formation and Destruction in a Fixed Bed Reactor Simulating Downdraft Gasification: Effect of Reaction Conditions on Tar Cracking Products. *Energy & Fuels* **2014**, *28*, 1970–1982.
8. Luz, C.; Cordiner, S.; Manni, A.; Mulone, V. Biomass fast pyrolysis in a shaftless screw reactor: A 1-D numerical model. *Energy* **2018**, *157*, 792–805.
9. Gao, L.; Volpe, M.; Lucian, M.; Fiori, L.; Goldfarb, J.L. Does Hydrothermal Carbonization as a Biomass Pretreatment Reduce Fuel Segregation of Coal-Biomass Blends During Oxidation? *Energy Conversion and Management* **2018**, *IN PRESS*.
10. Raveendran, K.; Ganesh, A.; Khilart, K.C. Influence of mineral matter pyrolysis characteristics on biomass. *Fuel* **1995**, *74*, 1812–1822.
11. Qi, M.; Luo, H.; Wei, P.; Fu, Z. Estimation of low calorific value of blended coals based on support vector regression and sensitivity analysis in coal-fired power plants. *Fuel* **2019**, *236*, 1400–1407.