Evaluation of the Energy Recovery of Composted Materials

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Abstract

Today's medium- and high-income society generates large amounts of household waste that must be treated with associated costs. Household waste, mostly food, comprises fruits, vegetables, and woody cellulosic garden waste. Composting, a complex biodegradation process, of this waste generates high-value humic compounds and a woody lignocellulosic residue that can be valorized in producing renewable fuels. A household compost, composted for six months in the spring and summer seasons, was subjected to solid/liquid extraction processes (water, acetone, methanol, tetrahydrofuran; room temperature) and liquefied with aqueous solutions of H_2SO_4 and NaOH (room and boiling temperature) in order to extract the humic compounds and to convert the cellulosic ligneous. The solid and liquid fractions were characterized by infrared spectroscopy (ATR-FTIR). The solids were characterized by thermogravimetry, and the composition was determined from DTG curves (rate of thermal degradation) considering the pseudo components model (moisture, extractives, hemicellulose, cellulose, lignin, and inorganics). At boiling temperature, the solid materials resulting from the treatment with NaOH and with H2SO4 have been subjected to pyrolysis kinetic studies by thermogravimetry applying the Kissinger equation to each cellulosic lignin pseudo component.

The results showed that the compost treatment with aqueous H_2SO_4 solution at boiling temperature efficiently converts the solid compost residue to generating lignin.

Keywords: Domestic solid waste; composting; liquefaction; lignin; pyrolysis; Kissinger

1. Introduction

For the past few decades, fossil fuels have been chosen to fulfill world energy demands, but since these resources are limited and generally have a negative impact on the environment, recent dramatic developments in renewable energy production occurred. These are supported by policies aiming to change the energy mix,

especially for electricity production [1]. Biomass has a major advantage over other renewable energy sources, as it can be stored and used on demand to give controllable energy. It is therefore free from the weather conditions intermittency, a problem for all other forms of renewable energy [2-4].

Bioenergy source is any fuel derived from biomass – recently living organisms or their metabolic byproducts. Being highly available and diverse, biomass is becoming a promising renewable source due to its capability to be linked with many economic sectors like agriculture, forestry, food processing, paper and pulp and, of course, the energy sector [5]. In order to support the growth of bioenergy, biomass supply has to grow as well, but not all the available biomass from forests and fields can be removed. Agricultural and forest residues and energy crops planted on idle or released cropland are an attractive alternative [4, 6]. Additionally, biomass can be upgraded through conversion processes, like pyrolysis, to increase its value as a fuel.

The energy policies in Portugal have been targeting mainly the development of solar and wind power [5], which may explain the low share of biomass in the energy mix. Much work needs to be done in the Portuguese bioenergy sector, however, an important limitation can be the investment costs and in the specific case of Portugal, there is still lack of governmental support and incentives to ensure the interest from private investors in bioenergy technologies.

Figure below shows the biomass conversion technologies. The final products of the

conversion technologies are used mainly for the production of heat, power, fuels and chemicals, where the unconverted residues can be used for soil amendment. Pyrolysis can be found in the group of thermochemical conversion, along with gasification. Figure 1.1. shows the technology variance for the biomass conversion.
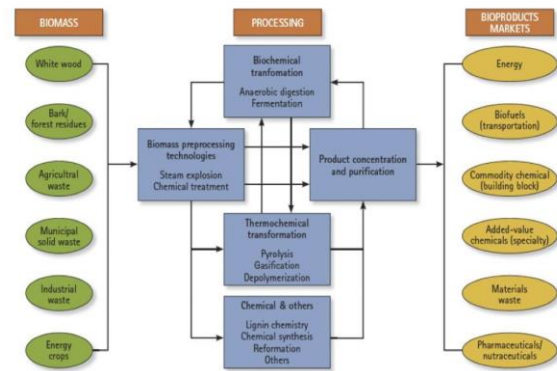

Fig 1.1. Biomass conversion technologies

2. Pyrolisis Kinetic

Pyrolysis kinetics analyzes how the thermal conversion evolves through studying reaction rates, order of reaction and other parameters that can influence those rates [7]. The heating rate can affect the distribution of the pyrolysis products; therefore, the activation energy values may also differ. Consequently, the reaction rate can vary as well. However, many authors have obtained good first-order results [8, 10-12]. For example, Di Blasi [13] noticed that activation energies are higher when first-order reactions are assumed. The conversion can be described by one process or multiple, depending on the species taken into consideration. Empirical and predictive models have already been developed to study the pyrolysis process. Empirical models are based on apparent kinetics, using estimation methods to find global kinetic parameters. In

contrast, predictive models are developed to be able to describe in detail the decomposition process using multiple species without any fitting procedure.

Several empirical pyrolysis kinetic models with exceptional levels of complexity and unprecedented levels of complexity are available in the literature. The simplest one is the single first-order reaction model (SFOM) [13, 15, 16, 22, 35] which considers only one stage of decomposition. Another one is the three parallel reactions model (3PM) [12-14, 18] describes the global decomposition of cellulose, hemicellulose, and lignin. Finally, the decomposition of extractives can be added, as in the work of Grønli et al. [9], who considered five parallel reactions (5PM). The Arrhenius law describes the reaction rate constant of each component:

$$k_i(T_p) = A_i T_p^{\gamma} \exp\left(-\frac{E_i}{RT_p}\right)$$

where $k_i(T_p)$ is the reaction rate constant of the ith component, A_i the pre-exponential factor (s^{-1}), E the activation energy (kJ/mol) and R is the ideal gas constant (J.K^{-1}mol^{-1}) [16]. A slightly more complex model is the distributed activation energy model (DAEM) [17,18,19]. This approach can be applied to the total amount of volatiles released or simply to the volatiles released from a single component. Like the previous models, DAEM considers the Arrhenius law but allows expressing the distribution of the activation energy in a Gaussian form as:

$$f_i(E) = \frac{1}{\sigma_i 2\pi^{1/2}} \exp\left(\frac{-(E - E_{i,0})^2}{2\sigma_i^2}\right)$$

Where E is the activation energy (J/mol), $E_{i,0}$ the mean activation energy (J/mol) and σ the standard deviation (J/mol) [37]. But this distribution is symmetric, and since the asymmetry of reactivity distributions has to come into consideration, the Weibull distribution is used in the form:

$$f(E) = \frac{\lambda}{\eta} \left(\frac{E - \varepsilon}{\eta}\right)^{\lambda-1} \exp\left[\left(\frac{E - \varepsilon}{\eta}\right)^2\right]$$

where λ is the shape parameter, η is the width parameter, and ε is the activation energy threshold (E ≥ ε) [18]. Some multi-component mechanisms can predict product yields of the three main components of biomass (hemicellulose, cellulose, and lignin). Di Blasi [13] proposed this model based on an extensive examination of literature data

The first step of the decomposition (depolymerization) does not lead to chemical composition changes but rather physical properties, such as porosity. This scheme was initially developed for cellulose but also can be applied to hemicellulose and lignin. Extractives and ash contents are integrated into the hemicellulose component. This mechanism can also consider secondary reactions of the vapor phase of tars that account the complete decomposition of tars.

The Bio-PoliMi mechanism is a predictive multistep devolatilization model that considers 43 species and 14 chemical reactions to describe, in detail, the devolatilization process of cellulose, hemicellulose, and lignin, including product speciation. Due to the complexity of lignin structure, three differentiated structures were identified as LIG-C, LIG-O and LIG-H,

being rich in carbon, oxygen, and hydrogen [38]. The figure below shows the chemical structure of all the components.

The devolatilization of cellulose involves multiple reactions that lead to the formation of the levoglucosan, decomposition products, char and water. The volatile products include CO, CO_2, CH_4, CH_3CHO, C_3H_6O, among others.

The devolatilization of hemicellulose involves multiple reactions that lead to the formation of xylose, char and other decomposition products. The volatile products include CO, CO_2, CH_4, CH_2O, C_2H_5OH, and CH_2OH, among others.

3. Material and Method

The sample used in this studied is home compost materials consisting of fruits and dry leaves from the household. The compost materials was composted for 30 days and had several layers. The bottom layers of the compost was used as the sample for this study. In the beginning the sample was separated for each pretreatment. For each pretreatment, 50 mg of raw compost material was mixed with the solvent of 100 ml. In this study, there are nine pretreatment that had been done which consist of:

- Water treatment with room temperature and boiling temperature

- Acid treatment (Sulfuric Acid (H_2SO_4)) with room temperature and boiling temperature

- Alkaline treatment (Sodium Hydroxide (NaOH)) with room temperature and boiling temperature

- Ionic liquid treatment (Acetone, Methanol, and Tetrahydrofuran)

Each sample was mixed together with the solvent in the room temperature condition. After this process, the sample was stirred with magnetic stirrer with the temperature setting according to each pretreatment condition for 1 hour. The mixture was filtered to separate the solid and liquid residue. The solid residue was dried naturally in room temperature and sieved. The liquid residues were stirred again with rotary evaporator machine to efficiently remove the solvents from samples with evaporation.
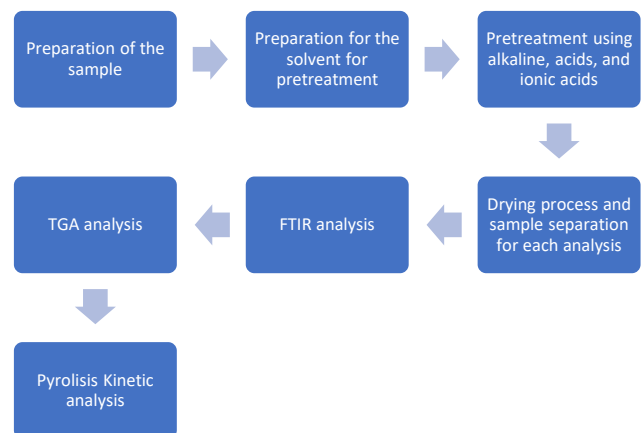

Figure 3.1. Flow process of the study

Figure 3.1. shows the flow process from the sample preaparation until all the analysis methods performed.

4. Result

4.1. FTIR

Figure 3-2 shows the FTIR spectra for the dry extract of raw and pretreatment compost

material. the figure is separated into 2 range area to analyze clearly in those range. Between 3700- and 2700-mm bond area all the extract shows similar peak area in around 3200 – 3390 mm which can identify the existence of oxygen-related bonding or the presence of moisture. Table 3-1 compliment figure 3-2 to show the list of peaks that informed specific bonds compound. The figure shows within this range, the raw material shows the largest amount of moisture compared to pretreatment compost material. Methanol and water-washed pretreatment shows effectivity to reduce moisture from the sample.

room T water extract — boiling water extract — H2SO4 room T extract — H2SO4 boiling extract — NaOH room T extract — NaOH boiling extract — Methanol extract — Acetone extract — THF extract
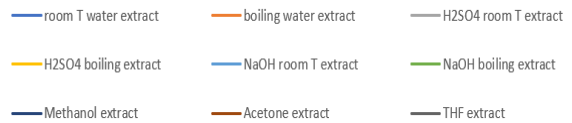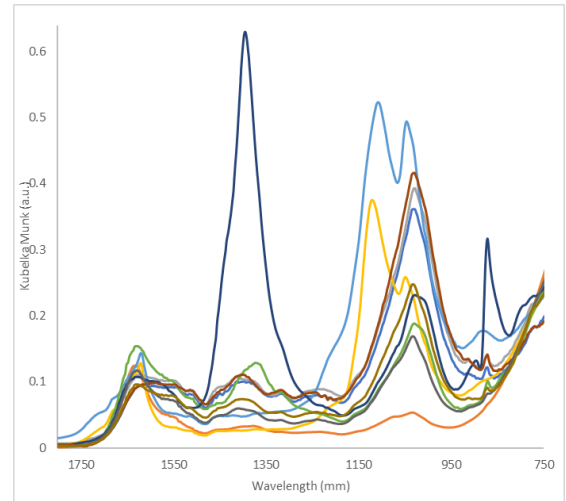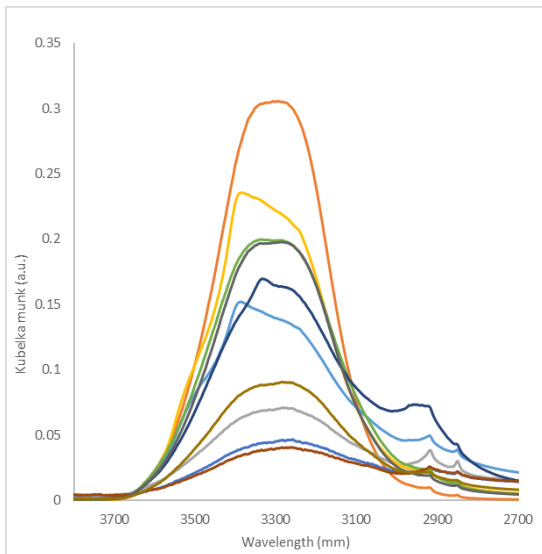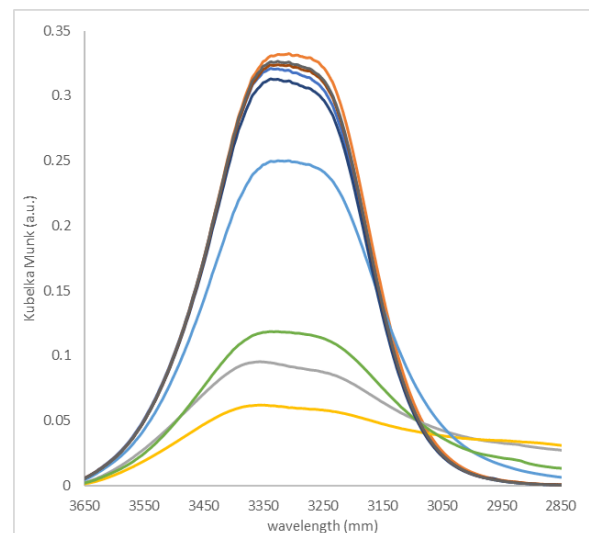
Figure 4.1. FTIR spectra with the wavelength for dry extract of compost material with pretreatment

The next range is between 750 – 1750 mm wavelength. In the graph, acids pretreatment sample shows 2 sharp peaks at 1109 which shows the aromatic C-H bonds and 1047mm with the same aromatic C-H plane deformation.
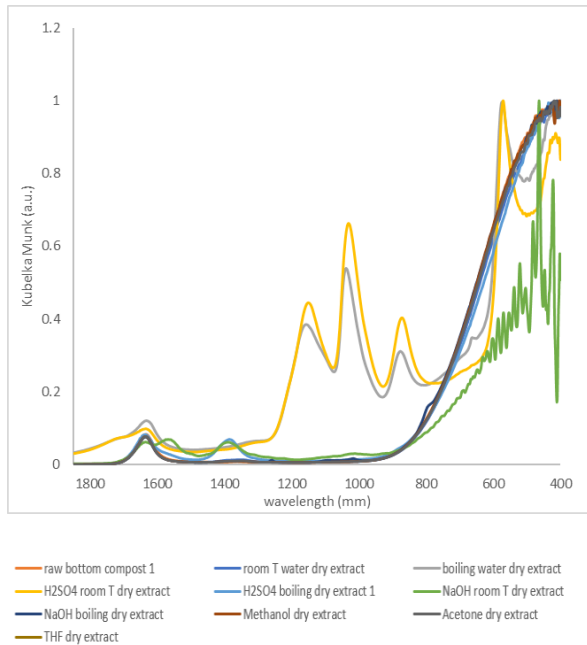
Figure 4.2. FTIR spectra with the wavelength for liquid extract of compost material with pretreatment

This peak number is also can identify the activity of lignocellulose in the region. There is significant peak for the alkaline pretreatment extract at 1396 mm which showing the C-H bonds bending

4.2. Thermogravimetry

To analyze the thermochemical process between each sample, the derivate of the thermogravimetric profile is chosen. Previously there are nine samples, but in this analysis methanol and THF are not included in the figure because the insignificant change for lignocellulose after pretreatment. Figure 3-4 shows the impact of each pretreatment on each component within component such moisture, extractive volatile, lignocellulose.

As in the literature study, pretreatment using acetone increase formation of the extractive volatile significantly. The extractive volatiles which can be the inorganic residues usually appear after water or moisture extraction. The release of the extractive volatile generally increase after pretreatment including sulfuric acid and sodium hydroxide in the boiling temperature. The impact of using higher temperature pretreatment substantially reducing the cell wall of lignocellulosic biomass which enhance the saccharification of polysaccharides. It is proven by the following process of lignocellulose formation.

The hemicellulose after pretreatment have been significantly reduced by almost 50%. Table 3-3 shows the change percentage for each component and pretreatment. In addition, there are two processes happening for the cellulose as it seen in the graph. The first cellulose experienced the polymerization as it is decreased 50-70% whereas the second cellulose crystallinity increased. The alkaline pretreatment break and reduce hemicellulose especially in the boiling temperature treatment.

For the lignin, the pretreatment using acetone, and alkaline create and modify the lignin structure as it is breakdown and reduced but not significantly. Pretreatment using acids shows the dissolution of lignin which increase the percentage by almost 50% of it. As lignin generates more energy while burning in comparison with cellulose, this value can be useful for further study to produce more energy
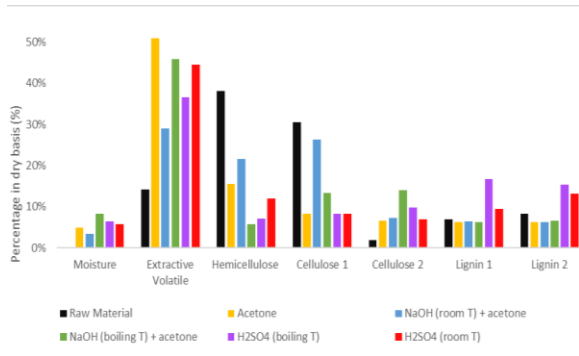
Figure 4.3. Comparison on moisture, extractive volatile, and lignocellulose percentage for each pretreatment

Dry Basis	Weight composition (%)						
Drying substance	Moisture	Extractive Volatile	Hemi cellulose	Cellulose 1	Cellulose 2	Lignin 1	Lignin 2
Raw compost		14.1	38.1	30.6	1.9	6.9	8.3
Acetone	4.98	50.9	15.6	8.3	6.7	6.2	6.2
NaOH (room T) + acetone	3.35	29	21.6	26.3	7.2	6.5	6.2
NaOH (boiling T) + acetone	8.36	45.9	5.7	13.3	13.9	6.2	6.6
2SO4 (boiling T)	6.36	36.5	7.1	8.2	9.8	16.6	15.3
H2SO4 (room T)	5.77	44.5	12	8.2	6.9	9.4	13.2

Table 4.1. Moisture, extractive volatile, lignocellulose weight composition percentage component before and after pretreatment
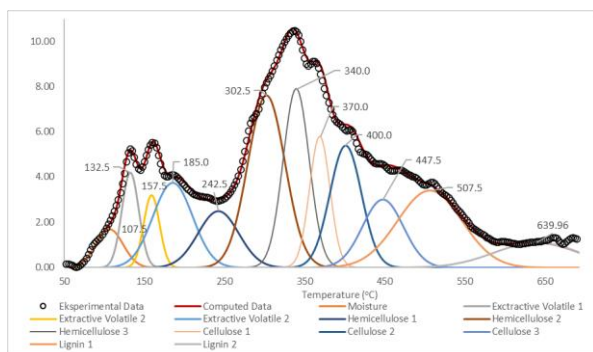
4.3. Kinetic Pyrolysis

Figure 4.1. DTG curves as a function of temperature for raw compost material for 50K/min
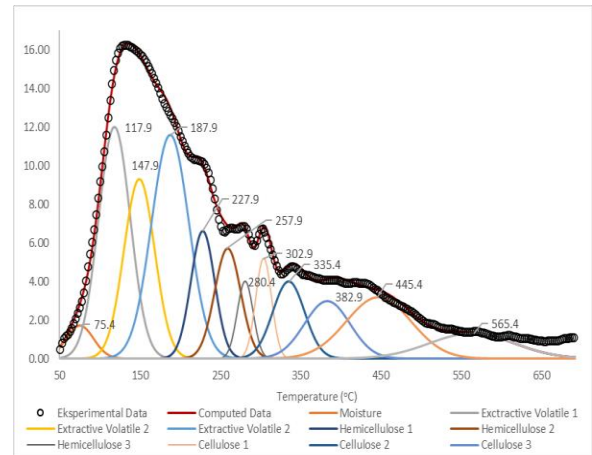

Figure 4.2. DTG curves as a function of temperature for compost material with H_2SO_4 for 50K/min

Figure 4-1 – 4-2 shows the DTG curves for raw compost material, and compost material with acid and alkaline treatment. In this part of study only three samples were taken to the experiment because time limit and based on the thermogravimetry and FTIR study, both H2SO4 and NaOH compost material with the boiling temperature treatment. The experiment was done for the heating rates of 10, 20, 30, 40, 50 K/min.

Table 4-1 shows the kinetic parameters obtained by fitting the Kissinger method to the experimental data for the three samples for lignocellulose component. The result of cellulose and lignin activation energy shows the similarity of literature study. From the temperature, it is shown that while using acids as pretreatment, the pyrolysis process got started earlier. The pretreatment with alkaline, also showing different initial temperature for each lignocellulose breakdown process.

The energy activation result from acids sample shows the smallest Ea compared to the pure raw material compost or alkaline – wash compost. This can be beneficial for energy production, because the smaller the activation energy it means the smaller energy needed for the conversion process of the component. The energy activation result from acids for the hemicellulose part is smaller than the other compost sample. One of literature study mentioned that there is amino acids reaction which produce glycine and other amino acids compound which could be detected in the diagram as hemicellulose.
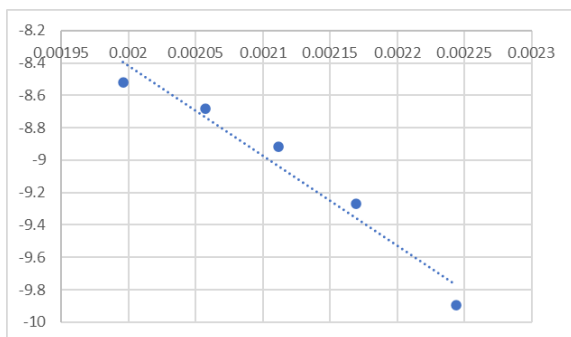

Figure 4.3. Arrhenius plot method applied to experimental TG curves for hemicellulose to calculate the activation energy.

5. Conclusion

The evaluation of the energy recovery for composted material as a potential source for sustainable fuels was done by FTIR, thermogravimetry, and pyrolysis kinetics. Pretreatment using acids (H_2SO_4), alkaline (NaOH), and ionic liquids (acetone, methanol, acetone) have an influence on lignocellulose conversion process especially with the boiling

temperature treatment. It is shown in the thermogravimetry analysis that hemicellulose and cellulose can be reduced by almost 50% after pretreatment.

Also, there is possibility to increase the production of lignin by using alkaline treatment. From thermogravimetry and pyrolysis kinetics it is shown the production of inorganics and extractive volatile increase after pretreatment. The FTIR shows that methanol and water washed pretreatment effectively reduce moisture from the sample. The result from pyrolysis kinetic process shows that the activation energy reduces after pretreatment with acid (H_2SO_4). The reduction of activation energy can make less energy in energy conversion process for lignocellulose and enhance the energy production.

In the future, more experiment for the pretreatment sample can be conducted to see the detail compounds within. It is also interesting to look deeper in to the composting days impact on the lignocellulose value within. Furthermore, an pyrolysis with Kissinger-Akahira-Sunose method and Flynn-Wall-Ozawa method can be implemented to have more pyrolysis parameter.

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