Evaluation of the Energy Recovery of Composted Materials

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I declare that this document is an original work of my authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa

To the alternative energy development…

Acknowledgments

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

Resumo

A sociedade atual, com médio e elevado poder económico, gera grandes quantidades de resíduos domésticos que tem de ser tratados o que tem custos associados. Os resíduos domésticos, maioritariamente alimentos, são compostos por frutos, vegetais e sobras lenho celulósicas de jardinagem. A compostagem, um processo complexo de biodegradação, destes resíduos gera compostos húmicos de elevado valor e um resíduo sólido lenho celulósico que pode ser valorizado na produção de combustíveis renováveis. Um composto doméstico, com 6 meses de compostagem nas estações de primavera e verão, foi sujeito a processos de extração sólido/líquido (água, acetona, hexano; temperatura ambiente)e liquefeito com soluções aquosas de H_2SO_4 e NaOH (temperatura ambiente e de ebulição) de modo extrair os compostos húmicos e a converter os lenhos celulósicos. As frações sólidas e líquidas foram caracterizadas por espectroscopia do infravermelho (ATR-FTIR). Os sólidos foram caracterizados por termogravimetria e a composição determinada, a partir da velocidade de decomposição térmica (curvas DTG), considerando o modelo dos pseudo componentes (humidade, extrativos, hemicelulose, celulose, lenhina e inorgânicos). Os materiais sólidos resultantes do tratamento com NaOH e com H_2SO_4, à temperatura de ebulição, foram sujeitos a estudos cinéticos de pirólise por termogravimetria aplicando a equação de Kissinger a cada pseudo componente lenho celulósico.

Os resultados mostraram que o tratamento do composto com solução aquosa de H_2SO_4, à temperatura de ebulição, é eficiente na conversão do resíduo sólido da compostagem gerando lenhina.

Palavras-chave: Resíduos sólidos domésticos; compostagem; liquefação; lenhina; pirólise; Kissinger

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List of Acronyms

C   Carbon

DAEM   Distributed Activated Energy Model

DTG   Derivative Thermogravimetry

Ea   Activation Energy

FTIR   Fourier Transform Infrared Spectroscopy

H   Hydrogen

IR   Infrared spectroscopy

O   Oxygen

N   Nitrogen

T   Temperature

TGA   Thermogravimetry Analysis

1. Introduction

1.1. Overview

For the past few decades, fossil fuels have been chosen to fulfill world energy demands. Still, since these resources are limited and generally harm the environment, recent dramatic developments in renewable energy production occurred. These are supported by policies that change the energy mix, especially electricity production [1]. Moreover, biomass has a significant 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 ability to be linked with many economic sectors like agriculture, forestry, food processing, paper, pulp, and energy [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. Therefore, agricultural and forest residues and energy crops planted on idle or released cropland are attractive alternatives [4, 6]. Additionally, biomass can be upgraded through conversion processes, like pyrolysis, to increase its value as a fuel.

The figure below shows the energetic Portuguese balance related to the final energy consumption in 2013; biomass only contributes 6.6%. 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, a significant limitation can be the investment costs, and in the specific case of Portugal, there is still a lack of governmental support and incentives to ensure the interest from private investors in bioenergy technologies.
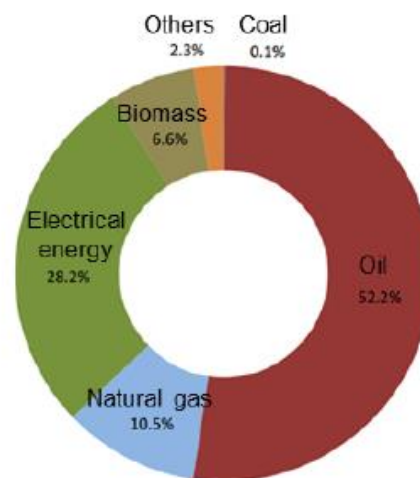
Figure 1-1 Portuguese energy balance in 2013

Figure below shows the biomass conversion technologies. The final products of the conversion technologies are used mainly for producing 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.
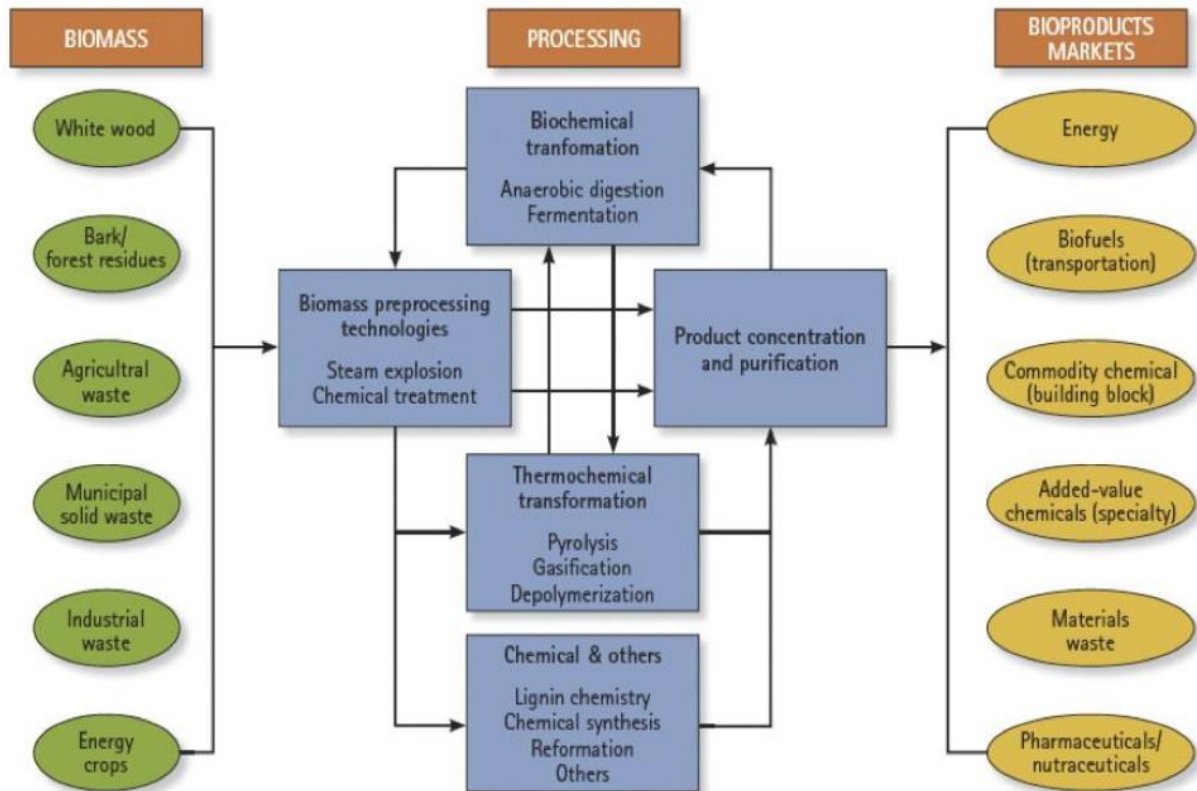
Figure 1-2 Biomass conversion technologies

Pyrolysis is a form of thermochemical treatment that decomposes organic materials into liquid, solid and gaseous forms without oxygen. Due to its versatility, pyrolysis is becoming a more relevant process since all three-output fractions have potential as fuels for transport, power generation, and combined heat and power [7]. Fast pyrolysis, in particular, is a relatively mature technology on the verge of commercialization [8], primarily located in the North of Europe [9-11]. However, despite showing great potential to adopt this technology with an estimated dry biomass production of 5630 thousand tons, Portugal has yet to start developing this industry [27].

The most common reactors used in industrial facilities for the pyrolysis process are the fluidized bed reactors and the rotating cone reactors for bio-oil production. In fluidized bed reactors, the biomass feedstock needs a pretreatment that involves drying (< 10% moisture), milling and/or sieving (particle size between 1 and 2

mm). This feedstock is then fed into the reactor, generally with a screw, heated to approximately 500 ºC in the absence of oxygen and decomposed into gaseous vapors and char particles, separated in the cyclone chamber. At this point, charcoal is collected while the gases move on into the condensers, turning them into bio-oil.

The non-condensable gases are recirculated into the main reactor chamber to be reused for pre-heating. In rotating cone reactors, the pyrolysis process occurs in the rotating cone while mixing biomass particles and hot sand in the absence of oxygen. The charcoal and the sand resulting from the previous stage, are recycled into the combustion chamber, where charcoal is burned to reheat the sand. The gaseous vapors are led to the condenser yielding the bio-oil. The non-condensable gases and the extra heat coming from the chamber can be used to generate steam for power generation or for drying the biomass.

Some industrial facilities adopted these technologies to produce electricity, bio-oil, and district heating. For instance, Fortum, founded in Joensuu (Finland) in 2013 [9], is a combined heat and power production plant (CHP) that produces electricity and district heating and also aims to create, in the future, 50,000 tons of bio-oil per year from the conversion of lignocellulosic biomass in a fluidized bed reactor. In addition, Dynamotive Energy Systems Corporation [10] in Canada is a leader in bio-oil production via a fluidized bed reactor, while BTG – Biomass Technology Group [11] in the Netherlands uses a rotating cone reactor to produce bio-oil.

1.2. Objectives

The objective of this work is to study the kinetic pyrolysis of compost biomass experimentally. The specific objectives are:

- Perform pretreatment on the compost biomass with different solvents and under different temperature

- Perform Fourier Transform Infrared experiment in FTIR to analyze the characteristic of the biomass compost with FTIR (Fourier Transform Infrared)

- Perform thermogravimetric experiments in a TGA to analyze the lignocellulosic characteristic of the biomass compost with TGA (Thermogravimetry Analysis)

- Estimate the activation energy from the kinetic pyrolysis using the Kissinger Method.

1.3. Bibliographical review

Previous changes in the proportion of energy produced by various sources, such as in the nineteenth century when coal surpassed biomass, provided the largest share of the global energy supply in the twentieth century. The process took when petroleum overtook coal, but this condition might be characterized

as energy additions rather than transitions. Nevertheless, the overexploitation and overuse of fossil fuels, especially coal, significantly impact climate change, such as extreme heat waves, heavy precipitation, droughts, sea-level rise, polar melting, expanding health risks, and other dangerous climate impacts.

Di Blasi [13] extensively reviewed a significant number of studies focused on modeling the biomass pyrolysis process based on thermogravimetric studies. In this review, the author describes one component and multiple component mechanisms. The assumption of a single component behavior inevitably introduces imprecisions in the decomposition rates (and conversion time), since it considers only one decomposition zone. Therefore, multicomponent mechanisms of biomass pyrolysis have been developed to describe different decomposition zones based on the pseudo components hemicellulose, cellulose, and lignin that compose biomass. Thermogravimetry provides one single curve of mass loss (and rate) over the residence time, and the different component-specific decompositions will overlap in this single curve.

The figure below shows typical thermogravimetric (TG) and differential thermogravimetric (DTG) curves. Hemicellulose and cellulose are associated with the shoulder and the peak of the DTG curves, respectively, meaning that the rate curves of these two pseudo components overlap during their decomposition process. On the other hand, lignin decomposes slowly over an extensive range of temperatures. The accuracy in the predictions of weight loss characteristics is improved as the number of model parameters increases. However, simplicity is always desired for global reaction mechanisms. Di Blasi [13] pointed out that the application of these kinetic models to the study of pyrolysis/devolatilization processes has been mostly concentrated on wood species and, in a small number of cases, on agricultural residues. Therefore, it is necessary to develop general reaction schemes that can be applied to other biomass fuels and broaden the current application. Given the wide variety in chemical composition among the different species, this matter is of particular practical importance.
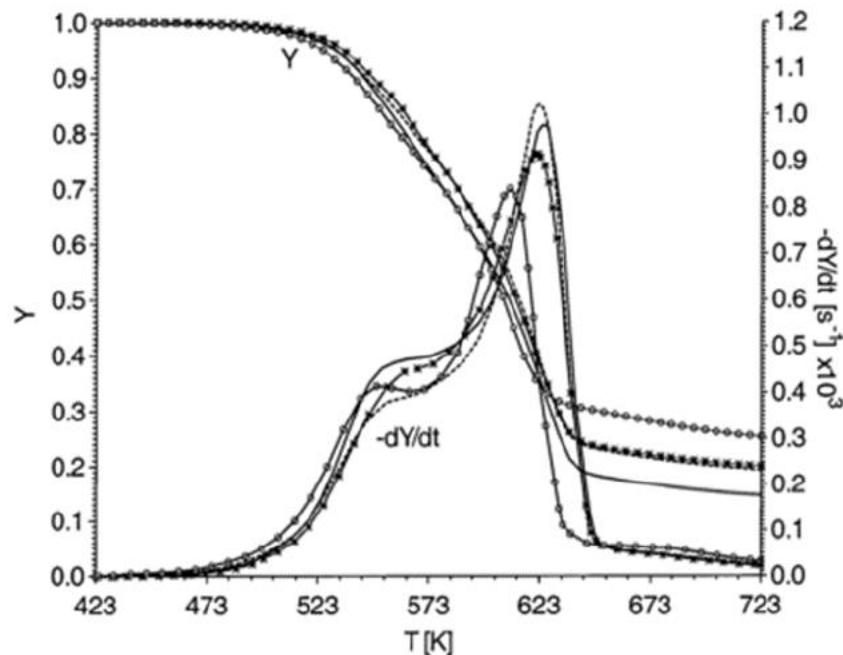
Figure 1-3 Typical TG and DTG curves [13]

In the remainder of this section, a number of relevant studies will be reviewed. The focus was given to studies that, in their kinetic analysis, implemented a single first-order reaction (SFOM), considering only one stage of decomposition, a three-parallel model (3 PM) that describes the global decomposition of cellulose, hemicellulose, and lignin, and a five parallel model (5 PM) that adds extractives.

1.3.1. Heating rate effects

Most of the referred authors studied the effects of the heating rates on pyrolysis behavior. Sharma et al. [22], Li et al. [19], Seo et al. [15], Mani et al. [21], and Damartzis et al. [18] concluded that transition temperatures slightly increase with increasing heating rate, shifting the DTG profiles. These biomass constituents have characteristic individual decomposition peaks in certain temperature ranges. It has been shown that an increase in the heating rate tends to delay thermal decomposition processes toward higher temperatures [12, 14, 18, 19, 21]. Furthermore, the distinct peaks associated with the different constituents may not appear at higher heating rates because some of them can be thermally decomposed simultaneously, overlapping each other in DTG profiles. This behavior was observed by Grønli et al. [14], Vamvuka et al. [20], Li et al. [19], Seo et al. [15], Mani et al. [21], Burhenne et al. [12] and Guerrero et al. [16].

Seo et al. [15], Damartzis et al. [18], and Guerrero et al. [16] concluded that lower heating rates lead to higher volatile matter production due to the fact that when the heating rate decreases, the required time to reach a particular temperature value increase, enabling other chemical reactions to occur (for example, dehydration). As a consequence, the amount of devolatilized matter is increased.

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Sharma et al. [22] and Damartzis et al. [18] studied the effect of the heating rate on the activation energy. The former authors concluded that increasing the heating rate generally leads to increasing the activation energy. Conversely, the latter authors concluded that a higher heating rate increased the activation energy values for hemicellulose and cellulose decomposition, decreasing the activation energy values for lignin decomposition.

2. Theoretical Foundation

2.1. Waste to Energy

2.1.1. Compost biomass

Compost is a process of biodegradation and transformation that convert lignocellulosic biomass into value-added products, such as humic substances. As the population increases, a large amount of organic solid waste, primarily from agriculture or food, also increases. Household organic waste usually consists of fruit, vegetables, and plant residues from the tree in the garden. Generally, people will collect the organic waste and dump it directly, but it can also traditionally be composted to reuse.
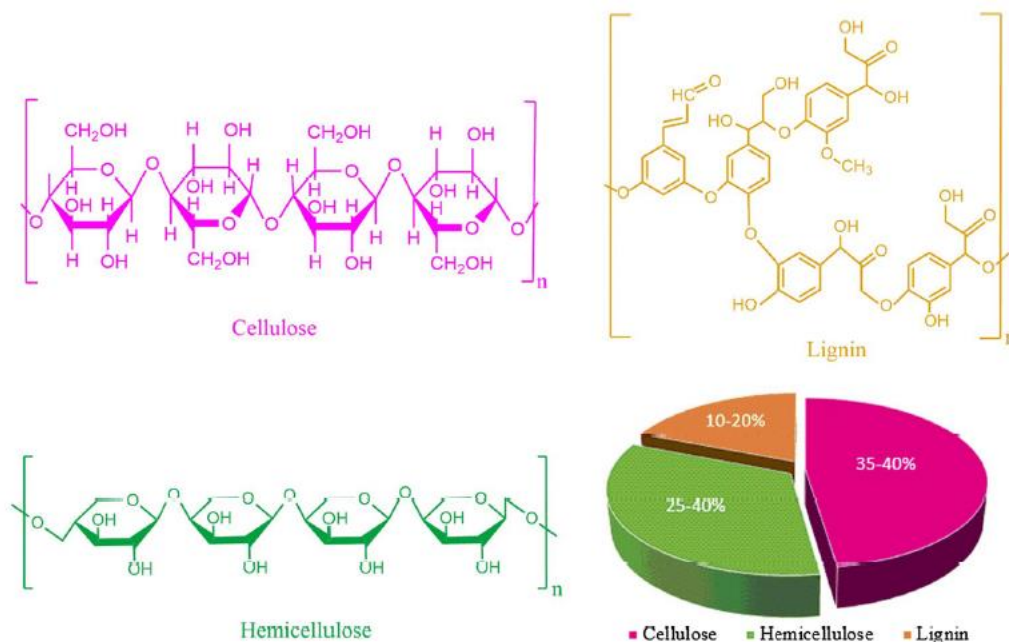
Figure 2-1 Lignocellulose composition: cellulose, hemicellulose, and lignin

2.2. Waste to Energy Conversion Process

2.2.1. Gasification

Gasification is one of the well-known and implemented biomass treatments commercially. The primary product is syngas which are usually used to produce electricity generators, or the syngas will be used in a boiler to produce energy and used as a chemical feedstock.

The gasification process can be divided into oxidation, drying, pyrolysis and reduction. Through this process, biomass goes through several physical and chemical changes, lead, and other gasing to CO, CO2, H2

production. These gasses are processed well for different fuels, including methanol, pure hydrogen for fuel, and methane production.

2.2.2. Pyrolysis

A pyrolysis is a form of thermochemical treatment that decomposes organic materials into liquid, solid and gaseous forms without oxygen. Due to its versatility, pyrolysis is becoming more relevant since all three-output fractions have potential as fuels for transport, power generation, and combined heat and power.

Fast pyrolysis is a relatively mature technology on the verge of commercialization, primarily located in the North of Europe. Despite showing great potential to adopt this technology with estimated dry biomass production of 5630 thousand tons, Portugal has yet to start developing this industry. The most common reactors used in industrial facilities for pyrolysis are the fluidized bed reactors and the rotating cone reactors to produce bio-oil. In fluidized bed reactors, the biomass feedstock needs a pretreatment that involves drying (< 10% moisture), milling, and sieving (particle size between 1 and 2 mm). Next, this feedstock is fed into the reactor with a screw, heated to approximately 500 ºC without oxygen, decomposed into gaseous vapors and char particles, and separated into the cyclone chamber. At this point, charcoal is collected while the gases move on into the condensers, turning them into bio-oil. Finally, the non-condensable gases are recirculated into the main reactor chamber to be reused for pre-heating.

In rotating cone reactors, the pyrolysis process occurs in the rotating cone while mixing biomass particles and hot sand without oxygen. The charcoal and the sand from the previous stage are recycled into the combustion chamber, where charcoal is burned to reheat the sand. The gaseous vapors are led to the condenser yielding the bio-oil. The non-condensable gases and the extra heat from the chamber can generate steam for power generation or drying the biomass. As with most biomass upgrading processes, pyrolysis plants are typically optimized to woody biomass.

However, other biomass sources need to be considered, as discussed above. But the use of "difficult" biomass fuels can bring complications in the operating system of these reactors, mostly operational problems caused by high ash content typically found in agricultural biomass and the yield/composition of the obtained products. In this context, fundamental research needs to understand the pyrolysis process of non-woody biomass better. Thermogravimetric studies and kinetic analysis can better understand the governing circles of the pyrolysis of alternative biomass.

2.3. Pretreatment Process

Pretreatment is a process in which carbohydrates, mainly cellulose, get ready for an enzymatic or microbial attack. This process is mainly used to improve ethanol and biogas production; however, it can also be used to improve the production yield of all biochemicals from lignocelluloses and improve animal feed, fiber properties, and compositing.

Figure 2.2 shows the pretreatment that can be done to break lignocellulosic biomass. In this study, the experiment will combine some of the treatments.
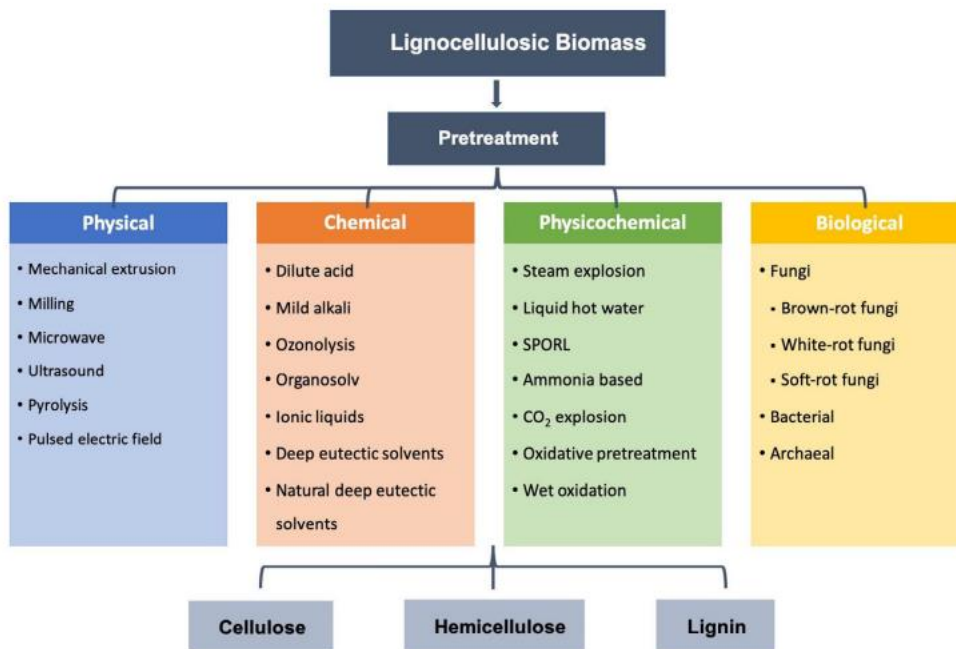

Figure 2-2 Pretreatment methods available for lignocellulosic biomass.

2.4. Analytical Tools

2.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is one of the essential analytical techniques for researchers. This type of analysis can be used for characterizing samples in the forms of liquids, solutions, pastes, powders, films, fibers, and gases. FTIR is also possible for analyzing the material on the surfaces of a substrate. FTIR is well known for characterization analysis for rapid, good accuracy, and relatively sensitive analysis.

In the procedure, the samples are subjected to contact with infrared radiation. The infrared radiation will impact the atomic vibrations of a molecule in the model, which will make absorption or transmission of energy between each molecule which will create the specific absorption or transmission of energy. Therefore, FTIR is also useful for determining particular molecular vibrations contained in the sample.

FTIR analysis's primary purpose is to understand the meaning of the FTIR spectrum. Figure 2-2 shows an example of a schematic mid-IR spectrum. The spectrum can result in "absorption versus wave number" or "transmission versus wavenumber" data.

IR spectrum divided into three wavenumber regions: far-IR spectrum (<400 cm^{-1}), mid-IR spectrum (400-4000 cm^{-1}), and near-IR spectrum (4000-13000 cm^{-1}). The mid-IR spectrum is the most widely used in the

sample analysis. The mid-IR spectrum is also divided into four regions: the single bond region (2500-4000 cm^{-1}), the triple bond region (2500-4000 cm^{-1}), the double bond region (2500-4000 cm^{-1}), and the fingerprint region (2500-4000 cm^{-1}).
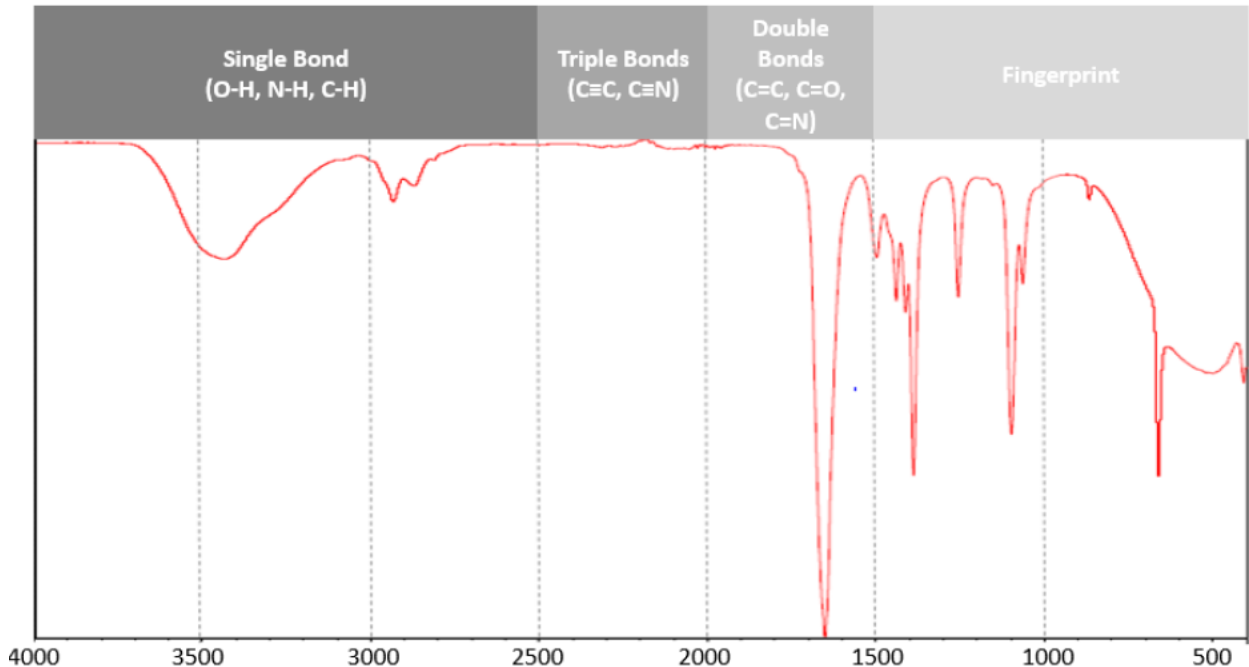

Figure 2-3 Mid-IR spectrum regions

2.4.2. Thermogravimetric Analysis (TGA)

Thermogravimetry is a technique that can measure heat flows and weight changes that occur in a material as a function of temperature and time in a controlled atmosphere]. This technique is usually referred to as differential scanning calorimetry – thermogravimetry (DSC-TGA). This combination identifies endothermic and exothermic events associated with weight losses, like melting or decomposition. Thermogravimetric analysis is an advantageous technique for determining the composition of multicomponent systems, atmosphere effects on materials, reaction kinetics, and other materials such as ash, moisture, and volatile contents of materials. For this reason, a potent tool for studying biomass thermal conversion processes like pyrolysis.

The thermogravimetry technique is simple: A small amount of the sample (~ 5 mg) is placed on a crucible supported by a precision balance inside a high-temperature furnace. Specifically, for the pyrolysis process, the atmosphere in the furnace must be inert, generally using Nitrogen or Argon. The temperature is measured with a thermocouple placed near the crucible. The temperature and mass variations information is sent to a computer unit to process the data in thermogravimetric (TG) and differential thermogravimetric (DTG) curves.

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Due to the considered low amount of the sample, this process should be repeated several times to obtain a representative pyrolysis behavior. These curves represent the mass variation and the mass loss rate, respectively, with temperature. They allow identifying the main reactions involved in the pyrolysis process and estimating its corresponding kinetic parameters. However, this process is limited since the number of responses co-occurring during a simple pyrolysis process is greater than the ones identified. Thus, pyrolysis is typically studied using models in which the overall pyrolysis behavior is considered as the combination of each component.

2.4.3. Pyrolysis Kinetics

Pyrolysis kinetics analyzes how the thermal conversion evolves through studying reaction rates, order of reaction and other parameters that can influence those rates [34]. 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 [12, 14-16]. 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}) [35]. A slightly more complex model is the distributed activation energy model (DAEM) [14,36,37]. 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:

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

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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:

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

where λ is the shape parameter, η is the width parameter, and ε is the activation energy threshold (E ≥ ε) [36]. 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. Figure 2-4 shows a general scheme of the decomposition of a component. v_c is the volatile matter.
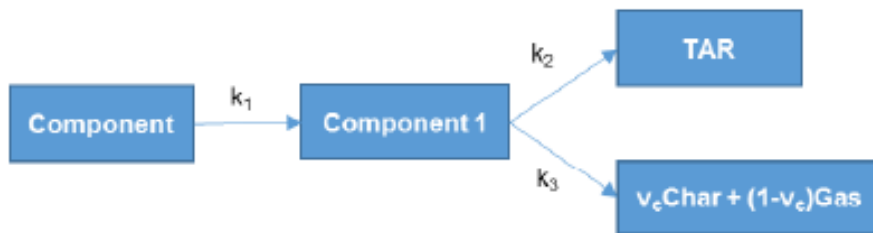

Figure 2-4 Scheme of decomposition of component

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.

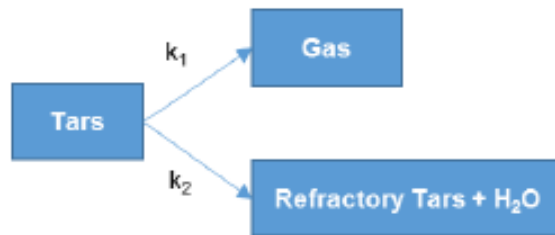*Figure 2-5 Scheme for secondary reactions of the vapor phase of tars*

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.
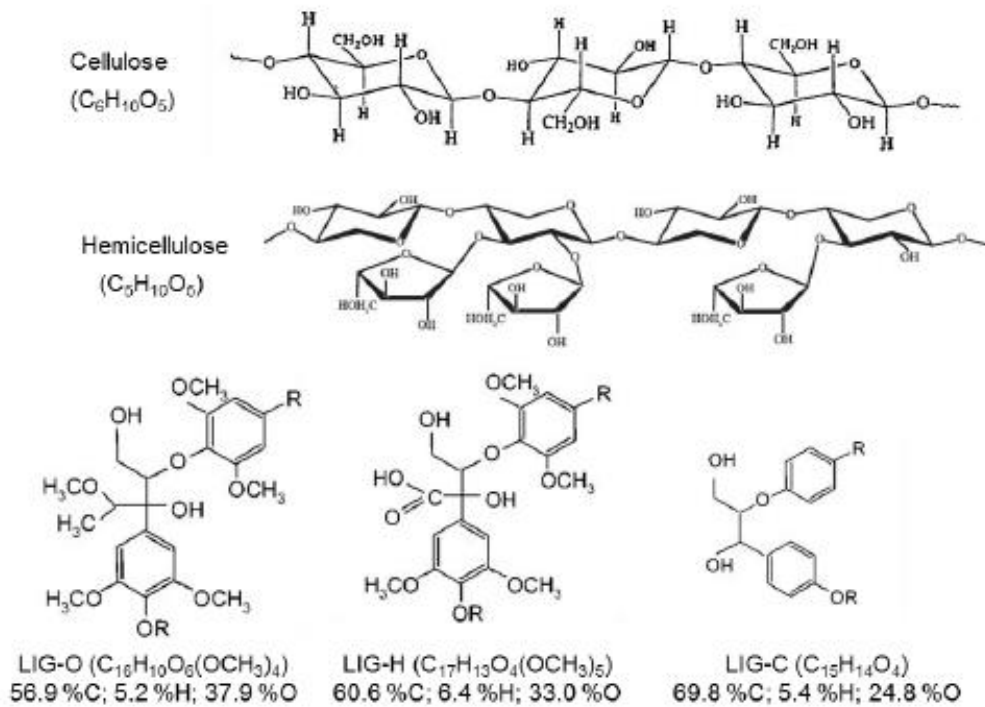
Figure 2-6 Chemical structure of lignocellulose components

Figure below shows the multistep mechanism of cellulose pyrolysis. 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.
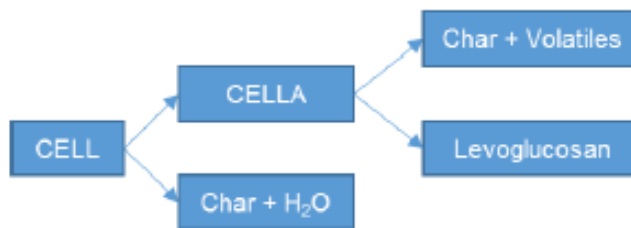
Figure 2-7 Multistep mechanism of cellulose pyrolysis

Figure below shows the multistep mechanism of hemicellulose pyrolysis. 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.
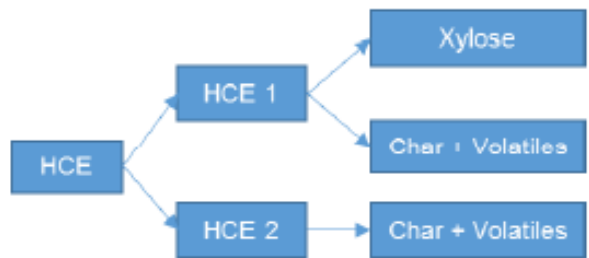
Figure 2-8 Multistep mechanism of hemicellulose pyrolysis

Figure below shows the multistep mechanism of the pyrolysis of the three lignin reference components. The devolatilization of hemicellulose involves multiple reactions that lead to the formation of intermediate lignin species, char and other decomposition products. The volatile products include CO, CO_2, H_2, CH_4, CH_2O, phenols, and some acids.

Figure 2-9 Multistep mechanism of the pyrolysis of LIG-H, LIG-O, and LIG-C

3. Materials and Methods

3.1. Materials and Pretreatment

The sample used in this study is home compost materials consisting of fruits and dry leaves from the household. The compost materials were composted for 30 days and had several layers. The bottom layers of the compost were used as the sample for this study.
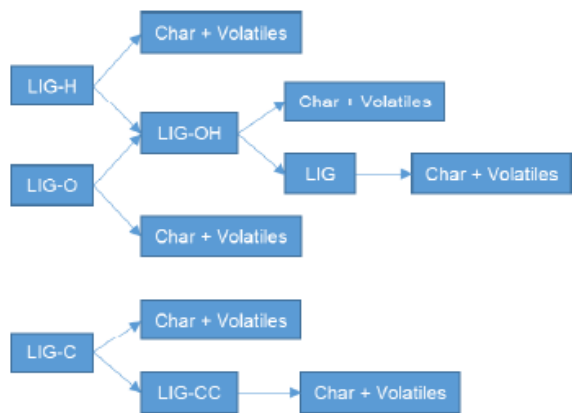
The below shows the process from the preparation of the raw compost material, the pretreatment, and the analysis methods used in this study.

Preparation of the sample	→	Preparation of the solvent for pretreatment	→	Pretreatment using alkaline, acids, and ionic liquids

TGA analysis	←	FTIR analysis	←	Drying Process & separation sample for each analysis

Pyrolysis analaysis
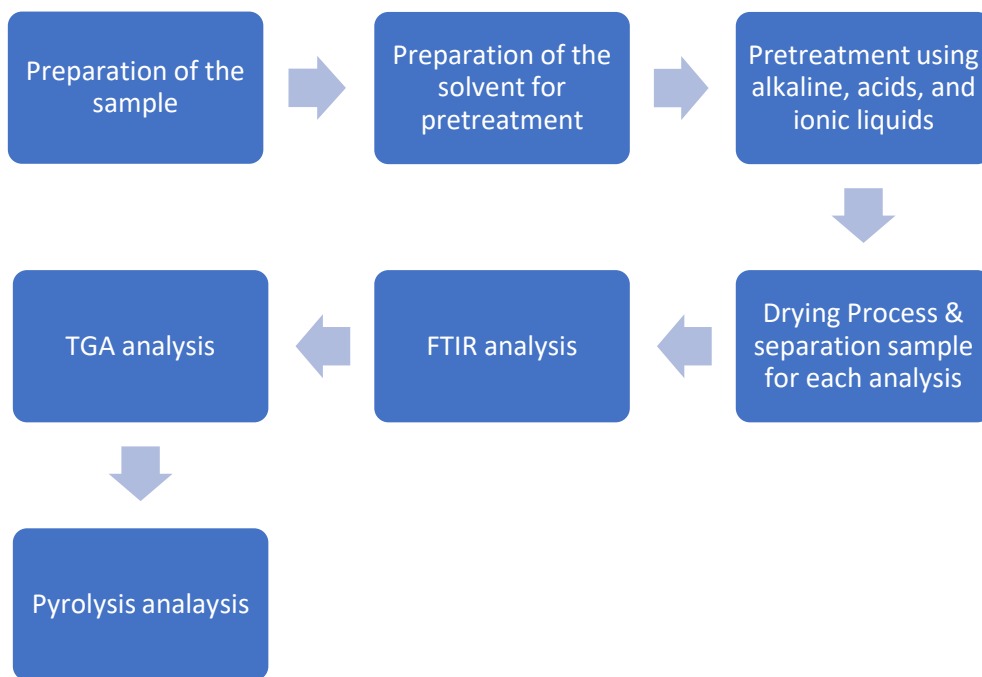
Figure 3-1 The flow process

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, nine pretreatments 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)

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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 a rotary evaporator machine to remove the solvents from samples with evaporation efficiently.

3.2. FTIR Study

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 presence of moisture. Table 3-1 compliment figure 3-2 to show the list of peaks which informed specific bonds compound. The figure shows within this range, the raw material show the largest amount of moisture compare to pretreatment compost material. Methanol and water washed pretreatment shows effectivity to reduce moisture from the sample.

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. 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.

Table 3-1 Wavelength of peak bands FTIR for dry compost material with pretreatment

Wavelength (cm-1)										Assignment
H₂SO₄		NaOH		Water		Methanol, Acetone, THF			Raw Compost	
H2SO4 room T	H2SO4 Boiling	room T	boiling	room T	Boiling	Methanol	Acetone	THF	-	
3390	3388	3342	3338	3257	3283	3265	3278	3284	3306	O-H stretching
2918	2918	2918	2919	2919	2918	2918	2918	2920	2918	CH₂ asymetrical stretching
2850	2850	2850	2850	2850	2850	2850	2859	2851	2850	CH₂ symmetrical stretching
1621	1621	1632	1632	1616	1627	1589	1629	1634	1630	C-C ring stretching; C-N deformation; N-O stretching and O-H deformation
1121	1109	1373	1396	1415	1415	1401	1412	1401	1561	
1049	1047	1030	1031	1317	1318	1323	1317	1320	1458	C-C stretching and C-H deformation from quinazoline ring; CH₂ scissoring
666	882	871	897	1240	1238	1248	1239	1245	1035	C-H deformation from quinazoline ring; C-C and C-N deformation and CH₂ rocking from radical ring
595	666	504	872	1030	1028	1031	1032	1033	519	
515	583	483	719	873	873	872	872	873	494	[
455	458	462	691	500	526	525	509	517	482	
448	454	451	645	483	473	512	460	475	474	
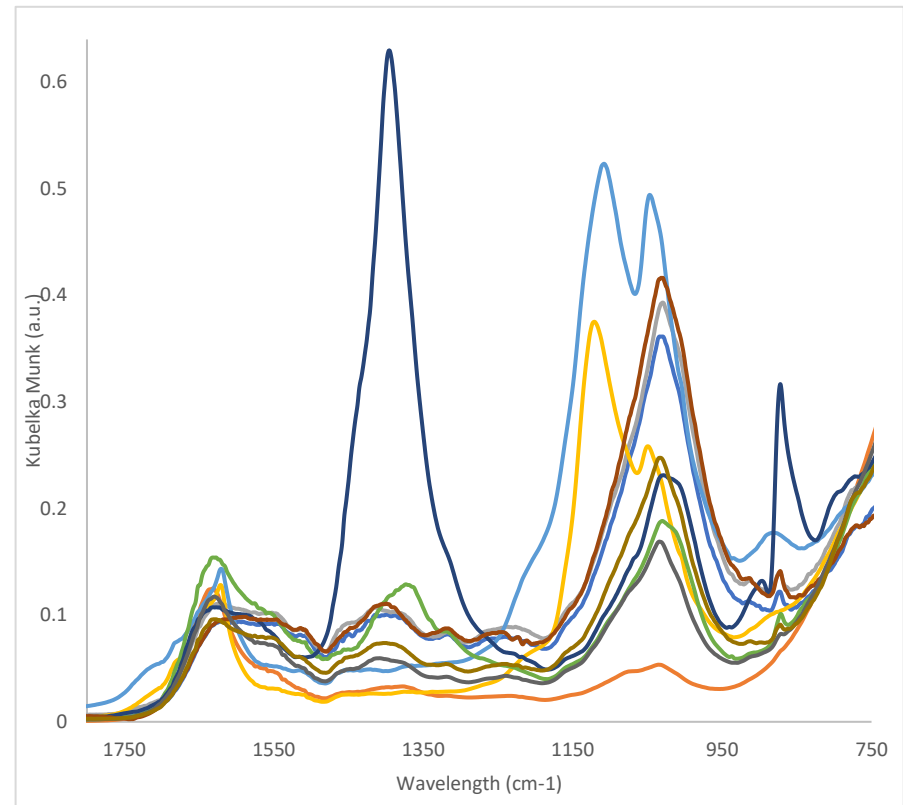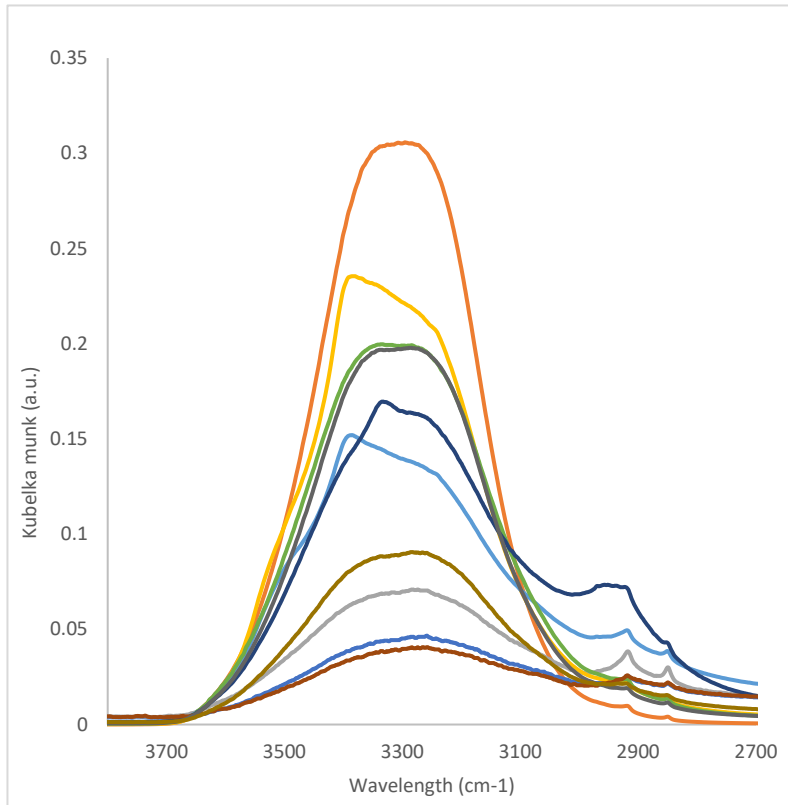
Figure 3-2 FTIR spectra with the wavelength for dry extract of compost material with pretreatment

Table 3-2 Wavelength of FTIR for liquid extract compost material with pretreatment

Wavelength (cm-1)									Assignment
H2SO4		NaOH		Water		Methanol, Acetone, THF			
room T	boiling T	room T	boiling T	room T	boiling T	Methanol	Acetone	THF	
3360	3360	3325	3326	3338	3324	3327	3338	3337	O-H stretching
2327	2327	1635	1637	1635	1635	1638	1637	1635	C=O stretching,
2100	2101	1388	1569	1355	1362	1260	1338	1348	C-C stretching and C-H deformation from quinazoline ring; CH2 wagging
1992	1986	475	1388	483	498	1094	495	503	C-C ring deformation; C-N deformation; N-O deformation; CH2 wagging and rocking
1633	1638	467	1011	474	490	1016	484	492	
1158	1151	462	633	467	479	796	475	482	
1040	1032	455	618	455	474	495	467	471	
877	873	443	603	439	459	486	462	467	
666	571	436	586	430	454	478	455	462	
575	451	427	570	423	447	467	447	450	
451	438	420	554	418	439	451	430	442	
431	430	412	538	411	431	443	423	434	
425	423	407	521	407	423	438	411	429	
419	415		504		411	427	403	423	
403	404		482		407	422		419	

			464			415		414
			447			411		407
			441			406		
			422			403		
			402					
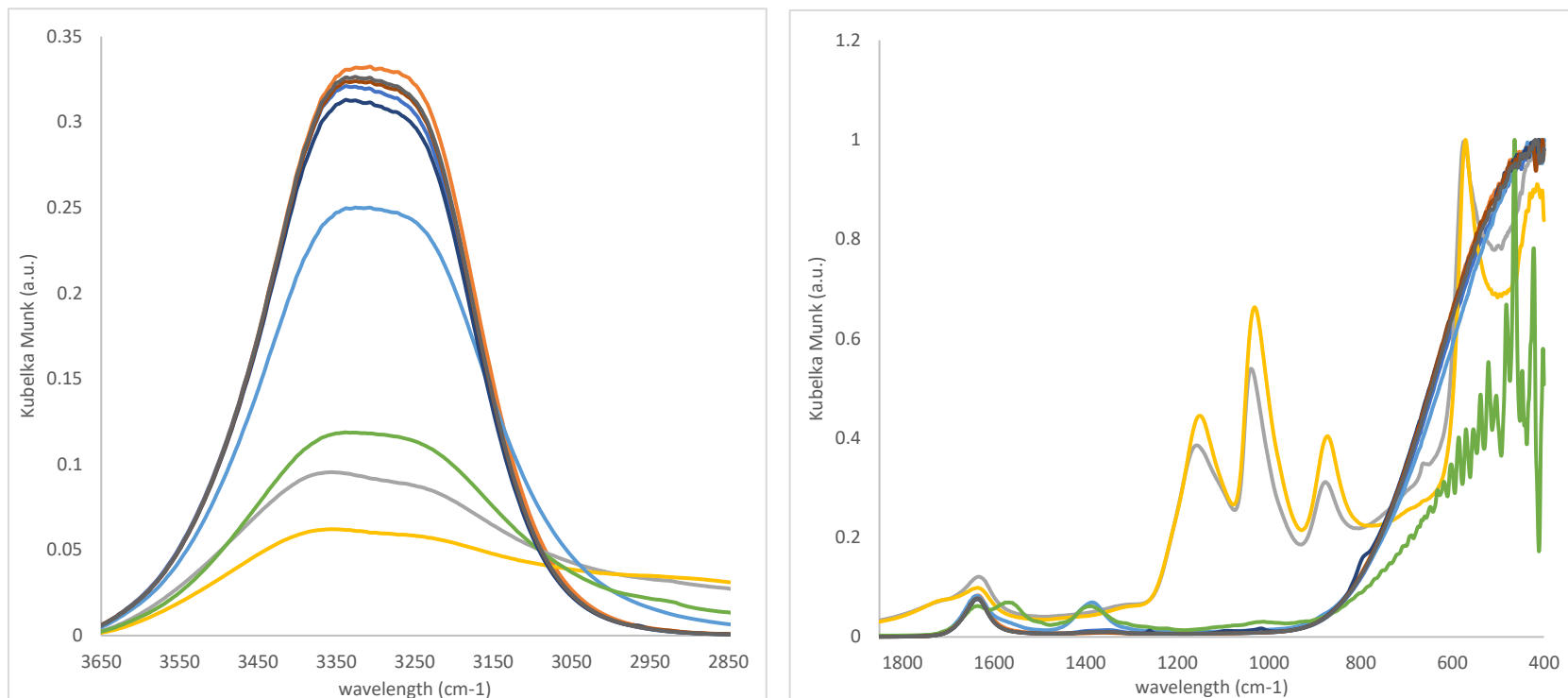
Figure 3-3 FTIR spectra with the wavelength for liquid extract of compost material with pretreatment
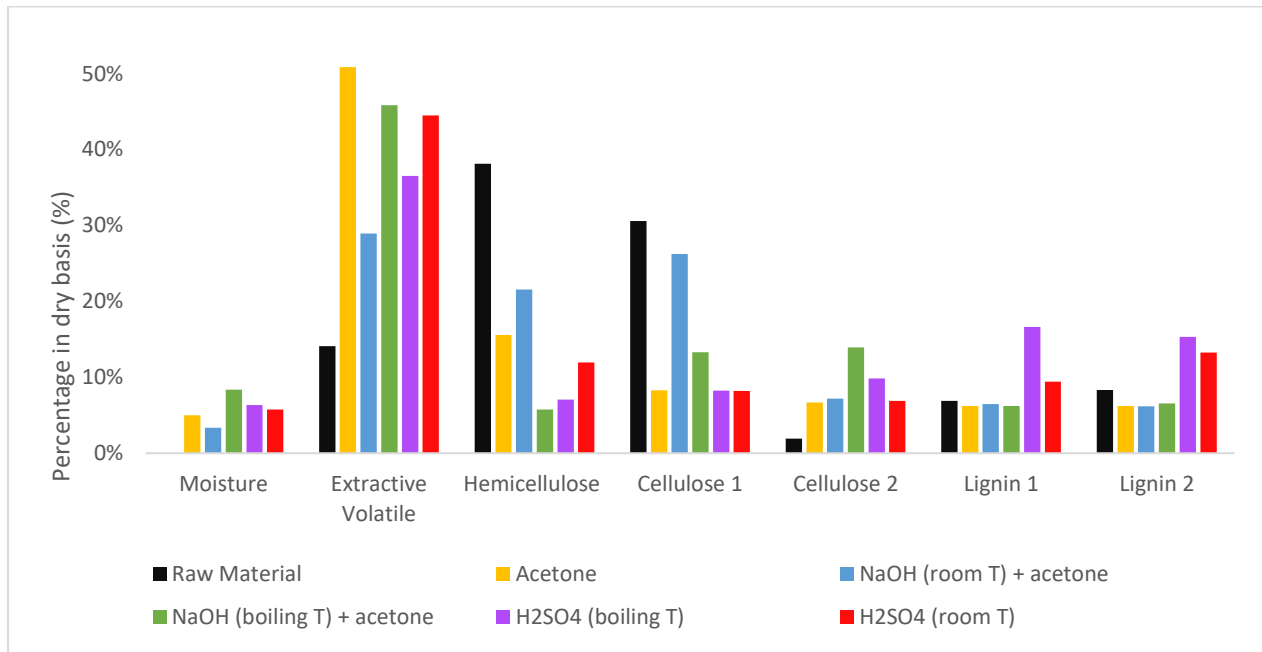
3.3. Thermogravimetry Study

Figure 3-4 Comparison on moisture, extractive volatile, and lignocellulose percentage for each pretreatment

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.

Table 3-3 Moisture, Extractive Volatile, Lignocelullose percentage component before and after pretreatment

Dry Basis	Weight composition (%)						
Drying substance	Moisture	Extractive Volatile	Hemicellulose	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	29.0	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
H2SO4 (boiling T)	6.36	36.5	7.1	8.2	9.8	16.6	15.3
H2SO4 (room T)	5.77	44.5	12.0	8.2	6.9	9.4	13.2

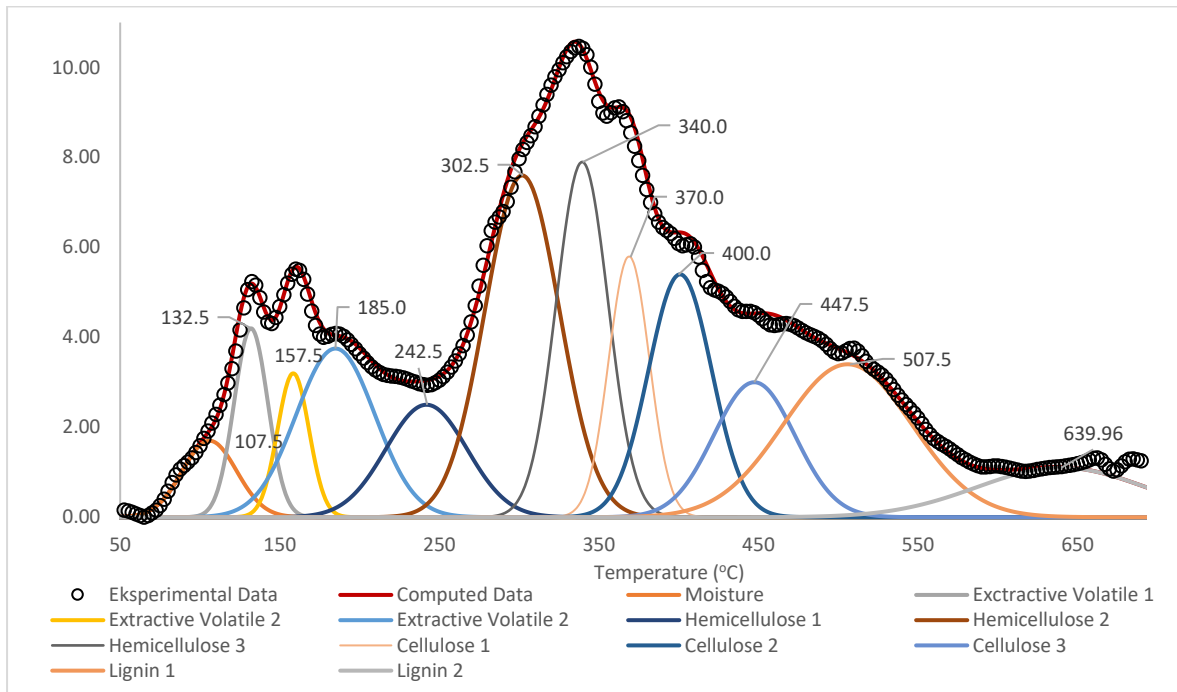# 4. Kinetic Analysis

4.1. Kinetics Pyrolysis

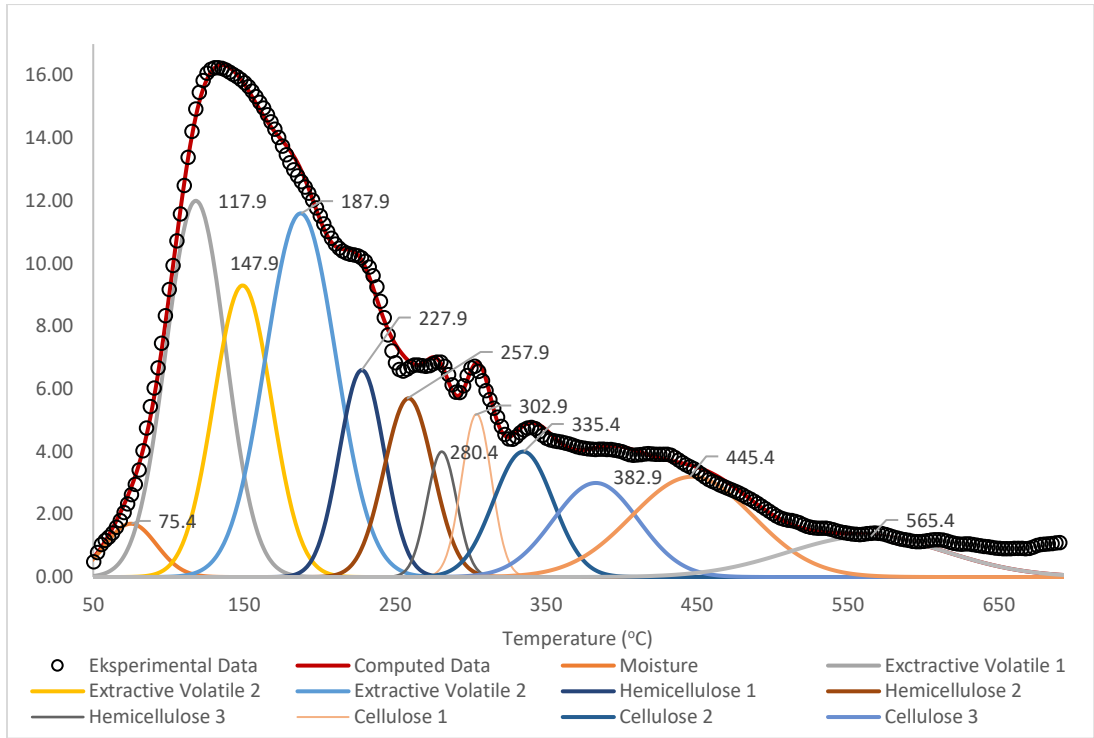*Figure 4-1 DTG curves as a function of temperature for raw compost material for 50K/min*

Figure 4-2 DTG curves as a function of temperature for compost material with H_2SO_4 for 50K/min
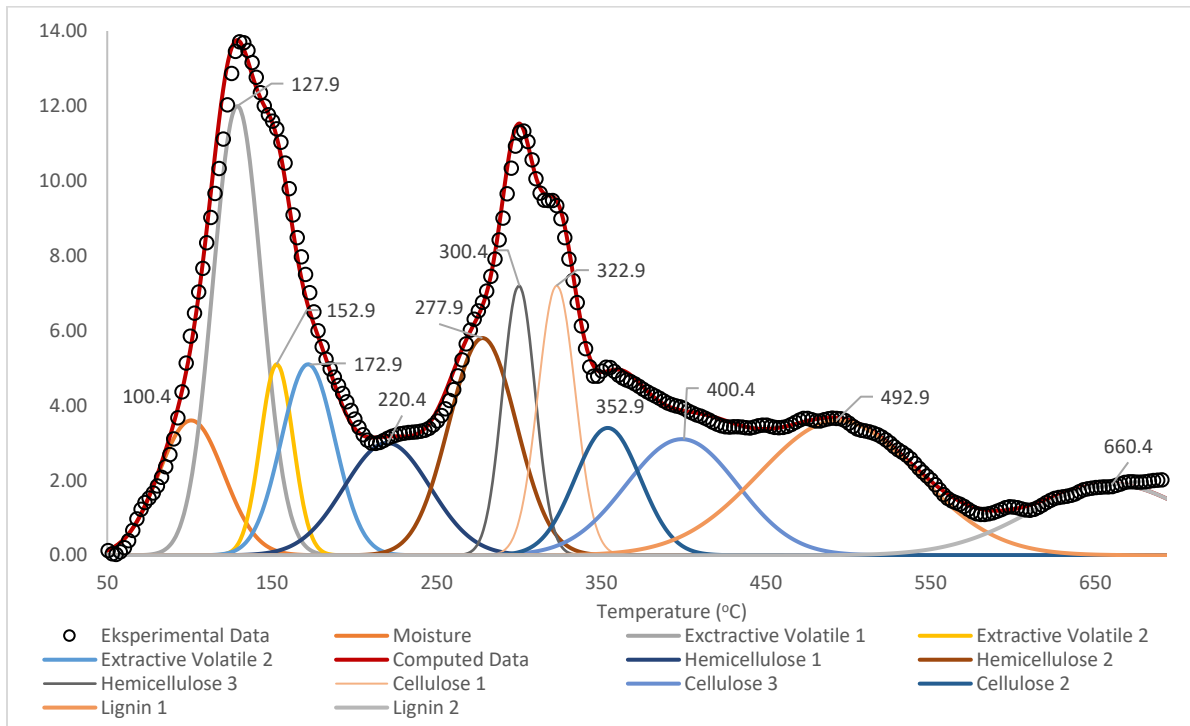

Figure 4-3 DTG curves as a function of temperature for compost material with NaOH for 50K/min

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 H_2SO_4 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.

From this study there is also possibility that Lignin 2 is the residual of combustion process from early process of inorganics or extractive molecule. Further study and analysis needed in this particular component to be sure of the classification.

Table 4-1 Kinetic parameters estimated with Kissinger method

	Raw material compost		NaOH		H_2SO_4	
	Tmax (C)	Ea (kJ/kmol)	Tmax (C)	Ea (kJ/kmol)	Tmax (C)	Ea (kJ/kmol)
Hemicellulose 1	242	96.2	220	113.9	227	46.2
Hemicellulose 2	302	115.4	277	110.2	257	59.2
Hemicellulose 3	340	115.1	300	129.5	280	79.4
Cellulose 1	370	108.7	322	123.3	302	97.3
Cellulose 2	400	134.8	352	152.2	335	102.6
Cellulose 3	447	136.8	400	175.1	382	119.1
Lignin 1	507	158.7	492	194.4	445	170.9
Lignin 2	640	238.5	660	200.3	565	178.8

5. Conclusions and Future Work

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. From thermogravimetry and pyrolysis kinetics it is shown the production of inorganics and extractive volatile increase after pretreatment. It is also showing that H_2SO_4 pretreatment have impact on the lignin growth which can be used as a potential source of energy. 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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