Effect of mechanical fractionation and torrefaction on the biomass composition

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Challenge the future

Effect of mechanical fractionation and torrefaction on the biomass composition

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Abstract

In the Netherlands, green residues such as verge grass are a possible alternative to (partially) replace traditional fossil fuels. A feasible way of doing this, without large modification costs on existing power plants, is biomass co-firing. However, grass has high moisture content, poor grindability properties and high ash content, which have prevented it from being directly co-combusted. Pre-treatments consisting of mechanical dewatering and thermal treatment (torrefaction) could greatly improve the feedstock properties in an energy efficient way. This study firstly investigates the effect of mechanical fractionation on the biomass composition, with focus on the mass losses of carbohydrates, lignin, extractives and inorganic matters during pressing. Secondly, an experimental bench-top, batch torrefaction setup was built. This test rig could provide valuable data from drying and torrefaction experiments, which could be used for modeling purposes and operating experiences for designing a larger-scale torrefaction plant in the future. Also, a preliminary study on the biomass torrefaction behavior was done by analyzing the experimental products.

Mechanical dewatering was found to be quite effective for handling herbaceous biomass feedstock as it removes approximately 30% of the moisture; this pre-treatment also improves the biomass quality by removing about half of the inorganic matters, which could cause slagging and fouling problems during combustion. Besides this, chemical analysis incorporating extraction, hydrolysis and High Performance Liquid Chromatography (HPLC) showed that pressing had removed about 10wt% of the carbohydrates and 20wt% of acid insoluble lignin. In addition, studies on extractive free samples proved that extractives had a catalytic effect on the thermal reactivity of biomass, which means that removal of extractives could lead to (slightly) higher thermal decomposition temperature.

Depending on the process conditions, dried biomass will suffer a 20% - 50% mass loss during torrefaction. Results from the chemical analysis on the torrefied grass had shown the reduction of carbohydrates content at different torrefaction temperatures. The resulted solid product, biochar, has a higher energy density than the primary feedstock and it is easier to store and transport. Also, torrefaction makes the biomass feedstock more brittle and less fibrous, which would benefit the fuel preparation for co-firing.

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Used symbols and abbreviations

Symbol or Abbreviation	Unit	Description
AIL		Acid Insoluble Lignin
AIR		Acid Insoluble Residues
ASL		Acid Soluble Lignin
ar		As received
$C_{4\%}$	g/L	concentration of 4% w/w H_2SO_4
$C_{72\%}$	g/L	concentration of 72% w/w H_2SO_4
C_{HPLC}	mg/mL	concentration of a sugar as determined by HPLC
CV%	%	Coefficient of Variation
D2 lamp		Deuterium Discharge lamp
d.a.f		Dry and ash free
d.b		Dry basis
DFG		Dried Fresh Grass
DPS		Dried pressed Solids
DTG		Differential Thermogravimetric curve
EFG		Extractives Free dried fresh Grass
EFP		Extractives Free dried Pressed solids
FG		Fresh Grass
GC		Gas Chromatography
GJ		Green Juice
HHV	MJ/kg	Higher Heating value
HPLC		High Performance Liquid Chromatography
i		Angle of incidence
LC		Liquid Chromatography
NREL		National Renewable Energy Laboratory
ODW	g	Oven dried weight
PS		Pressed Solids
r		Angle of refraction
$R_{ave.sugar}$		average recovery of a specific SRS component
RI		Refraction Index
SRS		Sugar Recovery Standards
Std. Dev	% mass basis, d.b	Standard Deviation
T	°C	Temperature
TC		Thermal Couple
TGA		ThermoGravimetric Analysis
UV		Ultraviolet
UV-VIS		Ultraviolet Visible
$V_{72\%}$	mL	Volume of 72% acid to be added
V_S	mL	initial volume of sample or standard
w.b.		Wet basis
wt%		Weight percentage
XRF		X-Ray Fluorescence Spectrometry
Y_{mass}	% mass basis, d.b	Mass yield

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1 Introduction

This chapter starts with an introduction to the background of this study, where the research motivation is also explained. The second part presents the research objectives and research questions. The last section provides an overview of this thesis and presents what methods were used for solving the problems.

1.1 Introduction

In the past few decades, concerns about global warming and climate change have reached a new level. Humanity is starting to realize the importance of emission gas reduction. At the Kyoto Conference in 1997, the European Union (EU) and its member states committed themselves to significantly reduce greenhouse gas emissions [UNFCC, 1997]. To be more specific, the Dutch government has made a commitment to the reduction of CO_2 emissions and set a goal of producing 14% (380 PJ) of the total energy consumption from renewable sources by 2020, up from less than 1% in 1999 [Rijksoverheid, 2013]. The new energy policies have stimulated interest in using biomass for energy production. Energy from biomass will have to provide 25 PJ per year, equivalent to 1.7 million tons of biomass per year.

Biomass energy is close to “carbon neutral”, which means that it can be used for energy production while only releasing carbon to the atmosphere that has been captured during the growing cycle of the plant, whereas traditional fossil fuels emit carbon that has been locked away from the atmosphere for millions of years. As the global fossil fuel reserve is depleting rapidly, people see biomass as one of the possible substitute energy resources and start to do a variety of researches / experiments. In big countries such as the UK and USA, energy crops such as willow and maize are planted and used to make biofuels. In a small and densely populated country like the Netherlands, there is very limited space for growing energy crops. Import of biomass is a viable option, but this could be economically unattractive due to its high transportation costs. Thus prioritize the utilization of locally available biomass resources is the right research direction.

Available biomass utilization technologies nowadays can be roughly divided into the following four ranges [Susta et. al, 2009]:

- Direct Combustion: most direct process for converting biomass into usable energy.
- Gasification:
- Anaerobic Digestion
- Ethanol production

Direct Combustion is the most direct process for converting biomass into usable energy. Gasification is the production of combustible gas from carbon containing materials; it contains three main successive stages: oxidation, pyrolysis and gasification. Bio refinery based on Anaerobic Digestion is a biological process that produces a gas principally composed of methane (CH_4) and carbon dioxide (CO_2) otherwise known as biogas, which can be used for production of energy. Starch content of Biomass feedstocks like corn, potatoes and similar can be converted by fermentation process into alcohol (ethanol). Bioethanol can be used as a hydrogen source for fuel cells or for direct combustion and is mainly produced in countries which have low sugar prices. This study will focus on thermal energy conversion in the form of direct combustion.

Direct combustion is the oldest and probably the most important biomass energy conversion technology. Historically, humans have started using biomass-derived energy since the time when people began burning e.g. wood to make fire. Currently, it is still the primary source of energy in rural areas. Biomass is mainly used in small-scale applications such as a domestic stove, where biomass is used as firewood. Large scale commercial use, though growing especially for heating and for electricity production, is still not the dominant application of biomass. As mentioned earlier, the motivation for the use of biomass to replace fossil fuels in steam power plants, cement industries and iron making is growing because it could reduce the carbon footprint of those industries. However, building a plant that burns biomass fuels requires a large initial cost and thus will not be economically beneficial. Combusting biomass fuels in an existing, fossil fuel fired power plant is challenging and could result in major performance penalties due to the large difference in combustion properties of biomass and fossil fuels. A viable option at this moment is partial replacement by cofiring biomass in an existing fossil fuel fired combustion plant. Recent studies [Al-Mansour and Zuwala, 2010; Berndes, et.al, 2010] on biomass co-firing with coal have shown that this technology generates high-efficiency biomass electricity and effectively reduces CO_2 emissions by replacing coal; this also leads to an increase in the share of renewable energy sources in energy balance.

For the choice of biomass, wood pellets made from residual wood are the most popular fuel for co-firing because of their homogeneity, good calorific value, low moisture, low ash content and they are available in considerably large volumes for trading [Sikkema, et al., 2011]. Since wood pellets are essentially compressed sawdust, it can easily be grinded by using the existing coal mills. However, for the countries which do not have a logging industry such as the Netherlands, wood could be a biofuel with high transportation and import/export costs that require incentives or direct subsidies for its large scale utilization. As such, the search for a cheaper alternative biomass fuel is necessary in order to sustain operations with biomass in the future.

Short rotation herbaceous fuels and agricultural waste may become possible alternatives to woody biomass as they are available locally at low cost. In addition, their utilization might have a positive impact on a regional level, not only by displacing fossil fuels, but also by providing new jobs on a regional level. Verge grass is a typical example of this kind of biofuels. It is an attractive biomass resource which generally comes in the form of waste and has a low to negative value (-5 to -55 Euro per ton fresh) [Koppejan et al., 2009]. Harvesting the grass is necessary to maintain short vegetation for traffic safety and also reduces nutrient availability, which decreases biomass production. The total area of verge grass mown in the Netherlands is approximately 50.000 ha, producing approximately 240.000 tons (dry matter), which is collected [Koppejan et al., 2009]. Some 20% of this grass is used as cattle feed. The remaining 80% is composted at high costs. These costs range from approximately 0 to 40 Euros per ton fresh weight. [Koppejan et al., 2009]. Furthermore, there are extensive natural areas covered with grass vegetation where removal of the vegetation is part of the necessary maintenance [Elbersen et al., 2002].

Despite all the advantages of verge grass, it has the same problem as any other kind of non-woody, green residue: high moisture and ash content, low bulk density and poor grindability due to its fibrous and tough structure [Bergman et.al, 2005a]. These unfavorable fuel qualities have been the obstacles that prevent verge grass from being widely used. High moisture content in biomass requires certain de-watering procedures before it can be used as fuel for co-firing, because high moisture will cause the overall temperature in the boiler to decrease. Also, untreated biomass can cause health and safety problems during the storage period. Low bulk density biomass leads to higher transportation costs and requires covered bunkers. Subsequently, green residues are often difficult to grind and thus require higher milling costs or they will cause a reduced burnout in the furnace. In addition, verge grass often has low ash

agglomeration temperatures, which could cause slagging in the combustion system and thus lead to higher maintenance costs. Finally, the high chlorine content will also cause more corrosion and HCl emissions. The reaction between alkali metals and chlorine could cause fouling and corrosion as well. [Tarleton and Wakeman, 2011]. In conclusion: biomass waste properties must be improved before they can be used as feedstock for co-firing.

Suitable techniques for removing the moisture in biomass can be either mechanical fractionation or thermal treatments. The latter is shown to require much less energy demand [Yoshida et.al, 2010]. Mechanical fractionation is a dewatering step which uses mechanical energy to separate the primary raw samples into a liquid fraction, *green juice* and a solids fraction, the *pressed solids*. This technique is often used prior to the thermal treatments to achieve overall lower energy consumption for biomass drying.

A typical thermal treatment is torrefaction, which is a thermal process operated at 200 °C to 300°C in absence of oxygen and at relatively long residence times, typically up to one hour. This technology has been used for tea and coffee making for hundreds of years, yet only recently its potential for preparing bio-fuel has been discovered and has been studied extensively. However, most torrefaction studies have focused on woody biomass and their experiments were carried out on analytical instruments such as Thermo Gravimetric Analysis (TGA) (often) combined with Fourier transform infrared spectrometer (FTIR). This type of setup generally uses only few milligrams for the experiments, which means that torrefaction research on a larger scale setup could be useful.

In a previous study [Mangkusaputra, 2014], the effect of mechanical fractionation (pressing) on the fuel properties (moisture content, ash content) and torrefaction behavior of verge grass were studied. Results have shown that pressing had not only removed the moisture, but also part of the inorganic matters in verge grass, which means a significant improvement of biomass fuel properties could be achieved through pressing. Mangkusaputra's study had employed TGA as its main analyzing technique for qualitative characterization of the organic matters in biomass. This technique is, however, based on studying the shape of the graphs and not meant to be used for quantifying the exact proportion of each component withdrawn from pressing/torrefaction. This means that other analytical methods should be considered in order to quantitatively determine the compositional changes of verge grass.

1.2 Research objectives

The primary objective of this thesis is to investigate the impact of torrefaction on the biochemical composition of verge grass. Biomass torrefaction is carried out on the experimental setup that has been specifically designed for this project. The obtained results in this study will be used for modeling purposes and as reference data for building a large-scale pilot torrefaction plant which runs on a continuous system. Furthermore, as a follow-up research of the previous study [Mangkusaputra, 2014], several open issues such as the effect of extractives on torrefaction and the exact changes of components in verge grass after pressing and/or extraction, will be covered in this study. To sum up, the following questions should be answered in this thesis:

1. What is the effect of extractives on the thermal reactivity of dried verge grass during torrefaction?
2. How is the biochemical composition of verge grass going to change after pressing and extraction?
3. How is the biochemical composition of verge grass going to change at different torrefaction conditions?

1.3 Approaches & thesis outline

This thesis starts by presenting the background of this research, with a general introduction on biomass co-firing and the torrefaction process. Chapter 2 provides the literature study on biomass properties, the torrefaction process and analytical techniques for carbohydrates determination. Acquired information from this literature study should enable a basic understanding of the nature of biomass analysis and torrefaction. Also, the literature study should be an inspiration for further refining the research methodologies.

Using the acquired information from literature study, series of experiments are designed in chapter 3 in order to seek the answers of the research questions. In general, pre-treatments such as pressing and torrefaction must be carried out prior to the analytical experiments. The effect of extractives on the thermal reactivity of dried verge grass could be investigated by first obtain the extractive free sample through extraction. Then compare the thermal decomposition rates of the extractive free sample and the primary sample, which can be performed on TGA.

For the second and third question, biomass compositional analysis requires multiple series of experiments for determining different kinds of components. The carbohydrates and lignin content can be determined through chemical analysis by means of hydrolysis and High Performance Liquid Chromatography (HPLC). Sample's ash content can be measured after combustion; this provides information on the quantity changes of inorganic matters after the pre-treatments. Also, since different inorganic compounds have different effect to the ash behavior of the biomass, incorporation of mineral matter analysis is thus necessary. This was carried out on the X-Ray Fluorescence (XRF) Spectrometry setup.

Chapter 4 starts with the background and motivation for developing the torrefaction experimental setup, followed by a detailed description of the test rig. Results from the drying and torrefaction experiments are given in the last paragraph. Torrefied grass prepared from this setup will be used for the compositional analysis in chapter 5.

Chapter 5 presents the results from all the experiments as well as the interpretation and discussion of the computational outcome. This chapter is arranged in more or less the same order as chapter 3 and contains all the (processed) data that is required to provide answers to the research questions.

In the last chapter, conclusions regarding the results are drawn and recommendations for further improvements are given.

2 Literature Review

This chapter presents the literature review on the topics related to this study. The first part starts with a general description and categorization of biomass, followed by more specific information about herbaceous biomass and its energy potential. Structure and components analysis will also be provided. The second part presents literature studies on biomass co-firing and torrefaction, and explains why torrefaction is necessary and how biomass behaves during torrefaction. Finally, the analytical techniques for carbohydrate content determination are given in the last paragraph.

2.1 Biomass

Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this definition is often used for plant based material, but biomass can equally apply to both animal and vegetable derived material. [Biomass Energy Centre, UK]

A typical plant material uses carbon to construct biomass by absorbing carbon dioxide (CO_2) from the atmosphere, using energy from the sun. If a plant is not eaten it is generally either broken down by micro-organisms or burned. In both ways, carbon is returned to the atmosphere as CO_2 or methane (CH_4). These processes have happened for as long as there have been plants on Earth and is part of what is known as the carbon cycle, which is a closed cycle with no net increase in atmospheric CO_2 levels [Biomass Energy Centre, UK].

2.1.1 Biomass categories

There is no established way of categorizing biomass, because categorization alternatives depend on the purpose and application. Generally there are two ways to categorize biomass: one is biological categorization based on types of existing biomass in nature (such as categorization according to ecology or type of vegetation), and the other is based on the use or application as resources. The latter is highly significant in terms of making effective use of energy [Yokoyama, 2008].

Based on the purpose of this study, an example of biomass categorization in terms of use and application is given in figure 2.1. In this categorization, biomass includes not only the

conventional product and waste from agriculture, forestry and fisheries, but also plantation biomass.

Table 2-1: Biomass categorization in terms of use and application [Yokoyama, 2008]

Biomass		
Conventional Biomass Resources	Agriculture, Forestry (Woody), Livestock farming	
	Food, Materials, Medicine, Timer, Pulp, Chip, etc.	
Biomass Waste (Derivatives)	Agricultural, Forestry, Fishery, Livestock residues (wastes)	
	Rice straw, Cattle manure, Lumber mill, Sawdust, Sewage sludge, Black liquor	
Plantation Biomass	Forestry	Eucalyptus, Poplar, Willow, Oil plam
	Herbaceous	Sugarcane, Switchgrass, Sorghum, Corn, Rapeseed
	Aquatic	Giant kelp, Water hyacinth, Algae

The underlined category is the one which this study is focused on, the herbaceous plants; these are the plants that have leaves and stems that die down at the end of the growing season to the soil level. Compared to woody biomass, they have no persistent woody stem above ground. In the next section, the structure and composition of this particular biomass is elaborated.

2.1.2 Biomass composition

Although there are many types of biomass, and their compositions are quite different, most of them do have some primary components in common such as cellulose, hemicellulose, lignin, starch and proteins. Just like other types of lignocellulosic biomass (such as trees), herbaceous plants mainly consist of *cellulose, hemicellulose* and *lignin*. Cellulose and hemicellulose are often also referred to as *structural carbohydrates (structural polysaccharides)*, because they are the main building blocks of plant cell walls. Figure 2.1 shows the structure of a typical lignocellulosic plant biomass. Apart from these three main components, lignocellulosic biomass also contains other components, such as *extractives*.

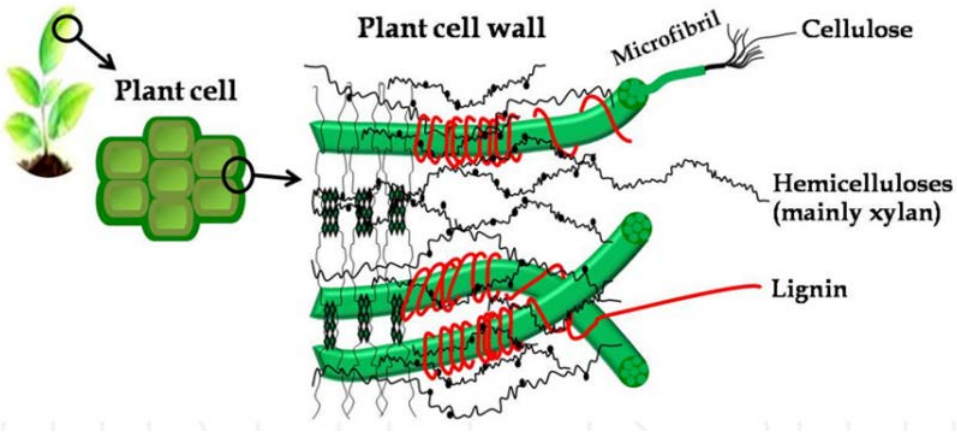


Figure 2-1: Lignocellulosic biomass plant structure. [Tomme et al., 1995]

Cellulose

Cellulose is the main constituent of the plant cell wall, it is the most abundant organic polymer on Earth [Klemm et al., 2005]. The cellulose content of cotton fiber is 90%, that of wood is 40-50% and that of dried hemp is approximately 45%. [Piotrowski et. al, 2011] Cellulose is a polysaccharide composed of linear glucan chains linked together by β-1,4-glycosidic bonds with cellobiose residues as the repeating unit at different degrees of polymerization, depending on resources. Its molecular formula is $(C_6H_{12}O_6)_n$. where n represents the degree of polymerization. The cellulose chains are grouped together to form microfibrils, which are bundled together to form cellulose fibers. The cellulose microfibrils are mostly independent but the ultrastructure of cellulose is largely due to the presence of covalent bonds, hydrogen bonds and Van der Waals forces. Hydrogen bonding within a cellulose micro fibril determines 'straightness' of the chain but inter-chain hydrogen bonds might introduce order (crystalline) or disorder (amorphous) into the structure of the cellulose. The crystalline structure makes cellulose great against acids and alkalis, but if it is an amorphous structure, cellulose is more susceptible to enzymatic degradation [Pérez et al., 2002]. In nature, cellulose appears to be associated with other plant compounds and this association may affect its biodegradation. Figure 2.2.a shows the structural formula of cellulose. Total hydrolysis of cellulose will break the chemical bond and yields D-glucose (a monosaccharide), but partial hydrolysis yields a disaccharide (cellobiose) and polysaccharides in which n is in the order of 3 to 10.

Hemicellulose

Hemicelluloses are the second most abundant polymers and differ from cellulose in that they are not chemically homogeneous. Hemicelluloses are branched, with 5-carbon monosaccharides (pentoses), including D-xylose and D-arabinose, 6-carbon monosaccharides (hexoses) including D-mannose, D-galactose and D-glucose and sugar acids mainly acetyl- and methyl- substituted groups. These polymers usually present themselves together in the hemicellulose structure, hence their noted names such as galactomannan, arabinoglucuronoxylan or glucuronoxylan.

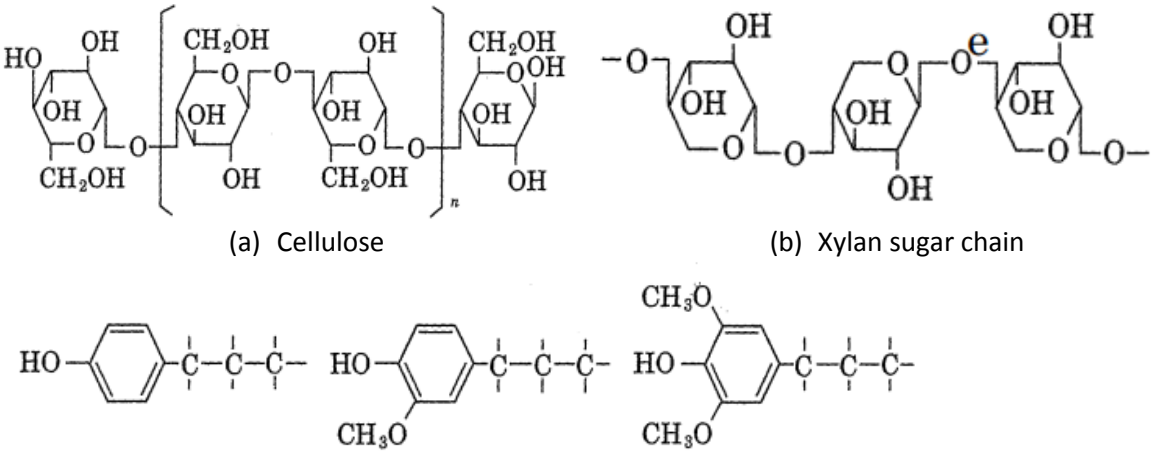
The average molecular formula for hemicellulose is $(C_5H_8O_4)_n$. Because the degree of polymerization n is 50 to 200, hemicelluloses have a lower molecular weight compared to cellulose and branches with short lateral chains that are easily hydrolyzed into monosaccharides [Saha, 2003; Scheller and Ulvsko, 2010], and many hemicellulose are soluble in alkaline solutions. Hemicelluloses in green biomass like straws and grasses are composed mainly of xylan, while softwood hemicelluloses contain mainly glucomannan. In many plants, xylans are heteropolysaccharides with backbone chains of 1,4-linked β-D-xylopyranose units. In addition to xylose, xylan may contain arabinose, glucuronic acid, or its 4-*O*-methyl ether, acetic acid, ferulic and *p*-coumaric acids. Figure 2.2.b shows the structural formula of xylan.

The most important biological role of hemicelluloses is their contribution to strengthening the cell wall by interaction with cellulose and, in some walls, with lignin. Hemicelluloses are bound via hydrogen bonds to the cellulose microfibrils in the plant cell wall, crosslinking them into a robust network. Hemicelluloses are also covalently attached to lignin, forming together with cellulose to form a highly complex structure.

Lignin

Lignin is the third most abundant polymer in nature. It is present in plant cell walls and confers a rigid, impermeable resistance to microbial attack and oxidative stress. Lignin is a complex polymer of phenyl propane units, which are cross-linked to each other with a variety of different chemical bonds. It constitutes the most abundant non-polysaccharide fraction in lignocelluloses [Pérez et al., 2002; Sánchez, 2009]. The three monomers in lignin are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol; they are joined through alkyl–aryl, alkyl–alkyl and aryl–aryl ether bonds. Lignin embeds the cellulose thereby offering protection against microbial and enzymatic degradation. Furthermore, lignin is able to form covalent bonds to some

hemicelluloses, e.g. benzyl ester bonds with the carboxyl group of 4-*O*-methyl-D-glucuronic acid in xylan. More stable ether bonds, also known as lignin carbohydrate complexes, can be formed between lignin and arabinose, or between galactose side groups in xylans and mannans.



(a) Cellulose (b) Xylan sugar chain

(c) Lignin structure unit (phenylpropane)

Figure 2-2: Chemical structures of major lignocellulosic biomass components

Due to its complex yet stable structure, lignin contributes to increased mechanical strength properties in such a way that trees with heights of even more than 100 meters can remain upright. Lignin is also proven to be highly correlated with higher heating value of biomass [Telmo & Lousada, 2010], and reduces the efficiency of hydrolysis [McMillan, 1994].

Extractives

Extractives are a heterogeneous group of substances which can be extracted from biomass by means of polar and non-polar solvents. The amount and types of extractives vary widely depending on the species; these extractives could include a veriety of organic compounds as waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and tall oil [Telmo and Lousada, 2010]. Classification of extractives based on the extraction method and the type of solvent used can be found in Table 2.2.

Previous study [Thammasouk, 1997] has shown the influence of extractives on the analysis of herbaceous biomass, it was advised to remove the extractives from the feedstock prior to the analysis (such as hydrolysis) in order to obtain more accurate estimates of the true lignin and cellulose content in the biomass. However, Thammasouk used three different kinds of biomass

for his study, switchgrass, corn stover and fescue feedstocks, the difference between their carbohydrates content in native substrate and extracted samples were around 5%, 10% and 15%, respectively, which is actually not that large.

Table 2-2: Classification of extractives [Fengel and Wegener, 1983]

Extraction Method	Main extractives group
Steam distillations	Terpenes
	Phenols
	Hydrocarbon
	Lignan
Ether extractions (lipophilic compounds)	Fatty acids
	Fats, oils
	Waxes
	Resins, resins acid
	Sterols
Ethanol extractions	Flavonoids
	Tannins
	Stilbenes
Water extractions (hydrophilic compounds)	Monosaccharides (arabinose, galactose, raffinose)
	Starch
	Pectin materials
	Protein
	Alkaloids
	Inorganic materials

Extractives could also affect the determination of higher heating values (HHV) of a feedstock [Dermirbas, 1999]. It was found that there was a highly significant correlation between HHV, Klason lignin and extractive contents, which means use of the native feedstock is recommended for heating value determination.

Biomass pyrolysis studies [Raveendran et al., 1996] have shown the importance of extractives in biomass char formation. Table 2.3 shows the biomass pyrolysis results, where Yield is calculated

in weight percentage (wt%) on a dry, ash free basis (d.a.f). It can be seen that approximately 27% of extractives are left as char, this means that extractive free biomass may therefore have a slightly lower char yield than that of the native feedstock. Also, since the extractives have the lowest initial decomposition temperature [Giuntoli et al., 2009; Saddawi et al., 2012], the native biomass sample should also decompose at a lower temperature than that of the extractive free samples, this shows that extractives have a catalytic effect by increasing the sensitivity of the reactions.

Table 2-3: Pyrolysis characteristics of biomass components in TGA [Raveendran et al., 1996]

	Yield wt% (d.a.f.)		Initial decomposition Temperature (°C)	Temperature at involution point (°C)
	Volatiles	Char		
Whatman cellulose	97.5%	2.5%	300	440
Wood cellulose	86.0%	14.0%	300	425
Alkali lignin	59.4%	40.6%	140	500
Acid lignin	52.9%	47.1%	200	427
Hemicellulose	68.0%	32.0%	175	277
Xylan	70.0%	30.0%	190	227
Extractives	73.0%	26.9%	120	302

Extraction could lead to lower biomass ash content as water extraction removes a large portion of inorganic matter from the biomass. Ash contents of the native biomass are shown to be higher in comparison with the extractive-free sample. [Thammasouk, Tandjo & Pnner, 1997]

2.1.3 Biomass Properties

The use of any biomass for conversion to energy carriers will be affected by the values of its physicochemical properties. These values will not only determine the conversion process but in general the investment evaluation, as a whole. The dependence of those properties on the different biomass resources which they come from is great and the in-depth understanding of them is essential before the thermochemical conversion process can be considered.

In general, the most important biomass properties are the following

- Moisture content
- Ash content
- Volatile matter content
- Heating value
- Bulk density
- Alkali metal content
- Halogen ion content (in particular Cl)

In this study, mainly moisture and ash content were taken into account during analysis.

Moisture content

Biomass moisture content is defined as the amount of water in the biomass expressed as a percentage of the material's mass. Moisture content has a significant effect on the engineering of the conversion process; either a thermochemical (i.e. combustion) or a biochemical (i.e. fermentation) process is considered. Actually, it has been estimated that an increase in the moisture content of biomass from 0% to 50% can decrease the heating value by about 66% [Sokhansanj, 2011]

The moisture content can vary from less than 20% for many of the agricultural wastes, like husks and straws, and up to 70% for switch grass. Wood, which is an important source of large quantities of biomass, has a moisture content of about 40-50%. Livestock waste biomass (like manure) or organic effluents have, in general, a high moisture content (above 85%) and thus provides them with pumpable characteristics, see table 2.4. Notice that the moisture content in the table is calculated on wet basis (w.b) and not on dry basis (d.b), as wet basis is the most commonly used basis.

Moisture in biomass could be divided into free water and bound water [Colin & Gazbar, 1995]. Free water is the part of moist that can easily be removed by weak mechanical strains. Bound water is a small proportion in the total moisture which needs extra treatments upon its removal. Rolf and Hlade [1979] distinguished three types of bound water:

- Chemically bound water, which is attached to solids by strong chemical bindings, and can be removed by thermal drying at a minimum temperature of 105°C.

- Physically bound water, which can be removed by thermal drying, and is fixed to the solid particles by adsorption or absorption.

- Mechanically bound water, which is found in both micro- and macro capillaries of capillary-porous bodies. This can be eliminated by strong mechanical strain.

Table 2-4: Typical moisture content of various biomass sources [Biomass Energy A]

Biomass source	Moisture Content (w.b.)	Biomass source	Moisture Content (w.b.)
Wood chips	10–60%	Cow manure	88-94%
Wood pellets	8–12%	Pig manure	90-97%
Straw	20-30%	Chicken droppings	75-80%
Sawdust	15-60%	Cheese whey	93-97%
Cotton stalks	10-20%	Maize silage	65-75%
Switch grass	30-70%	Sweet sorghum	20-70%
Bagasse	40-60%	Cardoon	15-20%

Moisture removal techniques applied in this study were mechanical pressing and oven drying. Further review on mechanical pressing is presented in section 2.3, and a description about oven drying is given in chapter 3.

Ash content

Ash content refers to the amount of inorganic matters in biomass including both the structural and extractable forms [Sluiter et al, 2005]. Structural ashes are inorganic substances that are fixed to the physical structural of biomass, and extractable ashes are the ones that can be removed by a washing or extraction method.

For biomass pellets, they need to have extremely low ash content is officially stated so as to meet European and national quality standards [Pellet Fuels Institute, 2008]. The lower the ash content, the less ash is produced from a residential pellet stove or burner so it becomes more convenient for the consumer. In case virgin wood is used as feedstock the standards can be easily met since the ash content in wood is usually less than 1%, while it can be very high in many green residues, see table 2.5. This is why wood pellets quality standards cannot be reached when using green residues as feedstock and another, specified quality standard for

pellets from green residue needs to be introduced. The ash contents were calculated in weight percentage on dried basis.

Table 2-5: Typical ash content of various biomass sources [Biomass Energy A]

Biomass source	Ash Content wt. (d.b.)	Biomass source	Ash Content wt. (d.b.)
Cotton stalk	7%	Douglas fir wood	1%
Wheat straw	4%	Barley straw	6%
Poplar wood	1%	Rice straw	3%
Switch grass	4%	Bagasse (sugarcane)	11%

The quantity and quality of ash in biomass depends on a large amount of factors including its type, its growing and harvest conditions, the fertilization type, the harvest techniques, its storage and transportation along with its pretreatment before it is introduced into a bioenergy conversion process [Biomassenergy, 2014].

High ash content generally makes a plant less desirable as a fuel [Demirbas, 2002]. This has to do with its effect on biomass energy value. Since ash content is a measure of assuming non-combustible inorganics in biomass, the higher the ash content the lower the energy value. In fact, if the ash and moisture content are not taken into account (d.a.f), most of the biomass resources would have similar energy values, since they all contain in various proportions the same substances (cellulose, hemicellulose and lignin).

Secondly, in many energy conversion processes it is not only the amount of ash, but also its chemical composition that must be carefully considered, since ash results in the production of a waste stream that needs to be treated or disposed. Ash composition affects thermochemical conversion processes (like combustion, gasification or pyrolysis) mainly at higher temperature ranges. In case of ash melting at these increased temperatures, this may substantially affect the operational costs of the plant and thus the whole investment profitability. Molten ash is reported to cause rapid fouling on heat transfer surfaces, furnace internals slagging and corrosion in boilers or gasifiers [Baxter et al., 1998; Daytong et al., 1999; McKendry, 2002]. These problems can be explained mainly by two reasons: the reaction between alkali metals and silica forms alkali-silicates which cause molten ash to stick and accumulate on furnace walls, and the reaction between alkali metals and sulfur oxides forms alkali sulfates on combustor heat

transfer surfaces. Besides silica and sulfur, chlorine in the biomass could cause corrosion and fouling as well. Slagging on the surfaces is difficult to remove and collect and may plug some of the mechanical equipment parts that will increase the maintenance costs.

Table 2.6 presents the common used ratios to classify fuels and their behavior upon combustion. These ratios have incorporated the species in the fuel which have been identified as responsible for the slagging and fouling phenomena. These ratios are relatively simple ratios of the mass fraction of serval species in the fuel matrix. The base acid ratio B/A, where B groups compounds with low melting temperature and A groups compounds with higher melting point. For biomass fuel the presence of phosphorus is often relevant. The index B/A (+P) takes into account the influence of increased P_2O_5 content adding it to the B groups as it enhances the development of low-melting-point phases in the fly ash.

Table 2-6: Ratios used in deposition indices [Tortosa Masiá, 20110]

Ratio	Description
B/A	$\frac{\%(Fe_2O_3 + CaO + MgO + Na_2O + K_2O)}{\%(SiO_2 + Al_2O_3 + TiO_2)}$
B/A + (P)	$\frac{\%(Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5)}{\%(SiO_2 + Al_2O_3 + TiO_2)}$

Table 2-7: Deposition indices [Tortosa Masiá, 2010]

Index	Description	Tendencies/Values			
		Low	Medium	High	Severe
R_S	$(\frac{B}{A}) \cdot S_{dry}$	<0.6	0.6-2.0	2.0-2.6	>2.6
S_R	$\frac{\%(SiO_2)}{\%(SiO_2 + MgO + CaO + Fe_2O_3)} 100$	>72	72-65	>65	
F_u	$(\frac{B}{A}) \cdot (\%Na_2O + \%K_2O)$	<0.6		0.6-40	>40
Cl content	$\%Cl_{dry}$	<0.2			>0.5

Using the described indices different correlations can be calculated, see Table 2.7. The correlations used most often are: the slagging index R_S, slag viscosity index S_R, the fouling index F_U, and the chloride content in biomass fuels, which also indicates the slagging inclination.

2.2 Torrefaction

Biomass can provide a large variety of convenient feedstock for energy, metallurgical and chemical industries on a sustainable basis. This feedstock can be in the form of solid, liquid or gases. People have been producing solid fuels (like charcoal) from biomass through pyrolysis for thousands of years. Torrefaction (French word for "roasting" is a mild form of pyrolysis at a temperature typically ranging between 200 and 300 °C. People have been using this technology for roasting green coffee beans, but in recent time, it has caught attention from power industries for pretreating biomass as a coal substitute. Torrefied biomass is used in fields such as [Basu, 2013]:

- Cofiring biomass with coal in large coal-fired power plant boilers
- Burning fuel in decentralized or residential heating system
- Gasifying it as a convenient fuel
- Providing feedstock for chemical gasification
- Substitute for coke in blast furnaces for reduction in carbon foot print of metallurgy industry.

This study is mainly focused on the application of torrefaction in the field of cofiring. The following sections discuss the torrefaction principle and conditions, biomass decomposition mechanisms, the torrefaction process and available torrefaction technologies.

2.2.1 Torrefaction principles and conditions

Basu [2008] has provided a very precise definition about torrefaction in his book "Biomass Gasification, Pyrolysis and Torrefaction", he described torrefaction as:

" a thermochemical process in an inert or limited oxygen environment where biomass is slowly heated to within a specified temperature range and retained there for a stipulated time such that it results in near complete degradation of its hemicellulose content while maximizing mass and energy yield of solid product."

From this definition, it is easy to derive the four important conditions for a torrefaction process, *temperature*, *oxygen concentration*, *heating rate and residence time*.

Table 2.8 has depicted some torrefaction studies where the researchers have suggested all different temperature ranges for a torrefaction process. Although their minimum temperatures are different, they have all set their maximum torrefaction temperature at 300°C. A typical torrefaction temperature range is between 200 °C and 300 °C [Bergman et al., 2005a], this is mainly due to the following two reasons: the first one is the decomposition temperatures ranges of the three main components of biomass, cellulose, hemicellulose and lignin; a detailed description about biomass decomposition mechanisms could be found in section 2.2.2. Another motivation for choosing this temperature range is to make the biomass lose its fibrous nature such that it is easily grindable, while it is still possible to form it into pellets without binders. These requirements limit the torrefaction temperature range.

Table 2-8: Torrefaction temperature ranges as suggested by different researchers

Researchers	Temperature Range (°C)
Arias et al. [2008]	220-300
Chen and Kuo [2010], Prins [2005], Zwart et al. [2006]	225-300
Pimchuai et al. [2010], Prins et al. [2006]	230-300
Bergman et al. [2005a], Tumuluru et al. [2011], Rouset et al. [2011], Sadak and Negi [2009]	200-300

Conventional direct heated torrefaction for making tea and coffee beans is carried out under atmospheric conditions; torrefaction of biomass in contrast, is carried out in absence of oxygen. However, some studies [Basu et al., 2013; Uemura et al., 2011] have shown that it is not essential to have an oxygen-free environment for torrefaction. Presence of a modest amount of oxygen can be tolerated and may even have a beneficial effect on design of commercial torrefier as low concentration of oxygen can be tolerated.

A biomass torrefaction process is traditionally characterized by a low particle heating rate, which is typically less than 50°C/min [Bergman et al., 2005]. Also the reactor residence time (about one hour) of the process is relatively long. This is to ensure that maximization of the solid yield is achieved during the process, a higher heating rate would increase the liquid yield at the

expense of solid products as is done for pyrolysis. A more detailed description about how energy and mass changes during a torrefaction process is given in section 2.2.3.

2.2.2 Biomass decomposition mechanism

A biomass would go through numerous reactions during torrefaction, its three main components, cellulose, hemicellulose and lignin all react differently to different temperatures, these reactions could be grouped into a few main reaction regimes, as is shown in figure 2.3. [Bergman et al., 2005a]

In this figure, reactions of a biopolymer are divided into five regimes, with green (A) being the lowest temperature regime and red (E) being the highest temperature regime. The green box represents the range of torrefaction temperatures, and the blue line splits this range into a low (<250°C) and high (>250°C) torrefaction temperature regime.

In temperature regime A, physical drying of biomass occurs. When temperature reaches C, the depolymerisation and recondensation regime, this means that the polymers will break into smaller (shorter) polymers and then condense within the solid structure. A further increase of temperature to regime D leads to limited devolatilisation and carbonization of the intact polymers and the solid structures formed in the temperature regime C. After that the temperature goes up even further to E, which is when extensive devolatilisation and carbonization of the polymers and formed solid structures in D will happen. For lignin there is an extra regime B defined between A and C, which is when softening of lignin happens. This would help the densification of biomass (via pelletization e.g.), as softened lignin is a good binder.

Based on figure 2.3, a simple comparison could be made between the three main components in a lignocellulosic biomass. Hemicellulose is the most reactive polymer followed by lignin and cellulose is the most thermostable one. By taking a look at the torrefaction box, it is observed that at a low temperature regime (below the blue line), the main biomass decomposition comes from the limited devolatilisation and carbonization of hemicellulose. Minor decomposition is to be expected for lignin and cellulose except for chemical changes in their structure, which however do not lead to a significant mass loss. In the high temperature regime, decomposition becomes more active as hemicellulose extensively decomposes into volatiles and a char-like solid product and also lignin and cellulose show limited devolatilisation and carbonization.

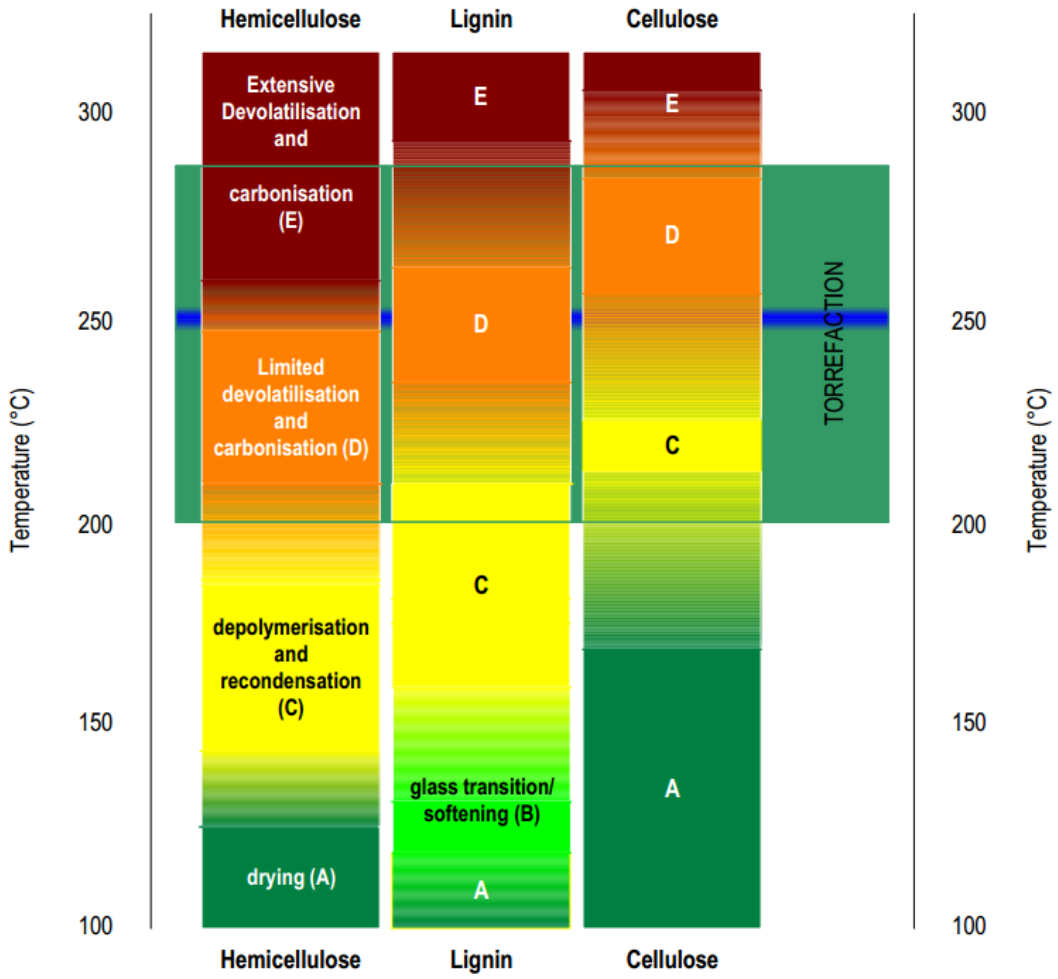


Figure 2-3: Main physical-chemical phenomena during torrefaction of lignocellulosic materials [Bergman et al., 2005a]

One thing that should be mentioned is that the transition from one to another decomposition regime happens much faster for hemicellulose than for lignin and cellulose, and this transition is very much species dependent. The transitions between the reaction regimes of hemicellulose in figure 2.3 represent hemicellulose of deciduous wood. Deciduous (willow, beech) wood has quite a different hemicellulose structure compared to that of the coniferous (spruce, larch) wood. Due to these differences deciduous wood is more reactive and results in significantly more devolatilisation (and carbonization). More details can be found in the study of Bergman et al. [2005].

2.2.3 Torrefaction product distribution

Torrefaction is a complex process with numerous reactions, many substances are formed and reacted again with each other. Torrefaction products can roughly be divided into three categories based on their states, solid, liquid and gas, based on their state at room temperature. Table 2.9 shows the classification of torrefaction products based on Bergman's study [Bergman et al., 2005a].

Table 2-9: Products formed during torrefaction of biomass [Bergman et al., 2005a]

State	Groups of components
Solid	• Original sugar structures • Modified sugar structures • Newly formed polymeric structures • Char • Ash
Gas (permanent)	• H_2, CO, CO_2, CH_4
	• C_xH_y, toluene, benzene
Liquid (condensable)	• Water • Organics sugars, polysugars, acids, alcohols, furans, ketones • Lipids terpenes, phenols, fatty acids, waxes, tanins

The solid phase torrefaction products consist of original sugar structures and reaction products. The reaction products in the solid phase are largely modified sugar structures, newly formed polymeric structures with possibly a certain degree of aromaticity, typical carbon rich char structures and the ash fraction.

Gas state torrefaction products are in general compounds with a boiling point below -33 °C, like H_2, CO etc. These substances are permanently in gas phase under normal circumstances (room temperature, atmospheric pressure). There are also small amount of light aromatic components, such as benzene and toluene in gas state, been detected as well.

Condensable fractions in the torrefaction products are called liquids. These compounds generally have a higher boiling point than room temperature, as they soon start to condense along the gas path when gas temperature decreases. Liquids can be divided into three sub-groups. One sub-group is reaction water as a product from the thermal decomposition (in addition to the freely bound water that has been released from the biomass by evaporation). The organics sub-group consists of organics that are mainly produced during devolatilisation and

carbonization. Finally, the lipids are a group of compounds which are not reaction products, but inert substances that are presented in the original biomass. They are evaporated under torrefaction conditions, such as fatty acids and waxes. These compounds are mainly liquids, but some can be solid at room temperature.

Prins [Prins, 2005] used the same classification as Bergman and provided an overall mass balance of three typical lignocellulosic biomass, willow, larch and straw, from several torrefaction experiments; this is shown in figure 2.4, where it can be seen that solid products account for at least 80wt% of the total reaction products, and the amount of lost material increases with temperature and residence time. In addition, Prins also provided the product yields of condensable products (weight formed divided by the dry- and ash- free weight of wood) for willow, see figure 2.5. In this figure, acetic acid and water are found to be the main liquid torrefaction products of willow, while smaller quantities of methanol, formic acid, lactic acid, furfural, hydroxyl acetone and traces of phenol are found. The product yields are calculated on dry basis.

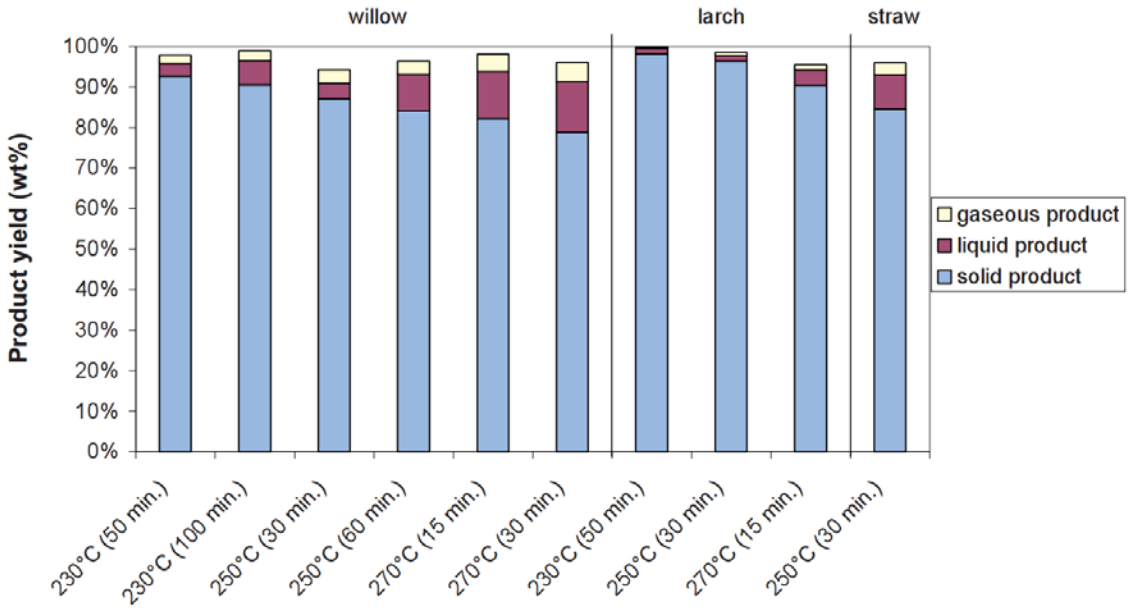


Figure 2-4: Overall mass balance of several torrefaction experiments [Prins, 2005]

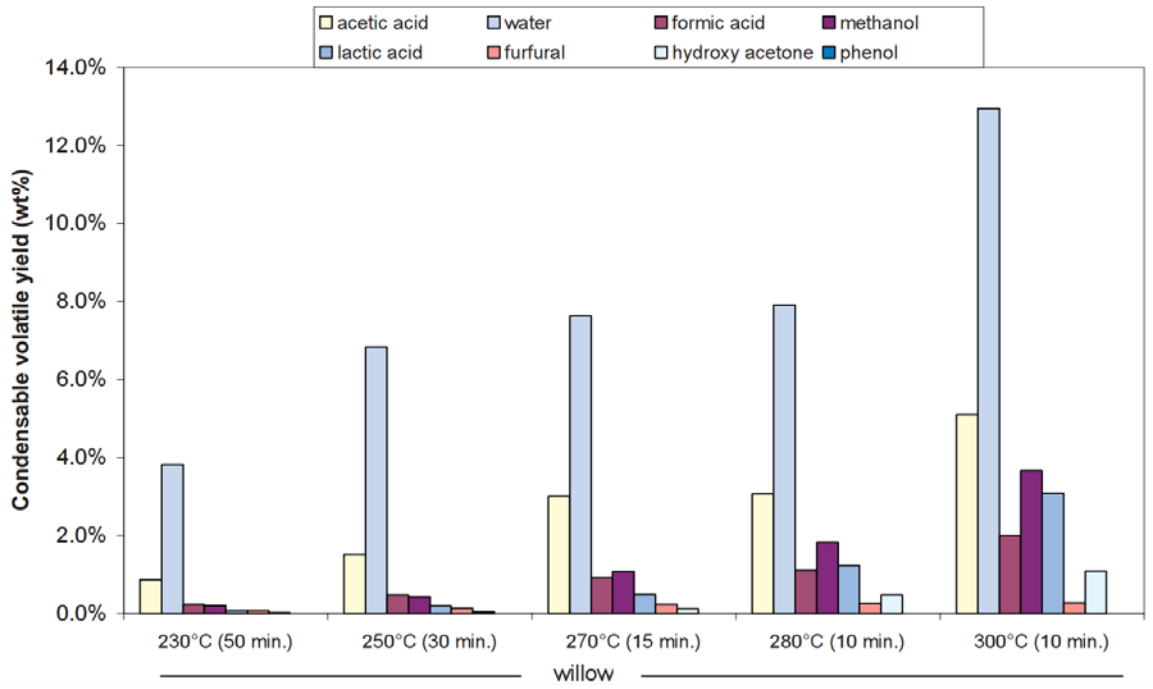


Figure 2-5: Product yields of condensable volatiles formed in torrefaction at different conditions, for willow [Prins, 2005]

2.2.4 Torrefaction process

Process overview

Figure 2.6 is a simple illustration of the torrefaction process, where one unit of biomass (dry wood) is used as input for the process. During torrefaction, the biomass will partly decompose and give off various types of *volatiles* and *gases*. Product of this process is referred as *torrefied biomass* or *char*.

Thermal treatments happen in the torrefier through (direct) contact of the biomass with the heating medium or heat carrier. The heating medium here could be a hot substance, dry or wet. For wet torrefaction, hot compressed water is used for heating up the biomass [Yan et al., 2009]. Dry torrefaction involves heating either by a hot inert gas (like nitrogen) or by indirect heating. The dry torrefaction process is currently being commercialized.

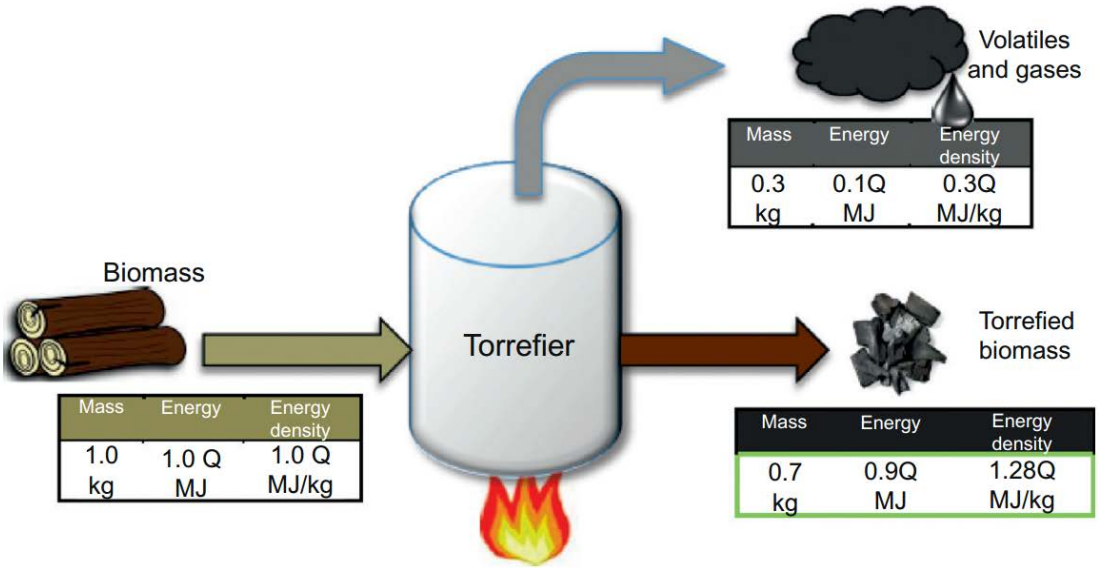


Figure 2-6: Mass and energy changes of a feed undergoing torrefaction [Basu, 2008]

Process yields

As mentioned in the previous section, different biomass species react differently to the torrefaction process due to their various compositions. Also the torrefaction temperature is a determining factor for the properties of the torrefaction products. Bridgeman et al [2008] conducted several torrefaction mass balance experiments, the data is reproduced in Table 2.10, which provides a summary of torrefaction products' mass and energy yields of three different biomass species, reed canary grass, wheat straw and willow.

It can be concluded from the table that biomass torrefaction has an overall higher energy yield than mass yield, this effect becomes more marked for higher temperature treatments, where the differences between mass and energy yields also become higher. Comparing the differences between species, woody biomass like willow shows higher yields than agricultural residues under the same torrefaction conditions, this is due to the higher volatile matter content in the agricultural residues and the decomposition of extractives and hemicellulose, the main fraction decomposed in the torrefaction temperature range.

Table 2-10: Mass and energy yields for reed canary grass, wheat straw and willow, treated at temperature of 230, 250, 270 and 290 °C (reaction time of 30 mins). [Bridgeman et al, 2008]

	Temperature [°C]			
	230	**250**	**270**	**290**
Reed Canary Grass				
Mass yield (d.a.f.)	92.6%	84.0%	72.0%	61.5%
Energy yield (d.a.f.)	93.5%	86.6%	77.1%	69.0%
Wheat Straw				
Mass yield (d.a.f.)	91.0%	82.6%	71.5%	55.1%
Energy yield (d.a.f.)	93.5%	86.2%	78.2%	65.8%
Willow				
Mass yield (d.a.f.)	95.1%	89.6%	79.8%	72.0%
Energy yield (d.a.f.)	96.5%	92.7%	85.8%	79.2%

Process heat requirement

The torrefaction process must provide both sensible heat to raise the feedstock's temperature, and latent heat to evaporate the water contained in the biomass. From the studies [Shah, Darr et al. 2012; Joshi 2014] which focused on heat utilization within the process and integration of waste heat sources, it was mentioned [Joshi 2014] that heat required for biomass drying at a relatively lower temperature accounts for a large proportion of the total heat requirement, with only a small quantity of heat being used to raise and maintain the temperature of biomass at the torrefaction temperature. In addition, torrefaction reactions were reported [Bates, R. B., & Ghoniem, A. F. 2013] to be mildly endothermic or exothermic depending on the extent of the reaction. Although the heat of the reaction may be an important variable with respect to process control, it accounts only for a small proportion of the entire process heat requirement.

Regarding the heat supply, this could be realized by either combusting additional fuel, combusting the torrefaction gases or recirculating heat. Additional fuel is mainly used by a stand-alone torrefaction plant, where the heat supplied by torrefaction gases may not be enough for successful operation. However, this method may lead to extra operational costs,

thus it has been suggested that the torrefaction process should be integrated with existing waste heat sources [Håkansson, K., et. al., 2010]. This is of course under the condition that the integration between the torrefaction unit and the primary process operation will not affect the waste heat production from the primary process. Furthermore, system integration would also contribute to a better utilization of the torrefaction gases, and together with heat recirculation, these would lead to an overall lower external heat requirement.

2.3 Analysis of carbohydrates

Herbaceous feedstocks are composed primarily of carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin). Lower concentrations of various compounds, such as proteins, acids, salts, and minerals, are also present.

Concentrations of cellulose, hemicellulose and lignin have major influence on the properties of biomass feedstocks and the changes of their concentrations during the torrefaction process are the key for torrefaction kinetic study. However, direct determination of carbohydrates can be quite difficult due to the complexity and diversity of their structures. [Hvizd, 2011]

Chromatographic methods are currently the most powerful analytical techniques to separate and identify different types of carbohydrates, the concentrations of these carbohydrates can also be derived from the output. Gas chromatography (GC) [Grob & Barry, 2004] and Liquid Chromatography (LC) [Snyder et. al., 2011] are commonly used chromatographic methods. The principles of these two methods are the same: they separate the samples by passing them through an analytical separation column. This column is either capillary or packed with certain types of particles which would retard some components in the sample more than others, these substances fixed in place for the chromatography procedure are called the *stationary phase*. Depending on the type of column, different types of constituents will have different retention times in the column, because their partition coefficients, polarities or sizes are different. A simple illustration of principles of LC is shown in figure 2.7 [Agilent Technologies, 2011]. The main difference between LC and GC is the physical state of *mobile phase*, which is liquid for LC and gas for GC. The mobile phase consists of the sample being separated/analyzed and the solvent that moves the sample through the column. The mobile phase moves through the chromatography column (the stationary phase) where the sample interacts with the stationary phase and is separated.

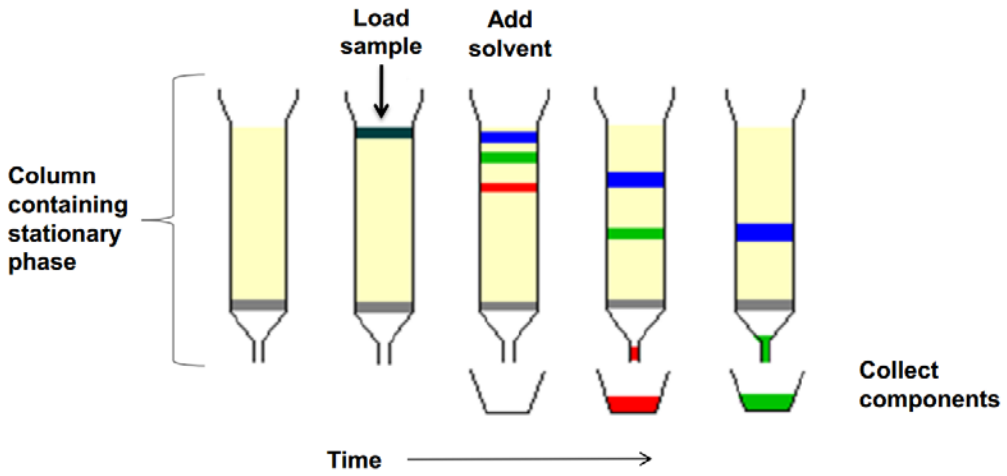


Figure 2-7: Principles of Liquid Chromatography [Agilent Technologies, 2011]

High Performance Liquid Chromatography (HPLC) is the modern variant of LC, it has been around for about 35 years and is the most used separation technique because of its fast, specific, sensitive and precise measurement. Just like LC, HPLC uses small volumes of liquid samples which are injected into a packed column with tiny particles (3 to 5 µm in diameter), where individual components in the sample move down the column with a liquid forced through the column by relatively high pressure delivered by a pump. Particles in the column packing interact physically and/or chemically with the sample components, this would result in each constituent having a different retention time. The exit of the column is connected with a flow-through device (*detector*), where the amount of these separated components is measured. An output from this detector is called a *liquid chromatogram*.

For the detection of the separated components after the column, there are two detectors available for HPLC setup in the laboratory of Process & Energy department: Ultraviolet (UV)/ Ultraviolet Visible (UV-VIS) detection and Refractive Index (RI) detection. The UV detector employs a deuterium discharge lamp (D2 lamp) as a light source, with the wavelength of its light ranging from 190 to 380 nm. The UV-VIS detector uses an additional tungsten lamp (W lamp), which can detect components at even higher wavelengths [Hitachi High-Tech, 2001a]. Since carbohydrates absorb only at wavelengths lower than 200nm, UV-VIS is not a suitable technique for detecting monosaccharides [Binder, 1980].

The Refraction Index of a material is the velocity of light in a vacuum divided by the velocity of light in the material ($n=c/c_m$. Theoretically , RI of a material is determined by the angle of

refraction (r) and angle of incidence (i) at a boundary between it and a material with known RI, this is referred to as the Snell's law ($\sin(i)/\sin(r) = n_2/n_1$). Based on this principle, RI detectors were developed to measure the changes in refraction of light in solution.

Figure 2.8 shows a typical RI detector optical system, where the flow cell of an RI detector is divided into the sample side and the reference side cells. Both cells are first filled up with equilibrium eluate flow, then the sample coming from HPLC is introduced to the sample side cell, this leads to changes in the chemical composition in the sample side solution, which also changes the photorefractive level. As a result, the amount of light which goes to the receiving element varies, and shows a peak which can be detected. Generally, the RI detector should be able to detect anything which has a different RI than the eluent, thus the RI detector is often called a universal detector" [Hitachi High-Tech, 2001b].

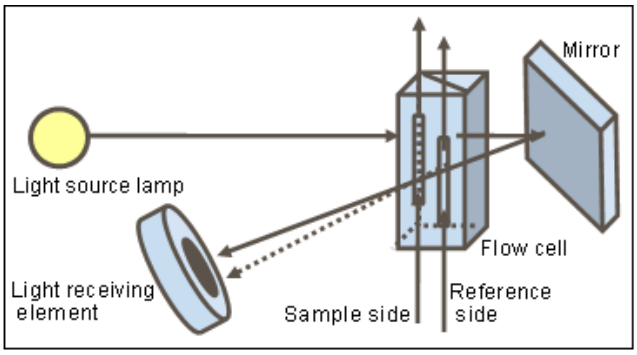


Figure 2-8: Diagrammatic illustration of a RI detector optical system [Hitachi High-Tech, 2001b]

3 Material preparation and analyzing methods

This chapter presents the detailed descriptions about the methods which were employed to answer the research questions. The first part of this chapter presents where and how the verge grass trimmings were collected, followed by introducing the pretreatment methods, including oven drying, grinding, pressing and extraction, this part will be as referred as the preparation steps. The third part is divided into four subsections, first part presents the Thermo Gravimetric Analysis (TGA) for characterizing the biomass pyrolysis, followed by laboratory analytical procedure for ash content determination, then the X-Ray Fluorescence Spectrometry (XRF) for mineral matter analysis and finally, High Performance Liquid Chromatography (HPLC) for determination of structural carbohydrates and lignin in the verge grass, the experiments listed in part three will be referred as the analyzing experiments.

3.1 Material

In this study, verge grass was chosen as the representative for the herbaceous biomass due to its abundant amount and availability, especially in the Netherlands. [Wolter Elbersen et al. 2002] The verge grass samples used for this study were collected in different period of the year from autumn 2013 until late summer 2014 (time when the sample was collected will be mentioned specifically in each experiment), at four different locations:

- Location A - Pavement in front of the Process and Energy building, which is located at Leeghwater straat 44.
- Location B - Pavement next to Aerospace Engineering building, along the Rotterdamseweg.
- Location C - South of kruithuispad, under the bridge of N470.
- Location D - Duck pond opposite to the baseball field on the intersection of Schoemakerstraat and Mekelweg.

Grass samples were trimmed manually using kitchen knife and ensured that none of the root part or other plants were taken, the samples were put in a 2.5L sealed plastic bag and processed according to the methods which will be introduced in the next section. Collected samples were

processed on the same day in batches, this is not only because of limited experiment apparatus, but more importantly, by taking average of these experiments, more accurate results could be They will be referred to as *fresh grass.* In case fresh trimmed grass was required by the experiment, sample was cut and put in the test rig the same day.

It should be mentioned that grass species at different locations are not always the same and weather conditions vary as well. Because of this, locations where the grass was collected were also recorded in the results. As for the weather conditions, although temperature varies through the year, grass were collected on the days when humidity, precipitation and wind conditions were similar. In this way, influences of external factors to the result were kept at its minimum.

3.2 Pretreatment methods

In this research, some pretreatments steps were adopted before the analyzing experiments. These pretreatments were not only needed for determining some basic material properties such as ash and moisture content, but also mandatory for preparing the samples for the experiments. The employed steps were oven drying; grinding, pressing and extraction, samples after pretreatments will be later referred as *pretreated biomass*.

Oven drying

Drying was the basic preparation step for biomass analysis, not only the moisture content was determined through drying, drying also make sure that samples could meet the requirements of the analysis experiments.

In this study, biomass feedstocks for the analyzing experiments were prepared following the procedure which was presented in “Preparation of Samples for Biomass Compositional Analysis” (Hames et al., 2008). This procedure worked with a drying temperature of 45 °C and started by putting the empty container in a pre-heated HEREAUS T-5050 oven at 45°C for 3 hours, then let it cool down to room temperature in a desiccator and recorded its weight to the nearest 0.1g. Second step was placing the container with biomass in the oven and let the material dry for 24 to 48 hours, provided that maximum depth of the biomass was1 cm. After this, container was cooled in a desiccator (vacuum and used silica as drying agent) and its weight was recorded. Hereafter, the container was heated up in the oven again for another hour, then cooled down, and its weight was again measured and registered. The last step was repeated when necessary,

until the change of biomass weight was less than 1% after 1 hour reheating. This procedure was a reliable alternative for the traditional air drying method, which was more time consuming (air drying method needs days before the biomass reaches a weight which changes less than 1% within 24 hours). Note that this procedure was only used for field collected biomass or pretreated biomass such as fresh grass and pressed grass, products / residues coming from the experiments were dried by following the below described procedure.

For determination of moisture content and total solids of the material, a much higher drying temperature than 45 °C was required. The procedure from "Determination of total solids in Biomass and total dissolved solids in liquid process samples" [Sluiter et al., 2008] described the steps for oven drying method at 105°C; the reason for choosing this temperature was that at ambient pressure, this temperature ensured that all the water (and possibly other components volatilized at 105 °C) present in the sample will be gone. Similar to the oven drying method at 45 °C, this procedure started with pre-drying the weighing dish at 105 °C, its weight was recorded after it was cooled down in a desiccator. Weight of the sample plus dish was recorded. After this, the dish was put in the oven for minimum of 4 hours, then cooled down to room temperature and its weight was measured again. Here after, the sample was put back into oven and being dried to *constant weight,* which was defined as less than 0.1% change in the weight percent solids upon one hour of re-heating the sample.

The used terminology, *total solids* refers to the amount of solids remaining after heating the sample at 105 °C to constant weight, the sample could be biomass feedstock, pretreated biomass or residue remained in the filter. Conversely, the *moisture content* was a measure of the amount of water (and other components volatilized at 105 °C) present in such a sample. The combined liquid and solid material resulting from biomass pretreatment was called *slurry;* the liquid fraction of biomass slurry was called *liquor.* The term *total dissolved solids* refereed to the amount of residue remaining from a filtered liquor sample after heating the sample at 105 °C to constant weight.

Formulas for calculating the percent total solids, or percent dissolved solids for a liquor sample, on a 105 °C dry weight basis were given:

$$\%Total\ solids = \frac{(Weight_{dry\ pan\ plus\ dry\ sample} - Weight_{dry\ pan})}{Weight_{sample\ as\ received}} \times 100 \qquad \text{(Equation 3.1)}$$

$$\%Dissolved\ solids = \frac{(Weight_{dry\ pan\ plus\ liquor} - Weight_{dry\ pan})}{Weight_{liquor\ as\ received}} \times 100 \qquad \text{(Equation 3.2)}$$

The percentage of moisture in biomass sample could be calculated as follow:

$$\%Moisture = 100 - \frac{(Weight_{dry\ pan\ plus\ liquor} - Weight_{dry\ pan})}{Weight_{liquor\ as\ received}} \times 100 \qquad \text{(Equation 3.3)}$$

Grinding

Some literatures sources [Grethelin, 1985; Dasari, 2007; Zhang, 2013] have shown that biomass particle size was correlated with the sugar yields from hydrolysis. Particle size was a determining factor for the Accessible Surface Area (ASA), which was the surface area of a biomolecule that was accessible to a solvent. For biomass hydrolysis, deviation to a smaller particle size might result in a low bias in carbohydrate content (and consequently high lignin bias) due to excessive carbohydrates degradation. Deviation to a larger particle size might also result in a low bias in carbohydrate content (and consequently high lignin bias) due to incomplete hydrolysis of polymeric sugars to monomeric sugars.

For this study, biomass grinding was performed by following the procedure from LAP "Preparation of Samples for Biomass Compositional Analysis" (Hames et al., 2008) though with different apparatus. According to the procedure, biomass feedstock should be fed into the knife-mill with 2 mm screen, unfortunately, this mill was not available in the P&E laboratory, alternatively, a generic coffee grinder (STROB – BG 701) was used instead. The oven dried fresh grass was put into the hopper and ground carefully until their average size met the experiment requirement ($\pm$2mm). During this process, grinding was stopped every five seconds in order to prevent large temperature rise of the grinder blades, since the heat could damage the biomass sample. After grinding, the samples were carefully collected and stored in a plastic sample bottle, sealed and kept in a refrigerator at -20 °C until needed.

One thing worth mentioning was that ground sample was not sieved. This is because that the entire biomass sample was analyzed, sieving can frequently cause fractionation and thus should not be performed.

Pressing

To study the effect of mechanical dewatering of biomass on torrefaction and ash content, samples were prepared by putting part of the fresh collected grass through *Samson gear GB 9002 juicer*, which is shown on the left in figure 3.1; this was a screw presser which presses fresh grass against a wire mesh creating pressure which facilitates liquid extraction. The juicer consisted of five components, which were auger, nozzle (only the bottom right nozzle was used), squeezing cap with three squeezing strength positions, a juicing screen and a pusher, see figure 3.1 (right).

Figure 3-1: Gear juicer (left) and its components (right)

Pressing of the fresh grass happened on the same day after the fresh grass trimming were collected. The grass samples were fed through the hopper and pushed downward using the pusher. Squeezing strength was set to be maximum, auger speed and pressing power was 80 RPM and 160 W, respectively. The fresh grass was then progressively separated into *grass juice* and *pressed solids* of which were collected in a separate container. A strainer was placed on top of the liquid container to make sure that the green juice will not have any large solids lumps in it.

After pressing, the pressed solids were dried at 45 °C following the procedure from oven drying. Small portions of the pressed solids were placed in a preheated oven at 105 °C for their moisture content and total solid percentage determination. Dried pressed solids were ground by following the grinding procedure, ground samples were ready for further analysis.

Grass juice was poured into a plastic sample bottle, sealed and immediately put in a refrigerator at 4 °C in case that analyzing experiments (such as hydrolysis) could carried out within two days; if not, grass juice was kept in a freezer at -20 °C for future use. Again, a small portion of grass juice was oven dried at 105 °C for moisture content and dissolved solids determination.

Extraction

Non-structural material in biomass which could be extracted by exhaustive treatments organic solvent or water is called extractives. A previous study [Thammasouk, 1997] has shown the effect of extractives on chemical characterization, and recommended removal of these materials prior to the analytical experiments.

This study followed the laboratory analytical procedure presented in "Determination of extractives in biomass" [Sluiter et. al, 2005b]. This procedure used a two-step extraction process to remove water soluble and ethanol soluble material. Biomass sample was prepared by following the drying procedure at 45 °C, and a Soxhlet extraction setup was used in this procedure (figure 3.2), a more detailed description for this setup can be found in appendix A.

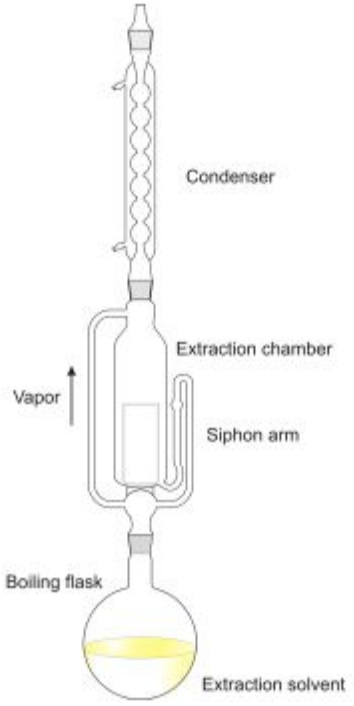


Figure 3-2: Soxhlet extractor

The extraction procedure started by adding 2-10 g samples to a tared extraction thimble, making sure that the height of the biomass in the thimble did not exceed the height of the Soxhlet siphon arm. The weight of added sample was recorded to the nearest 0.1 mg. The boiling flask was filled with 200ml HPLC grade water, the heating mantle was adjusted to provide a minimum of 4-5 siphon cycles per hour and reflux for 6-24 hours. After water extraction, the glassware was allowed to cool down to room temperature and the residual

water in the extraction chamber was removed as much as possible. The boiling flask was then replaced with another one containing 200ml of ethanol, the heating mantle was adjusted so as to provide a minimum of 6-10 cycles per hour and reflux for 16-24 hours.

After extraction, the thimble was carefully taken out and dried in a convection oven at 45 °C for a minimum of 24 hours, cooled down in a desiccator to room temperature and the sample was transferred into a tared sample bottle; again the sample weight was recorded to the nearest 0.1mg. Weight of the removed extractives was thus the difference of sample weights before and after extraction. Another method to determine the amount of extractives could be accomplished by first collecting the solvent (water and ethanol with extractives) after extraction in pre-weighed boiling flasks, and evaporating them using a rotary evaporator. Then cooling the flasks in a desiccator and recording the total weight of flask and solids inside. The amount of extractives could thus be calculated by subtracting empty flask's weight from the total weight after extraction. During the experiment, method one would be used for extractives content determination, as it was a simpler technique and distinguishing different kinds of extractives was not the main focus of this study. Method two would be only used for correction purposes (to check if its results corresponded with results from method one) and for determination of free sugar content in extractives, as extractives mainly consisted of free sugars, other water extractives and ethanol extractives. Details of this procedure would be given in the last paragraph of this chapter.

3.3 Analyzing methods

Biomass feedstock and torrefied products were analyzed using various methods. TGA showed how the weight of a (pretreated) biomass changes across a certain temperature range. XRF was used for the analysis of ash after combustion and HPLC was employed for carbohydrates determination.

3.3.1 Thermo Gravimetric Analysis (TGA)

TGA is a thermal analysis method by means of measuring the changes in physical and chemical properties of selected materials. These changes are recorded either as a function of time (with constant temperature and/or constant mass loss), or as a function of increasing temperature (with constant heating rate). Based on these principles, TGA is able to provide information about

various physical phenomena such as vaporization, sublimation, absorption etc. Similarly, chemical phenomena like desolvation, decomposition and oxidation can be analyzed with TGA as well.

The basic instruments that TGA needs are a precision balance with a pan loaded with the sample, a reference pan and a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time.

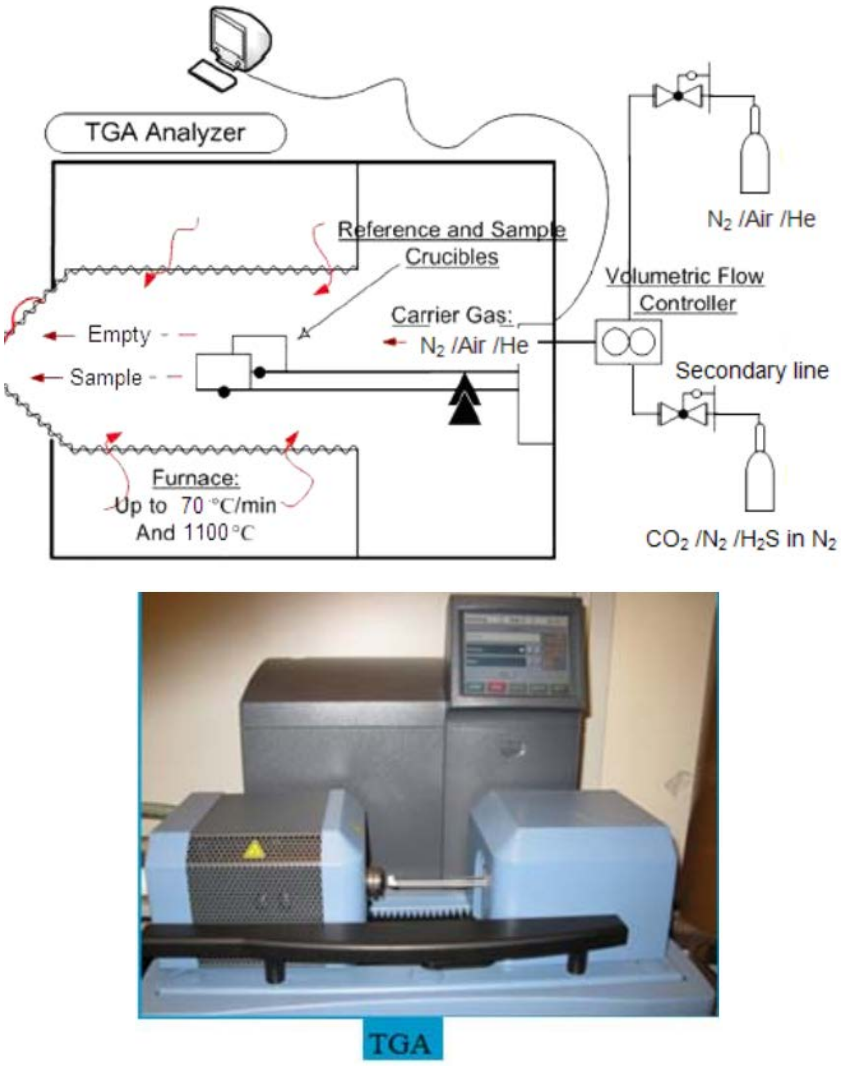


Figure 3-3: A schematic drawing of TGA system (TOP), and picture of TGA (bottom) [Meng, 2012]

In this study, TGA was mainly used for recording the decomposition (weight changes) of biomass samples during torrefaction and combustion. For these purposes, a TA Instruments TGA Q600 apparatus was selected as analytical tool, a schematic drawing and a picture of this tool was

given in figure 3.3. Some technical details of this TGA instrument are: Platinum/Platinum Rhodium (Type R) thermocouple, heating rate from ambient to 1000 °C at 0.1 to 105 °C/min and sample pans made of platinum (40 µL) or alumina (110 µL, 40 µL, and 90 µL) [Meng, 2012].

TGA data was analyzed and compared by using Universal Analysis 2000 software from TA instruments, which was specifically developed to analyse thermographs obtained from TGA experiments. In this study, only one type of thermograph was used, this is called Differential Thermogravimetric (DTG) curve. In this graph, the rate of weight loss was plotted as a function of temperature. This kind of graph was used for identifying the nature of organic mass loss. A typical DTG curve is given in figure 3.4. The three typical features shown in a DTG curve are: a *horizontal portion / plateau*, which indicates constant weight loss or no loss at all; a *peak* which indicates the change in weight loss rates and its top corresponds with maximum weight loss rate; and an *inflection point*, which shows the overlapping of two consecutives reaction. The inflection point of DTG curve can clearly be seen as a shoulder to a peak or as a tail of a peak.

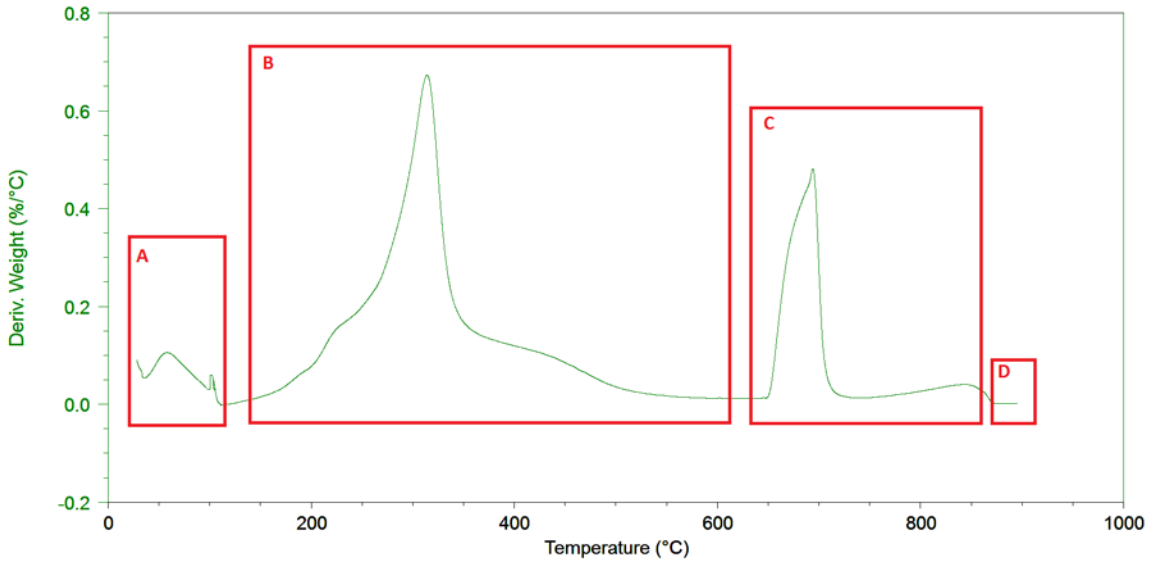


Figure 3-4: Typical DTG curve for organic matter characterization subject to pyrolysis

The four framed parts of the curve indicates the observed typical characteristics: Mass loss due to moisture evaporation (A), devolatilisation subject to pyrolysis (B), combustion of the remaining compound following pyrolysis (C), and a plateau which generally indicates ash content of the sample (D).

Now take a closer look at part B, which is given in figure 3.5. This part shows the DTG curve during pyrolysis and is the main focus of this study. In this figure, there are two main inflection points which indicates three overlapped reactions. Study [Carrier et, al., 2011] has shown that a wide curve ranging from temperature 150°C -600°C (A) represents devolatilisation curve for extractives in the lower temperature range and lignin in the higher temperature range. Two narrow curves, ranging from 220°C -315°C (B) and from 315°C -400°C (C) represent mainly hemicellulose and cellulose decomposition, respectively. The shoulders and tails of the main peak shown in this figure indicate that the devolatilisation curve of these three components overlapped each other.

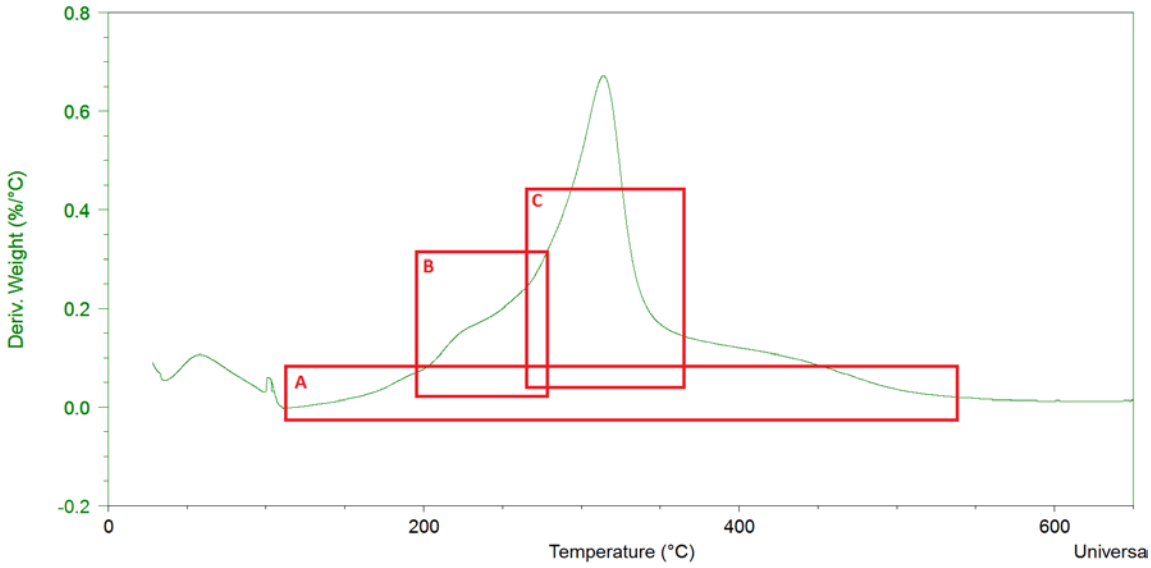


Figure 3-5: DTG curve during devolatilisation for organic matter characterization

In this study, TGA was used as an analytical tool in the following two series of experiments. Firstly, to find out the effect of extractives on biomass thermal decomposition behavior by comparing the DTG curves of dried fresh grass sample and extractive free grass sample. A second series of experiments was performed by comparing the DTG curves of grass torrefied at different conditions. This was to see the effect of changing the torrefaction conditions (temperature, retention time) on the organic matter content.

3.3.2 Determination of ash in biomass

As mentioned in chapter 2, ash content was a measure of non-combustible inorganics in biomass; high ash content not only lowers the energy value, it can also cause problems during energy conversion process.

Ash content of the sample was determined by following the procedure from NREL, "Determination of ash in biomass" [Sluiter et. al, 2005b]. For this procedure, the so called *oven dry weight* (ODW) of the sample was used, this weight was sample's oven dried weight at 105 °C. For any other samples which were dried differently (air dried or dried at 45 °C), their weights must be corrected by their total solids contents prior to this procedure. Procedure for determination of total solids content (in g) was described in section 3.2, equation 3.4 shows how this correction was done:

$$ODW = \frac{Weight_{dry\ sample} \times \%Total\ solids}{100} \qquad \text{(Equation 3.4)}$$

Sample ashing was carried out by using a NABERTHERM muffle furnace (model L9/12/B180), which was controlled by a ramping program. Experiment started with placing the empty crucibles in the furnace at 575 °C for a minimum of four hours, the crucibles were then removed into a desiccator and cooled down for an hour. Crucibles' weights were recorded and they were reheated in the furnace to constant weight. Constant weight here was defined as less than 0.3 mg change in the weight upon one hour of re-heating the crucible.

After the previous steps, crucibles were tared and filled up with certain amount of samples (0.5 – 2 g is recommended), the sample weight was recorded and the crucibles were placed in the muffle furnace. The furnace temperature was programmed to undergo the following procedure: ramp from room temperature to 105 °C and held at this temperature for 12 minutes; ramp again to 250 °C at 10 °C / minute and hold at 250 °C for 30 minutes; ramp to 575 °C at 20 °C / minute and hold at 575 °C for 3 hours; Finally, allow temperature to drop to 105 °C and hold at this temperature until samples are removed. Samples should be cooled in a desiccator to room temperature and the weight of crucibles plus ash was recorded to the nearest 0.1 mg. Again, the sample was reheated to constant weight. The percentage ash on an ODW can thus be calculated using equation 3.5:

$$\%\ Ash = \frac{Weight_{crucible\ plus\ ash} - Weight_{\ crucible}}{ODW_{sample}} \times 100 \qquad \text{(Equation 3.5)}$$

3.3.3 X-Ray Fluorescence Spectrometry (XRF)

In this study, the composition of ash from verge grass was analyzed in order to determine the removal rates of various inorganic compounds through mechanical fractionation. As explained in section 2.1.3, the presence of alkali metals, sulfur and silica would cause fouling, slagging and corrosion in heat transfer equipment. This was one of the main reasons why woody biomass was favored over herbaceous biomass, because wood had much lower ash content (generally around 1%, as compared to verge grass which has typically 10% ash). The high ash content in herbaceous biomass also made the pre-treatments necessary when it was used as feedstock for combustion. In addition, the mass of major inorganic species in fuel could be determined through ash analysis; these can be used for the calculation of ash deposition indices presented in section 2.1.3.

X-Ray Fluorescence (XRF) is a proven, widely used technique for elemental analysis and chemical analysis. It has a broad range of applications such as positive material identification, scrap metal sorting, measuring sulfur in oil etc, it is particularly suitable for the investigation of metals, glass, ceramics, building materials and fly ashes.

The principle of XRF is illustrated in figure 3.6. A stable atom comprises a nucleus and the electrons orbiting it. Orbiting electrons are organized into shells: each shell is made up of electrons with the same energy. When a high energy incident (primary) X-ray collides with an atom, it disturbs this stability. Because of the high energy level, an electron is ejected from low energy level (K-shell, the inner shell, see diagram). This creates vacancies which will soon be filled by electrons cascading in from outer electron shells. However, since electrons in outer shells have higher energy states than the inner shell electrons they are replacing, the outer shell electrons must give off energy as they fall into these vacancies. The energy is given off in the form of X-rays, this phenomena is referred as X-Ray Fluorescence. Since each element has different electron shell energies, the energy produced as the electron moves between the different shells is released as secondary X-rays which are characteristic of the element. In this way, the element present in the sample can be identified. [CLU-IN, 2013]

Biomass samples for the ash component analysis were prepared in the first week of February 2014. Grass was collected from location A, (see section 3.1) and divided into two parts. First part was oven dried and ground and kept at 105 °C for ashing. Second part was pressed; pressed

solids and grass juice were collected and dried separately at 105 °C. Ashing the samples happened fully according to the procedure described in 3.3.2 and ensured that at least 1.5 g ash could be obtained for each type of sample (Dried fresh grass, dried pressed grass and dried grass juice).

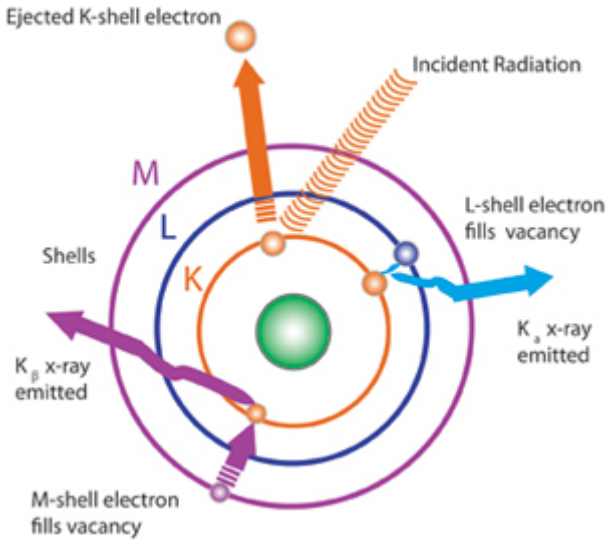


Figure 3-6: X-Ray Fluorescence illustration [CLU-IN, 2013]

XRF experiments were carried out at the "X-RAY FACILITIES" from the department of Materials Science and Engineering of Delft University of Technology. The measurements were performed with a Panalytical Axios Max WD-SRF spectrometer and the data was processed using SuperQ5.0i/Omnian software.

3.3.4 Determination of carbohydrates and lignin in grass samples

Carbohydrates in the biomass can be structural or non-structural, the latter also been named as soluble carbohydrates, since they can easily be separated from biomass by washing or water extraction [Lamaudière, 2012]. The challenge remained is to determine the amount of structural carbohydrates, which often represent the major portion of carbohydrates in biomass. Structural carbohydrates and lignin make up a major portion of biomass samples. Determination of these constituents in the *primary sample* (dried fresh grass) and their changes after mechanical (pressing) and thermal treatments (torrefaction) were the main research object for this study.

For the purposes of this study, LC/HPLC is a more suitable analytical method than GC. The main reason is that GC requires the samples to be volatile and thus cause more complications, whereas in HPLC samples can often be analyzed directly. Since the samples in this study are

mostly solids, employing GC would lead to unnecessary troubles. Notice that attention must be paid to sample solubility and sample concentration, and in case of the metal loaded cation-exchange columns, column heating is required.

However, only monosaccharides and oligosaccharides could be put through HPLC directly. Polysaccharides such as cellulose and hemicellulose must be "broken down" into monomers for them to become separable by HPLC. This was done through acid hydrolysis, which means the cleavage of chemical bonds by the addition of acid.

Experimental procedure – Sample preparation

It was proven in Thammasouk's study [Thammasouk, 1997] that extractives may lead to less accurate estimations of lignin and carbohydrates content of a feedstock; NREL's procedure complied this theory by recommending usage of extractive free samples. But in this study, both primary sample and extractive free sample were analyzed through the solid sample hydrolysis. There were two reasons for doing that; first, by comparing both chromatograms, it could be concluded whether the influence of extractives is significant, since extractives could lead to more and higher peaks, shifted base line, etc. . Secondly, the amount of non-structural carbohydrates could be determined by subtracting results of extractive free sample from these of the primary sample.

Grass juice that was produced during pressing also contained carbohydrates, lignin, extractives and other components. The total amount of soluble carbohydrates released into solution and the amount of monomeric sugars released into solution must be quantified as well. This was done by following the procedure for liquid sample hydrolysis. Grass juice should be filtered with a medium porosity filtering crucible after hydrolysis to gravimetrically determine the amount of acid insoluble material (mainly lignin) in the sample.

In order to correct the possible losses due to destruction of sugars during dilute acid hydrolysis, two different sets of sugar recovery standards (SRS) including D-(+) glucose, D-(+) xylose, D-(+) galactose and L-(+) Arabinose were prepared and hydrolyzed. The first set of SRS resembled the concentrations of sugars in solid sample, this would be referred as *SRS Low*, as compared to the SRS for liquid sample, where the concentrations of sugars were much higher, and this would be referred as *SRS High*, see table 3.1 for the exact sugar concentrations in each SRS. Notice that

since a fresh SRS was not required for every analysis, a large batch of SRS might be produced. SRS were decanted into sealed bottles and stored in a freezer and removed when needed. Hydrolysis of SRS was also carried out by following the same procedure as grass juice.

Table 3-1: Sugar concentrations for Sugar Recovery Standards

	Sugar concentrations (mg / mL)			
SRS type	Glucose	Xylose	Galactose	Arabinose
Low	1	0.5	0.2	0.2
High	50	20	10	10

Experimental procedure – Solid sample hydrolysis

For solid biomass hydrolysis, the laboratory analytical procedure from NREL, "Determination of Structural carbohydrates and lignin in biomass" [Sluiter et al., 2012] was employed with some necessary changes in experimental apparatus and reagents, which are further explained in this section.

NREL's procedure has employed a two-step acid hydrolysis to fractionate the carbohydrates into monomeric forms which are more easily quantified. Other components in the solution after hydrolysis are mainly lignin. Lignin is in nature very resistant to degradation, which means it cannot be broken down during acid hydrolysis. After hydrolysis, lignin fractionates are separated into acid insoluble material and acid soluble material. The acid soluble material may also contain acid soluble inorganic matters, which must be accounted for during gravimetric analysis. The analysis of lignin in biomass samples are presented later in this section.

The procedure started with sample preparation. Fresh grass was either oven dried at 45 °C or pressed first then dried at the same temperature, they were labeled as Dried Fresh Grass (DFG) and Dried Pressed Grass (DPG) respectively. 300 ± 10 mg of the sample was put into a tared pressure tube, this tube was cleaned and dried in the oven prior to the experiment. Notice that total solids of these samples must be measured for correction and each sample were analyzed in duplicate or in triplicate.

A large batch (approximately 60 ml) of 72% w/w sulfuric acid for hydrolysis was prepared by adding 25 ± 0.5 ml deionized water to 40 ± 0.1 ml 96% w/w sulfuric acid. Diluted acid could be

stored under ambient conditions for later use. 3.00 ± 0.01 ml (or 4.92 ± 0.01g) of 72% sulfuric acid was added to each pressure tube; a glass stir rod was used to mix until the sample was thoroughly mixed. The pressure tube was placed in a water bath set at 30 ± 3 °C and the sample was incubated for 60 ± 5 minutes. During this time, the sample must be stirred every 5 – 10 minutes without removing the sample from water bath, this was essential to ensure even acid to particle contact and uniform hydrolysis.

After the 60 minutes hydrolysis, the pressure tube was taken out and the acid was diluted to a 4% concentration by adding 84 ± 0.04 ml deionized water. Teflon cap must be placed on securely to prevent any leakage and the sample was mixed by inverting the tube several times to eliminate phase separation between high and low concentration acid layers. The tube was placed in an oil bath set at 121 ± 3 °C and the sample was incubated for 60 ± 5 minutes. (NREL recommended autoclave for hydrolysis instead of oil bath, which was unfortunately not available.) Upon completion of the second 60 minute hydrolysis, the tubes were removed from oil bath and cooled to near room temperature before the caps were removed.

Experimental procedure – Liquid sample hydrolysis

The hydrolysis of liquid samples and SRS were carried out by following the procedure from NREL, "Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples." [Sluiter et. al., 2006]. Grass juice and SRS were assumed to be degradation free samples, since they were either hydrolyzed on the same day when they were made, or stored in a sealed bottle in a freezer. Because of this, only analysis for total sugar content in the sample was performed. The equations used in this paragraph are from the procedure as well.

A pipette was used to inject 20 ml of liquid sample into a pressure tube, in duplicate or triplicate. The pH value of the sample was measured and recorded, then equation 3.6 was used to calculate the amount of 72% w/w/ sulfuric acid required to bring the acid concentration of the sample to 4%. The obtained amount of acid were added into the sample while it was been swirled. After this, Teflon cap was placed on to the pressure tube and this tube was placed in the oil bath set at 121 ± 3 °C for 60 ± 5 minutes. When it was done, tube was removed from oil bath and cooled down to room temperature.

$$V_{72\%} = \frac{[(C_{4\%} \times V_S) - (V_S \times e^{-pH} \times 98.08 g\ H_2SO_4 \quad / 2\ moles\ e^{-pH})]}{C_{72\%}} \qquad \text{(Equation 3.6)}$$

Where: $V_{72\%}$ is the volume of 72% acid to be added, in mL

V_S is the initial volume of sample or standard, in mL

$C_{4\%}$ is the concentration of 4% w/w H_2SO_4, 41 g/L

$C_{72\%}$ is the concentration of 72% w/w H_2SO_4, 1176.3 g/L

Experimental procedure – Lignin analysis

Lignin was quite acid resistant and thus would not be affected by hydrolysis, lignin in the sample was either soluble in acid, which could be detected using UV-Vis spectroscopy; or non-soluble in acid, which could be filtered out and measured gravimetrically. Unfortunately, UV-Vis spectrometry in the laboratory was broken, because of this, the amount of acid soluble lignin was assumed to be 0.5 wt% of fresh grass sample. Also the amount of protein in the grass was assumed to be negligible and thus was not taken into account. These assumptions were based on the experimental values obtained from ECN Phyllis2 database, Verge grass (#2541). [ECN, 2012]

The procedure for the determination of acid insoluble lignin started by placing an appropriate number of medium porosity filtering crucibles in the muffle furnace at 575 ± 25 °C for a minimum of four hours. These crucibles were then removed from the furnace and put directly into a desiccator and cooled for an hour. The crucibles' weights were measured and recorded to the nearest 0.1 mg. In order to obtain a reliable result, the crucibles were put back into the muffle furnace at 575 ± 25 °C and ashed to constant weight, which was defined as less than ± 0.3 mg change in the weight upon one hour of re-heating the crucible.

The hydrolysis solution was vacuum filtered through one of the above weighed filtering crucibles. The filtrate was captured in a filtering flask and transferred it into a sample storage bottle. This sample would be used for carbohydrates determination and could be stored in a refrigerator for a maximum of two weeks. Deionized water was used to quantitatively transfer all remaining solids out of the pressure tube into the filtering crucible. The crucible and acid insoluble residue was then dried at 105 ± 3 °C until a constant weight was achieved, this took

usually more than four hours. The samples were then removed from the oven and cooled in a desiccator. Weight of the crucible and dried residue was recorded to the nearest 0.1 mg.

The crucibles with residue were then placed in the muffle furnace with ramping function and ashed in the same way as described in section 3.3.2. At 105 °C, the crucibles were removed and cooled in a desiccator to room temperature. Total weight of crucibles and ash was measured and recorded to the nearest 0.1mg. And again, the crucible was put back into furnace and ashed to constant weight. The weight percentage of acid insoluble residue (AIR) and acid insoluble lignin (AIL) on dried basis (or in case of extractive free samples, extractive free basis) could be calculated using the following equations from the procedure:

$$\%\, AIR = \frac{Weight_{crucible\ plus\ AIR} - Weight_{\ crucible}}{ODW_{sample}} \times 100 \qquad \text{(Equation 3.7)}$$

$$\%\, AIL = \frac{(Weight_{crucible\ plus\ AIR} - Weight_{\ crucible}) - (Weight_{crucible\ plus\ AIR} - Weight_{\ crucible})}{ODW_{sample}} \times 100 \qquad \text{(Equation 3.8)}$$

Based on these results above on dried basis and assumption on acid soluble lignin (0.5 wt%), the total lignin value to a fresh grass sample basis is:

$$\%\, Lignin_{fresh\ base} = (\%\, AIL) \times \frac{100 - ODW_{sample}}{100} + 0.5 \qquad \text{(Equation 3.9)}$$

And in case of extractive free sample,

$$\%\, Lignin_{fresh\ base} = (\%\, AIL) \times \frac{100 - \%\, Extractives}{100} + 0.5 \qquad \text{(Equation 3.10)}$$

Experimental procedure – Carbohydrates analysis

In this paper, HPLC was used for carbohydrates analysis. The peak area in a chromatogram was linearly related with concentration of specific component in the sample. In order to translate HPLC outputs into sugar concentrations, two series of calibration standards containing the sugars that are to be quantified should be prepared. Similar to SRS, one series calibration standards would be used for solid sample results, the other would be used for grass juice. A five point calibration was used for both series to draw the calibration curves, concentration of sugar standards could be found in table 3.2.The calibration curves are given in appendix B, notice that the actual calibration points can be slightly different than the values given in the following table.

Table 3-2: Concentration points for calibration standards.

Components	Concentration points (mg / ml)	
	Solid sample	Grass juice
D-(+) glucose	0.1; 0.2; 0.5; 1; 2	5; 10; 15; 20; 30
D-(+) xylose	0.1; 0.2; 0.5; 1; 2	5; 10; 15; 20; 30
D-(+) galactose	0.01; 0.02; 0.05; 0.1; 0.2	0.5; 1; 1.5; 2; 3
L-(+) Arabinose	0.01; 0.02; 0.05; 0.1; 0.2	0.5; 1; 1.5; 2; 3

Liquid sample after hydrolysis was acidic and must be neutralized before injecting them into the HPLC, because the HPLC column required the sample to be pH neutral. NREL suggested using calcium carbonate as neutralizer, however, this badly interfered with the resolution of the sugar peaks in the chromatogram. The solid reaction product of sulfuric acid and calcium carbonate, calcium sulfate, was slightly soluble in water and could be detected by HPLC. Calcium sulfate showed irregular peak behavior (in the form of a slope) in the chromatogram and this slope overlapped with the glucose peak. For biomass sample that had low carbohydrates content, this slope became significant (visible in the chromatogram) and would interfere with the glucose peak, a sample chromatogram is given at the left hand side in figure 3.7. A suitable neutralizer suggested by Vergas Radillo in his paper [Vergas Radillo et al., 2011] was barium hydroxide. Theoretically, reaction between sulfuric acid and barium hydroxide will produce barium sulfate, which is insoluble in water, this lead to a "clean" sample solution and thus solve the above mentioned neutralizer problem, see the chromatogram at right for the result.

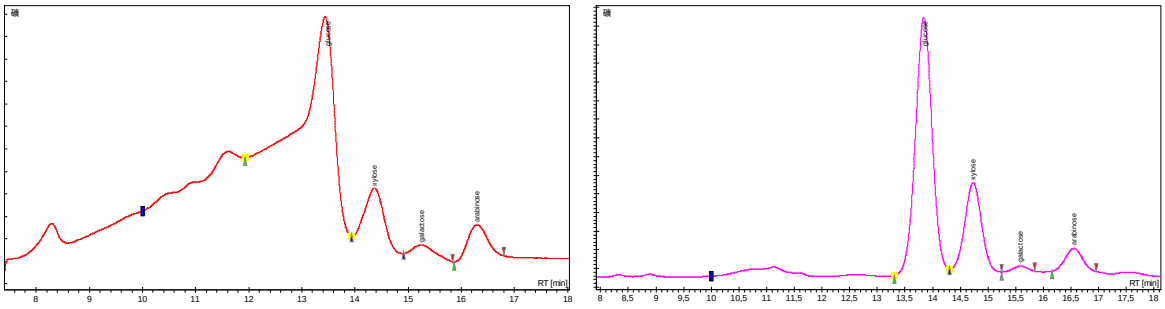


Figure 3-7: Chromatogram of sample neutralized with $CaCO_3$ (left) and $Ba(OH)_2$ (right)

Neutralization was done by first transferring approximately 20 mL sample of each liquor obtained after filtration into a 50 mL Erlenmeyer flask. Barium hydroxide powder was then used to neutralize each sample to pH 5-6. The addition of barium hydroxide needed to be carried out very slowly and the pH value of the solution was being constantly monitored with pH paper.

Neutralized sample was centrifuged in a mini laboratory centrifuge (Labnet, model C1301). A syringe with 0.4 µm syringe filter was used to transfer the sample into autosampler vials. These vials were then sealed and labeled. Notice that the samples for HPLC analysis were prepared in at least duplicate, samples which were not being directly analyzed were put in a refrigerator for not more than four days.

The calibration standards and samples were analyzed by HPLC using a Phenomenex Rezex RPM-Monosaccharide column equipped with the appropriate guard column. HPLC conditions are stated in table 3.3.

Table 3-3: HPLC conditions for monosaccharides determination

Injection volume	20 µL
Mobile phase	HPLC grade deionized water
Flow rate	0.6 mL/minute
Column temperature	80 – 85 °C
Detector temperature	As close to column temperature as possible
Detector	Refractive index
Run time	25 minutes

For the SRS, the amount of each component sugar recovered after dilute acid hydrolysis was calculated using the next equation:

$$\%\, R_{sugar} = \frac{concentration\ detected\ by\ HPLC, mg/mL}{known\ concentration\ of\ sugar\ before\ hydrolysis, mg/mL} \times 100 \qquad \text{(Equation 3.11)}$$

The obtained sugar recovery values, which are typically between 91% and 94%, were used to correct the corresponding sugar concentration values measured by HPLC for each of the hydrolyzed samples Notice that dilution made prior to HPLC analysis was accounted for as well; this was done by calculating the total amount of water (sum of added water and water produced during neutralization) in an HPLC sample, then multiplied by the HPLC detected sugar concentration. The amount of produced water during hydrolysis was calculated based on the following chemical equation:

$$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O \qquad \text{(Equation 3.12)}$$

The amount of a specific sugar monomer in the biomass sample could thus be calculated as:

$$Sugar_x = \frac{C_{HPLC} \times (added\ water + 72\%H_2SO_4 \times 2H_2O/H_2SO_4)}{\%R_{ave.sugar}} \times \frac{1g}{1000mg} \quad \text{(Equation 3.13)}$$

Where: C_{HPLC} = concentration of a sugar as determined by HPLC, mg/mL

$\%R_{ave.sugar}$ = average recovery of a specific SRS component

$Sugar_X$ = $Sugar_{corr}$, amount in g of a sugar in the neutralized sample after correction for loss on 4% hydrolysis.

$72\%H_2SO_4$ = amount of acid in 72% sulfuric acid solution

H_2O, H_2SO_4= molar mass of water and sulfuric acid, respectively

Concentration of the polymeric sugars was calculated from the amount of the corresponding monomeric sugars by using an anhydro correction of 132/150 for C-5 sugars (xylose and arabinose) and a correction of 162/180 for C-6 sugars (glucose, galactose and mannose). During hydrolysis, the conversion of polymers to monomers in the carbohydrates resulted in the addition of a hydrogen and a hydroxyl group to each monomer. An anhydro correction was used to mathematically convert the monomeric values back to a structural polymeric value in grams.

$$Sugar_{anhydro} = Sugar_x \times Anhydro\ correction \quad \text{(Equation 3.14)}$$

Calculate the percentage of each sugar on an as received basis

$$\%Sugar_{as\ received} = \frac{Sugar_{anhydro}}{ODW_{sample}} \times 100 \quad \text{(Equation 3.15)}$$

In case of extractive free samples, the percentage of each sugar on an as received basis could be calculated as followed,

$$\%Sugar_{extractive\ free} = \frac{Sugar_{anhydro}}{ODW_{sample}} \times \frac{(100 - \%Extractives)}{100} \quad \text{(Equation 3.16)}$$

Where: %Extractives = percent extractives in the prepared biomass sample, as determined in the procedure presented in 3.2.

Notice that extractives also contain certain amount of free sugars (see paragraph 2.1.1), and the quantity of this free sugar (in g) could be calculated by subtracting sugars in the extractive free samples from the sugars in the original sample.

$$Sugar_{free} = Sugar_{as\ received} - Sugar_{extractive\ free} \times \frac{(100 - \%Extractives)}{100} \qquad \text{(Equation 3.17)}$$

Once the amount of water and ethanol extractives were determined by using method two described in paragraph 3.2, with the amount of free sugar is known, composition of extractives could thus be derived.

The general procedure for converting the "raw" HPLC data in to cellulose and hemicellulose content are summarized in the following procedure:

1. HPLC data, the chromatogram, contains a graph with separated peaks. Obtain the peak area through integration
2. Calculate the sugar concentration based on peak area, using the corresponding calibration curve.
3. Correct the sugar concentrations using the obtained sugar recovery values
4. Take the average concentration from duplicated experiments, and calculate the amount of each monomeric sugar by multiplying its concentration with sample volume
5. Correct these quantities with sample's weight difference as compared to primary sample, DFG. This difference could come from mechanical fractionation, extraction and/or torrefaction.
6. Use anhydro correction to mathematically convert the monomeric values back to a structural polymeric value.

4 Experimental torrefaction setup

This chapter presents the bench scale experimental setup which is developed for drying and torrefaction experiments. It starts with elucidating the background and the motivation for developing this test setup, followed by a detailed description of the system in the second part. In the last section, lists of performed experiments were given together with summaries for drying and torrefaction experiments results.

4.1 Background and motivation

As mentioned in the introduction, torrefaction studies at this moment are mainly focused on the use of woody-biomass as feedstock, torrefaction of green residues and optimization of its associated process parameters are still left to be done for the researchers. This is the first reason for designing this experimental setup.

Currently, most of the biomass torrefaction experiments were carried out in analytical instruments such as TGA, which only uses a few milligrams for the experiments. These experiments provide good insight regarding the kinetics of torrefaction, but could not reveal much information about design considerations of a scaled up torrefaction setup. For example, heat and mass transfer limitations are essential for the gas-solid reaction during torrefaction, but they would not be reflected in TGA.

There are a few studies in which torrefaction was performed on a larger scale than TGA. Patuzzi [Patuzzi, 2014] has reported in his paper about a bench-scale torrefaction setup which he used for torrefying reed (*Phragmites australis*). This setup employed indirect heat transfer to the biomass by electrically heating the reactor wall. However, this concept is not suitable for larger scale reactors with much lower surface to volume ratio. Torrefaction on a large scale requires direct convective heat transfer. ECN TOP technology (Bergman, 2005c) was designed based on direct heating of the biomass during torrefaction by means of hot gas that is recycled. However, TOP technology used wood as its feedstock, torrefaction of herbaceous biomass or agricultural waste on a larger scale (than TGA) has not been studied extensively yet.

The last motivation for developing this test setup was to gain operating experiences with torrefaction processes, these experiences would become useful for designing a larger system in the future.

4.2 Bench-scale torrefaction setup.

The two reported experimental setups in the previous section both had useful designs which can be good references for the development of a new bench-scale torrefaction setup.

For a bench-scale reactor, electrical heating was considered safer and easier to control than combustion of fuel gas with accompanying heat transfer to the bed. The reactor had employed direct convective heating through heated media, since the same technique was planned to be applied in future (large scale) setups. Also, because this was a bench-scale reactor, a simple batch system was chosen instead of a continuous system to prevent the whole setup from becoming too complicated.

Construction of the setup is explained with the schematic drawing of the bench scale torrefaction setup shown in figure 4.1. Pictures of every major component are presented in figure 4.2. For the torrefaction experiments, nitrogen was selected as the primary heat transfer medium to ensure an inert environment for torrefaction and was controlled and measured by a mass flow controller (Aalborg, model GFC-57, 0-186 stdL/min). Addition of air and carbon dioxide (physical connection of CO_2 supply was not installed yet) to the system was also possible; they were both controlled and measured by one mass flow controller (Aalborg, model 37, 0-30 stdL/min). Both nitrogen and air/carbon dioxide flows could be controlled separately, and it was also possible to mix the flows to the desired composition by adjusting the mass flow controllers at a gas mixing station, see figure 4.2a.

An electric heater (Heating Group, TPE Flange Immersion Heater, 2000W, 230V, 50Hz) was employed for heating up the gases, heater's temperature was measured with the built-in thermocouple (TC 1). As can be seen in figure 4.2b, the thick, horizontal pipe which is been wrapped up with isolation material (Rockwool with aluminum foil) is the heat exchanger, it has a plug-in heater with a length of 900mm and diameter of 78mm. The heater's housing is made of stainless steel and has a length of 1000mm and diameter of 150mm. Torrefaction gases flew through this pipe were being heated and went up to the reactor. The vertical pipe which was

also being wrapped up with the same type of isolation material was connected with reactor column and it has a valve at its bottom which could be opened for collecting residues and moisture remained in the pipe. The power and control unit of the heater can be seen on the right of the picture and it has a built-in reset button. A set point of 700 °C was employed as the maximum temperature of the heater to prevent meltdown of the heating element. The inlet gas line (red line in figure 4.1) was twined with electrically heated wires in case when additional heating to the pipeline is required.

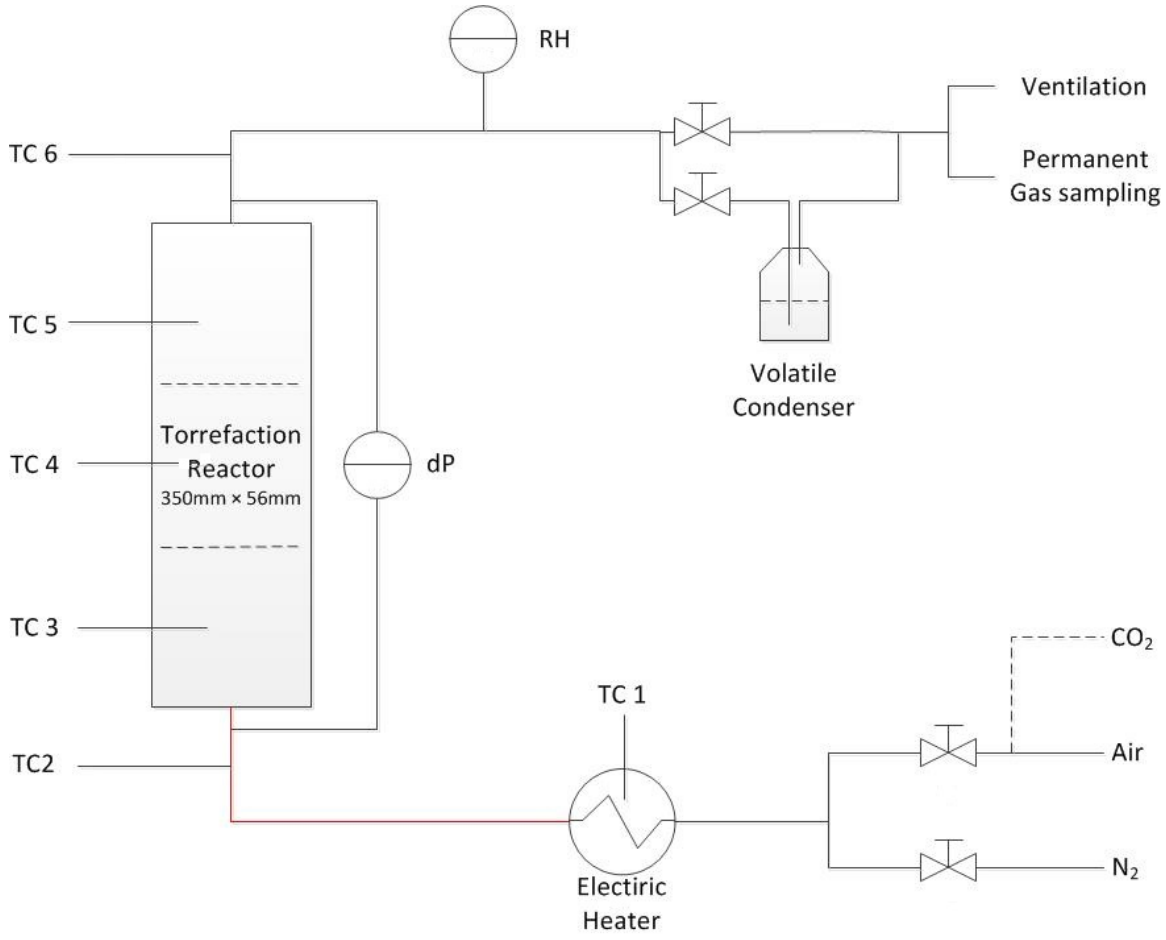
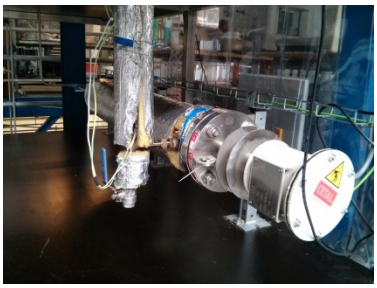


Figure 4-1: Schematic drawing of the bench-scale drying / torrefaction setup

The torrefaction reactor consisted of a vertically disposed stainless steel column, see figure 4.2c. This column was also made of stainless steel (AISI316) and is 350mm long with an inner diameter of 56mm and wall thickness of 2mm. It had flanges on both side with a diameter of 100mm and a thickness of 10mm; the flanges had six holes for M6 bolts. The column was wrapped with two layers of isolation material, with rock wool on the outside and glass wool on the inside. It could be filled with biomass up to a maximum of 0.87 liters, with two perforated

plates on either side to restrain the biomass to the specified volume. These plates were 2mm thick and had a radius of 73mm, they holes were 1mm holes with a center distance of 4.5mm. The column was equipped with three in-bed thermocouples which measured the temperature of biomass at different height in the column (T3, T4 and T5), see figure 4.2d. There were also another two thermocouples (T2 and T6) which were installed at the bottom and top of the reactor, these were used to measure the gas temperature difference after biomass heat treatment. In addition, a pressure drop sensor (dP, Endress & Hauser, model PMD70) shown in figure 4.2e was used to study the changes in the bed pressure drop throughout the process. This was done by measuring the pressure difference between top and bottom of the reactor. A relative humidity sensor (RH, Michell instruments, model WR283) was employed for monitoring the drying of the biomass bed by measuring the humidity of the flue gas.

a. Gas mixing station



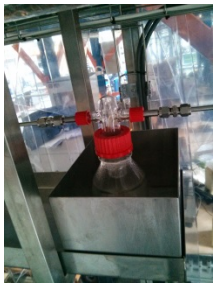
b. Gas heater

c. Packed bed

d. In-bed thermocouples

e. dP sensor

f. Relative humidity sensor



g. Volatile condenser

h. Ventilation (1) & Permanent gas sampling (2)

i. Experimental setup

Figure 4-2: Pictures of the experimental torrefaction setup

After the humidity detector, a bypass along the pipe line made it possible to collect the condensable compounds in the torrefaction gases. As described in section 2.2.3, these compounds (water, organics and lipids) were liquids or (dissolvable) solids at room temperature and thus started to condense as they passed through water. The sample collecting bottle was sat on ice to keep the water at low temperature, as shown in figure 4.2g. Gas flow after the condenser could also be collected at permanent gas sampling, the rest was ventilated (see figure 4.2h). It was also possible to directly collect the total torrefaction gas at gas sampling by closing the valve at bypass. Figure 4.2i presents the full view of the experimental setup; the letters indicate the locations of the corresponding components in the setup.

Two wire rings (dashed lines) were used when filling up the reactor column. They were placed in a way that the column was roughly divided into three equal compartments (bottom, middle and top) with the thermocouples (TC3, TC4 and TC5) in the middle. The biomass sample was divided into three equal portions and carefully filled up the column so that the density of biomass in each compartment was similar. Torrefaction products in different compartments showed different properties, as the torrefaction temperature decreased along the column.

Mass flows of all the gas supplies, heater and tracing power were all electronically controlled by the program LabVIEW 2012. Experimental data was first collected using the Data Acquisition (DAQ) system (module 9205 and 9472) from NATIONAL INSTRUMENTS, and then recorded also by LabVIEW.

4.3 Experiment procedure

In total there were two series of experiments been carried out using the bench-scale torrefaction setup, drying and torrefaction experiments. The drying experiments were meant to be performed for testing and commissioning the experimental setup, whereby also the effect of different operating conditions (gas temperature and flow rate) on the drying time of the grass sample was examined.

For the drying experiment, two different gas temperature (90 and 130 °C) and two flow rates (30 and 90 Nl/min) were chosen. For each experiment, the same amount (200g) of fresh grass trimming was used. It was equally divided into three portions and carefully put into the column to ensure that the sample was loaded with similar density in each part of the column (top, mid

and bottom). Experiment was carried out using heated air and the biomass was dried until the humidity had dropped to the off-set point, which was about 3%. The samples in different section were then carefully taken out and put into three sealable plastic bags. The drying time was recorded and the moisture content of the biomass sample in each bag was measured to ensure that the samples were dried.

As for the torrefaction experiments, the torrefaction temperature and retention time were chosen as the variables. The other parameters, such as flow rate and ramping rate, were set to be fixed. Through a previous study [Joshi, 2014], it was known that in case of grass a temperature of 230 °C was sufficient to initiate torrefaction. By consulting Bridgeman's study [Bridgeman, 2008], the torrefaction temperatures for this study were chosen to be 230 °C, 250 °C, 270 °C and 290 °C, and the residence times were chosen to be 15, 30 and 45 minutes. With the given temperatures and residence time, there were twelve experiments in total. For convenience's sake, experiment was labeled by first the temperature, then the residence time. For example, experiment 250-45 refers to torrefaction at 250 °C, with a residence time of 45 minutes. The samples were loaded and taken out in the same way as for the drying experiments.

Early trials of torrefaction experiments were done by first drying the fresh biomass in rig itself and then torrefy it. However, for each experiment, certain preparations must be undertaken in order to "switch" the system from drying to torrefaction. Firstly, the relative humidity sensor must be taken out and replaced by a cap to seal the pipe line. Since the working range of RH detector was only between -30 °C and 200 °C, high temperature during torrefaction (above 200 °C) and potentially corrosive atmosphere (volatiles from torrefaction) might damage the device. Secondly, torrefaction required inert atmosphere, thus the convective media must be changed from air to nitrogen. Finally, in order to collect sample volatiles released during torrefaction, by pass for the volatile condenser must be switched on.

The above mentioned steps led to more complicated experiments and drying the grass in rig itself took also a lot time. It was thus decided to dry the fresh grass samples prior to the torrefaction experiment. This was done in the oven at 105 °C by following NREL's procedure. The dried grass was then loaded into the reactor column in the same way as for the drying experiments. Take again 250-45 as example to explain the torrefaction procedure. This started with increase nitrogen flow to 60 nL/min. Then gradually increased the inlet gas temperature

(keep the heating rate between 3-4 °C/min) to 250 °C by controlling the heater power, the time needed to reach this temperature was recorded. Temperature was maintained at 250 °C for 45 minutes and then the heater and nitrogen supply was turned off. System was cooled down till room temperature before the sample was taken out and sorted according to its position in the column (bottom, middle and top). Each part of the sample was put into different bags, weighted and sealed. The mass yield of verge grass at different height in the column could thus be calculated using the following equation:

$$Y_{mass}(\%) = (\frac{m_{product}}{m_{feedstock}}) \times 100 \qquad \text{(Equation 4.1)}$$

5 Experimental result and discussion

This chapter presents the results obtained from analytical experiments, together with discussion which assesses how the results answer to research questions in chapter 1. Results are divided into five sections. First section presents properties of all the biomass samples, including primary sample, pressed sample, extractive free sample and torrefied sample. Second part shows the results obtained from TGA analysis, where the thermal decomposition of different samples are presented and compared. XRF results in the third section shows the ultimate result pf ash composition. The fourth paragraph contains the results obtained from the experimental setup described in chapter 4. Last part presents the results from HPLC, where the carbohydrates and lignin content in different samples are determined.

5.1 Biomass properties

In this study, five types of grass samples were obtained by following the preparation steps in section 3.2: fresh grass (FG), pressed solids (PS), grass juice (GJ), extractive free dried fresh grass (EFG) and extractive free dried pressed solids (EFP). Table 5.1 shows the biomass properties (total solids content, moisture content and ash content) of fresh grass, pressed solids and grass juice samples. Table 5.2 presents the extractives contents and ash contents of the DFG and DPS samples. All of the experimental data was recorded to the nearest 0.1mg, this means that for the experiments with bigger sample quantities (such as pressing), accuracy of the results were calculated until 0.01%, as compared to the extraction experiments with an accuracy of 0.1%. All results were reported on percentage by weight.

From table 5.1, it can be seen that fresh grass samples from location A & B (80% - 85%) had in general slightly higher moisture content than those from location C & D (70% - 75%). Their ash content shows minimum differences as they were all between 10% and 13%. The total solids and moisture content were calculated based on the receiving weights of the pressed products. The 4th column shows the percentage of pressed solids and grass juice based on the primary sample (fresh grass), where it is seen that pressed solid / grass juice ratio show large variations for experiments on different date. This was because of the juicer's condition; after it had been

used extensively in the previous study [Joshi, 2014] and in this study, the juicer started to have difficulties when squeeze strength is at maximum, sometimes the auger even stopped. The operator was forced to lower the squeeze settings and thus pressed solids with higher moisture content were produced. Despite all of this, the primary effect of water removal could still be clearly seen by comparing the moisture content between fresh grass and pressed solids. What also should be mentioned is that the liquid phase (grass juice) in case of mechanical fractionation did not only consist of the soluble components, but also of entrained solids. For this reason, it was expected that the green juice would also contain the pressed grass components in small amounts.

Table 5-1: Biomass properties of fresh grass, pressed solids and grass juice

Location	Date	Sample type	Percentage of sample as received	Total solids (a.r)	Moisture content (a.r)	Ash content (dry)	Ash content (fresh)
A	Nov.2013	FG	100.00%	16.02%	83.98%	12.95%	2.07%
		PS	23.65%	42.35%	57.65%	9.55%	0.96%
		GJ	76.35%	8.31%	91.69%	14.83%	0.94%
A	Jan. 2014	FG	100.00%	17.33%	82.67%	11.79%	2.04%
		PS	39.98%	31.51%	68.49%	8.75%	1.10%
		GJ	60.02%	9.65%	90.35%	13.95%	0.81%
A	Feb.2014	FG	100.00%	17.94%	82.06%	10.63%	1.91%
		PS	45.15%	28.91%	71.09%	8.09%	1.06%
		GJ	54.85%	10.24%	89.76%	13.46%	0.76%
B	Apr.2014	FG	100.00%	19.49%	80.51%	11.55%	2.25%
C	Aug.2014	FG	100.00%	25.38%	74.62%	12.37%	3.14%
		PS	44.85%	30.55%	69.45%	11.25%	1.54%
		GJ	55.15%	11.65%	88.35%	13.85%	1.49%
D	Aug.2014	FG	100.00%	27.01%	72.99%	11.38%	3.07%

Although the moisture contents in pressed solids were different, their ash content (directly measured on dry basis) were relatively stable and always lower than those of the fresh samples. But of course, it was incorrect to compare the ash content on dry basis of fresh grass with pressed grass, because the weight losses during drying and pressing were not taken into account.

This meant that in order to compare the ash content in those three samples types directly, all the ash contents must be calculated separately based on the initial weight of the fresh grass (wet basis). The percentage of ash which was leached away during pressing thus could be determined by comparing the obtained ash contents. This procedure is illustrated in figure 5.1, by using experiment on Nov 2013 as an example. All values in this figure were calculated on the weight of fresh sample, the top pie represents the products from pressing, bottom left pie shows the composition of the pressed solids and bottom right pie represents the composition of grass juice. From this figure, it can be seen that pressed solids contained almost the same inorganic matters (ash) as the grass juice; this means that about half of the inorganic matter was in the grass juice and got removed during pressing. The ash content on fresh basis of all the samples were given in the last column in table 5.1.

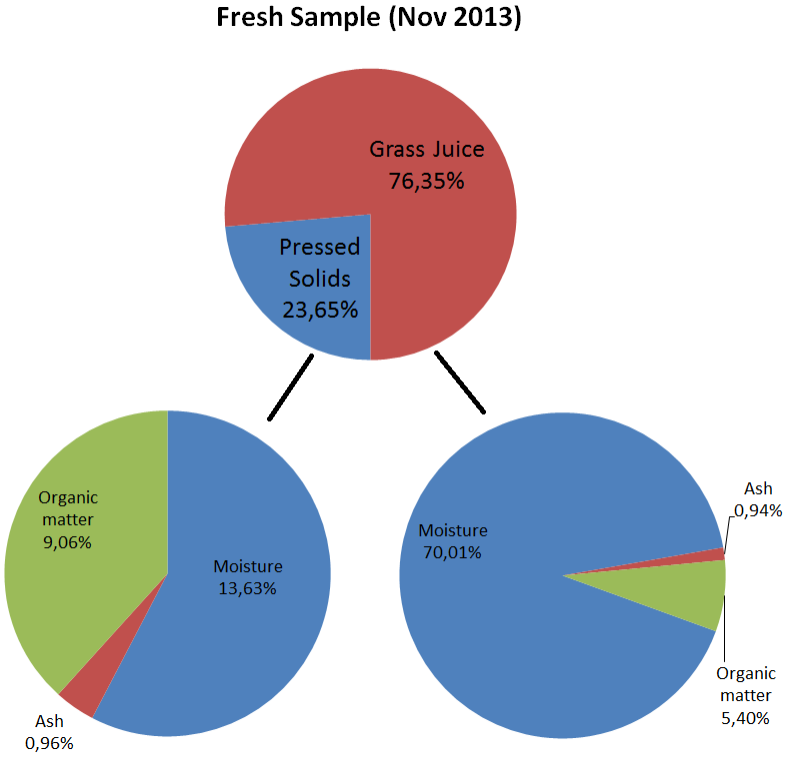


Figure 5-1: Compositional analysis for pressing experiment

Results from the extraction experiments were presented in table 5.2. EFG and EFP samples were obtained by extracting DFG and DPS respectively. The ash content was determined by first measuring the amount of ash measured from ashing the extractive free samples, and then multiplied with weight percentage of extractive free samples to obtain the ash content on dried basis. The ash content on fresh sample basis after extraction was calculated by following the

same method mentioned above. It was then possible to directly compare the ash content between dried, pressed and extracted samples. The removal rate through extraction could thus easily be calculated using the following equation:

$$Removal\ rate(\%) = 1 - \frac{Ash\ content\ before\ extraction}{Ash\ content\ after\ extraction} \quad \text{(Equation 5.1)}$$

The ash removal rates were given in the last column in table 5.2. It could be seen that for DFG, sequential water/ethanol extraction had removed approximately 80% of the inorganic matters in the original sample, as for DPS, this rate was between 71% and 78%.

Table 5-2: Extractives and ash content of DFG and DPS samples

Location	Date	Sample type	Extractives content (dry)	Extractive free (d.a.f)	Ash content (dry)	Ash content (fresh)	Removal rate
A	Nov.2013	DFG	40,8%	56,7%	2,5%	0,4%	81.0%
		DPS	39,9%	57,8%	2,3%	0,2%	75.8%
A	Jan. 2014	DFG	41,8%	55,8%	2,4%	0,4%	79.8%
		DPS	35,1%	62,4%	2,5%	0,3%	71.0%
C	Aug.2014	DFG	41,2%	56,3%	2,4%	0,6%	80.3%
		DPS	37,8%	59,8%	2,5%	0,3%	78.0%

5.2 Thermo Gravimetric Analysis (TGA) results

In this study, TGA analyses were performed to examine the effect of extractives on biomass decomposition and the effect of different operating conditions on the produced torrefied grass. The TGA results in this study are given in the format of the Differential Thermogravimetric (DTG) curve, where the sample weight loss rate is plotted as a function of temperature. More details about TGA data analysis could be found in paragraph 3.3.1.

Effect of extractives on biomass decomposition

The effect of mineral content on biomass thermal behavior had been reported in multiple literatures [Saddawi et al., 2012; Saleh, 2013]. In the previous study [Mangkusaputra, 2014], it

was mentioned that mechanical fractionation had removed most of the alkali minerals and thus had mitigated the catalytic effect from the alkali compound. However, the catalytic effect shown in Mangkusaputra's study was not very significant, which suggested that the removal of inorganic matters through pressing was not good enough.

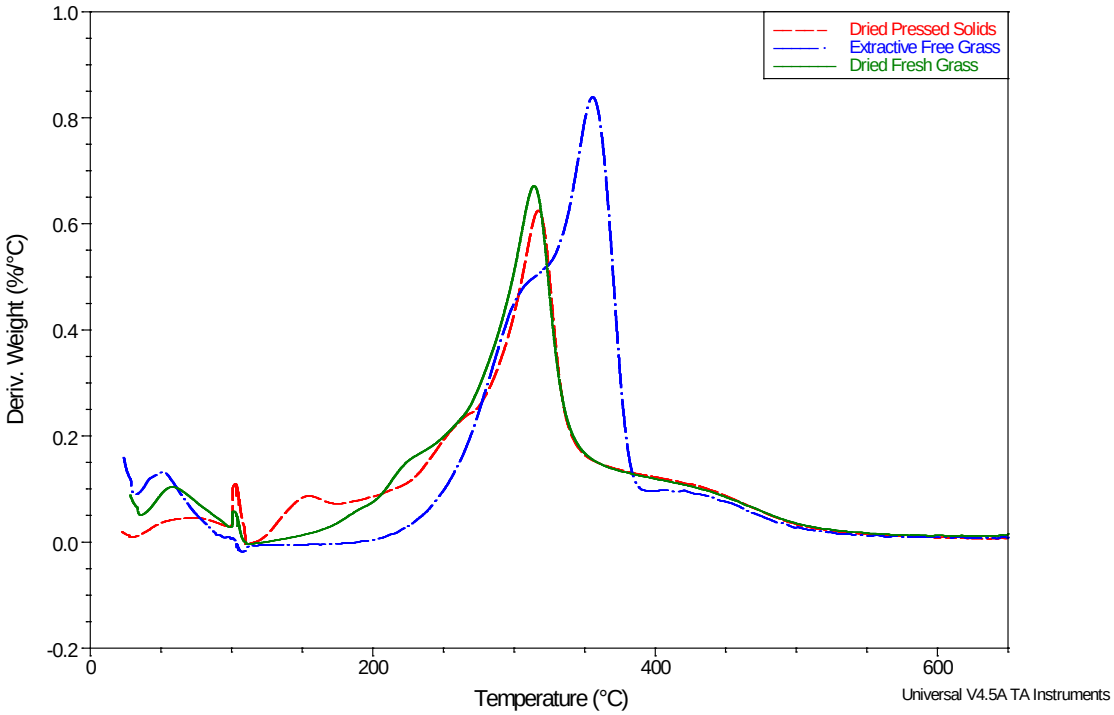


Figure 5-2: DTG curves of dried pressed solids (red), extractive free grass (blue) and dried fresh grass (green).

By comparing the TGA plots between DFG and DPS samples in figure 5.2, it can be seen that the peak of maximum devolatilisation for both plots occurs almost at the same temperature. This means that the partial removal of extractives resulting from pressing has almost no catalytic effect on the thermal reactivity of the biomass sample. However, second series of experiments had employed a more effective way to remove the mineral matters in biomass, sequential water/ethanol extraction, the exact removal rate through extraction is found in paragraph 5.5. The TGA result of the extractive free sample is given in figure 5.2. These DTG curves show that the peak of EFG has significant delay as compared to DFG's peak, which means that biomass becomes less reactive to thermal degradation after it has been extracted. This could be explained by the catalytic effect of extractives. Extractives have lower decomposing temperature than other components in the sample (see table 2.3 in paragraph 2.1.3); the

mineral content in extractives could also cause the major portion of the biomass to react at lower temperature. See chapter 2.1.2.

TGA analysis on verge grass torrefied at different conditions

The experimental setup for this study has torrefied verge grass at four different temperatures (230 °C, 250°C, 270°C and 290°C) with two retention times (15min and 45min). Figure 5.3 shows the DTG curves of the torrefied grass for the 15min series. Notice that with exception of DFG, same quantities of biomass sample were used for the experiments. This means that higher peak implies more material to decompose (react). Grass torrefied at lower temperature has less volatile removal during torrefaction and thus more material to react in TGA experiments. Following this theory, it is easy to speculate that if DFG had the same intial weight, it would have the highest peak in this plot. The shoulder in DFG's curve at 220°C shows the decomposition of hemicellulose, which is gradually removed during torrefaction as the temperature increases .

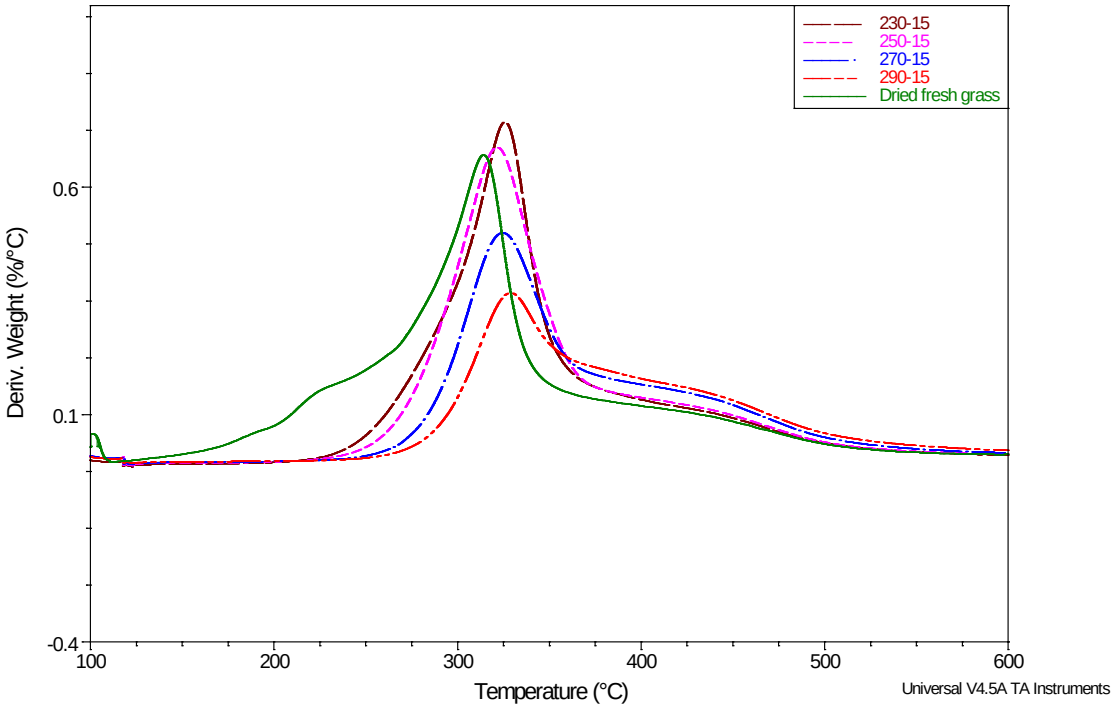


Figure 5-3: DTG curves of dried torrefied grass at different temperatures

Figure 5.4 demonstrates the DTG curves of torrefied grass during different retention times. For both the 230 °C series and 270°C series, the same initial weight was applied. It can be seen from the graph that longer retention time leads to slightly lower peak, which means that for the same

temperature, more volatiles will be removed as the retention time increases. However, this removal rate is very small.

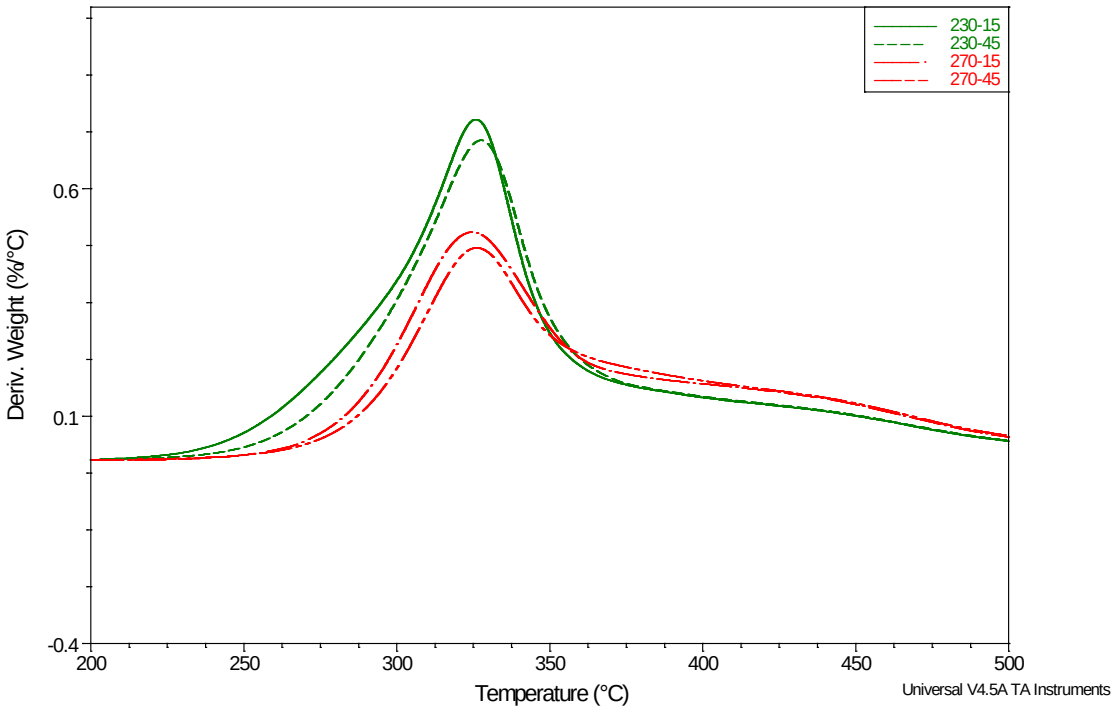


Figure 5-4: DTG curves of torrefied grass at 230°C and 270°C, during different retention times

5.3 X-Ray Fluorescence Spectrometry (XRF) results

In this study, the removal rates of inorganic matters were determined by analyzing the ash samples using X-Ray fluorescence spectrometry. Ash samples for the XRF test were prepared from the verge grass collected at location A, in February 2014 (see table 5.1 for the properties of the biomass sample). Fresh samples were split into two portions, with one portion first having been oven dried at 105 °C for a minimum of 24 hours, then ashed by following the ashing procedure presented in section 3.3.2. The other portion was pressed by consulting the pressing procedure in section 3.2, the obtained pressed solids (45.15 wt%) and grass juice (54.85 wt%) were also dried at 105 °C for more than 24 hours, then ashed by following the same procedure. The weights before and after drying of each sample were recorded to calculate the oven dry weight (ODW) and moisture content. Results from the calculation are given in table 5.1 in section 5.1, together with a brief discussion about the sample properties. Notice that there is 9.6% loss during pressing, which has been accounted for during calculation.

The obtained ash samples from dried fresh grass (DFG), dried pressed solids (DPS) and grass juice were analyzed using XRF equipment at the department of Materials Science and Engineering. XRF results were expressed in weight percentage of the total ash sample. These weight percentages are given in appendix C, together with the standard deviation (Std. Dev) and coefficient of variation (CV%) of mass balances for every major component. Notice that the concentrations of the inorganic elements in ash sample from pressed solids and grass juice were corrected with their weight percentages in the ash sample from fresh grass, which means that for any specific component, the summation of its weight percentages in pressed solids and grass juice should be close to its weight percentage in fresh grass.

Figure 5.5 depicts the results as columns; blue columns represent weight percentage of various inorganic elements retained in the ash from fresh grass sample. Red and green columns represent those percentages of pressed solids and grass juice respectively. They were stacked and the difference between the heights of stacked columns and blue columns represents the errors of XRF results. Percentages of removed inorganic constituents are shown on top of the columns.

In figure 5.5, it can be seen from the heights of the blue columns that alkali metals, principally potassium oxide (K_2O), are the most abundant inorganic compound in verge grass. Other inorganic constituents such as silica, sulfur, chlorine and calcium are present in the sample as well, only at lower levels. This figure shows that apart from the decrease of the moisture content, pressing also has partially removed minerals from the biomass. By taking a look at the inorganic matters removal rates, it can be seen that for almost every compound (except silica) in the ash, at least 35% of its quantity had been leached away by pressing. In particular, the reduction in K_2O, Cl, CaO and MgO were more than 50%. This is especially important for the biomass quality given that the reactions between alkali (K_2-O), alkaline earth elements (MgO) and other inorganic constituents, sulfur, chlorine and silica, resulting in unwanted deposits, slagging and corrosion in energy conversion facilities utilizing biomass fuels. Furthermore, most of silica was retained in pressed solids.

Results presented in table 5.3 are calculated by substituting the XRF results into the ash deposition indices given in section 2.1.3, it can be seen that slag viscosity S_R was increased from 53.87 to 73.11, this leads to less tendencies for the ash to deposit on the reactor. The slagging

index has shown that although pressing has dramatically decreased the possibility of slagging by about 65%, DPS still has a severe tendency to cause slagging. Finally, the chlorine content for both samples is proven to be extremely severe. Notice that B/A + P ratio was used because of the high P_2O_5 content in grass.

Table 5-3: Ash deposition ratio and indices for DFG and DPS samples

	B/A + P	S_R	F_U	Cl
DFG	3.74	53.87 (High)	126.33 (Extremely Severe)	13.97 (Extremely Severe)
DPS	1.72	73.11 (Low)	44.74 (Severe)	9.54 (Extremely Severe)

To sum up, from the XRF results it can be concluded that simple dewatering pretreatment could effectively reduce the inorganic compounds in the biomass sample, which would help improve the feedstock quality. However, verge grass (and pressed solids) are still not good enough to be used as the primary feedstock for combustion purposes due to its high possibilities for causing slagging and high chlorine content.

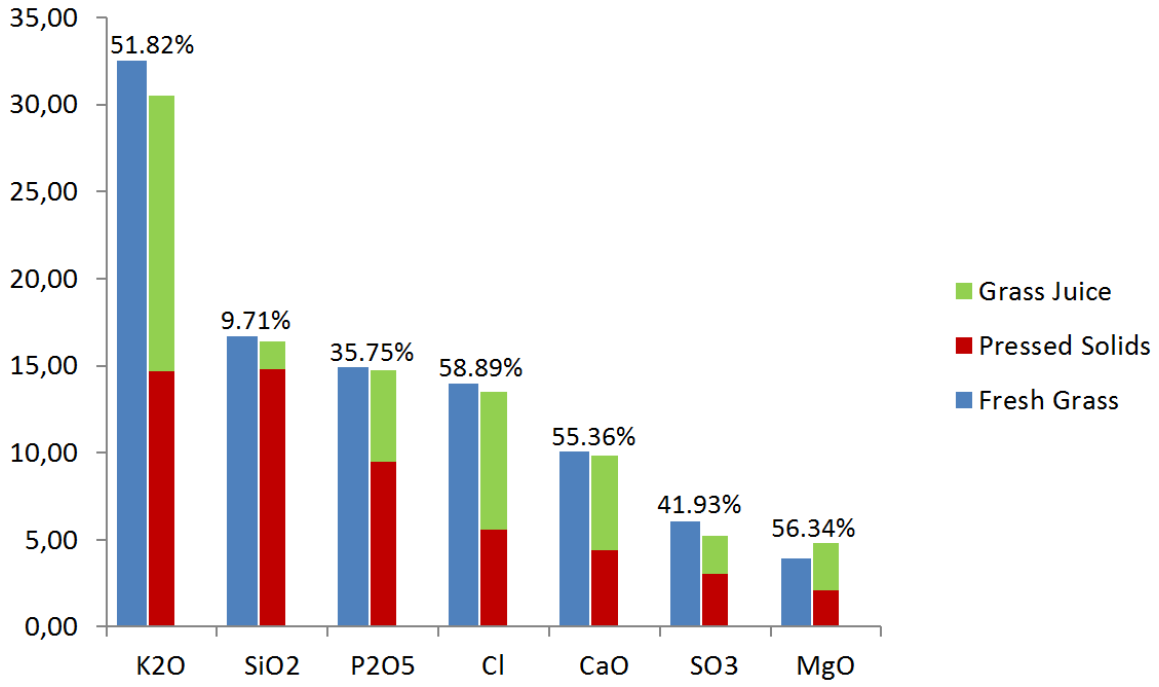


Figure 5-5: Ash composition of fresh grass (blue), pressed solids (red) and grass juice (green)

5.4 Experimental results from torrefaction setup

For this study, two series of experiments, drying experiments and torrefaction experiments were carried out on the experimental setup described in chapter 4 using fresh verge grass as feedstock, with varying flow rates and gas temperatures. Air was used for drying experiments and nitrogen was used for torrefaction experiments. This section presents the results from these two series of experiments in two paragraphs.

5.4.1 Drying experiments and results

The drying experiments were carried out in April 2014, with verge grass collected from location B (consult section 3.1 for detail location). Fresh grass samples contained approximately 80% moisture on average, the given volume of the reactor could accommodate approximately 0.2 kg of wet feedstock prior to drying, the exact biomass properties are given in table 5.1.

Experimental data from the drying experiments are presented in this section. for these experiments, fresh trimmed verge grass was dried with ambient air at flow rates of 30 and 90 Nl/min and gas temperatures (TC2) of 90 °C and 130 °C. It is common to represent the state of a packed bed by means of the breakthrough curves, as the curves represent the “breaking though” of the dryness and initial temperature of the convective media. Figure 5.6 shows one of the breakthrough curves of the drying experiment with air temperature of 130 °C and flow rate of 90 Nl/ min. The purple, red and green curves represent thermocouples placed near the bottom, middle and top of the bed, whereas the blue line represents the relative humidity as measured by the sensor over the top of the bed.

The humidity at the start of the experiments was relatively high, this was because of the presence of fresh samples in the column. The air above the sample is stagnant and its humidity increased due to the moisture in the grass. This soon was blown away due to the movement of air, thus the humidity decreased. However, the subsequent heating up of the bed led to rapid increase in drying rate, large amount of moisture thus led to complete saturation of the gas, which is shown as 100% humidity. The state of complete saturation persists until the top of the bed started approaching its *equilibrium moisture content* (EMC), which was approximately 3% depending on the humidity of air supply.

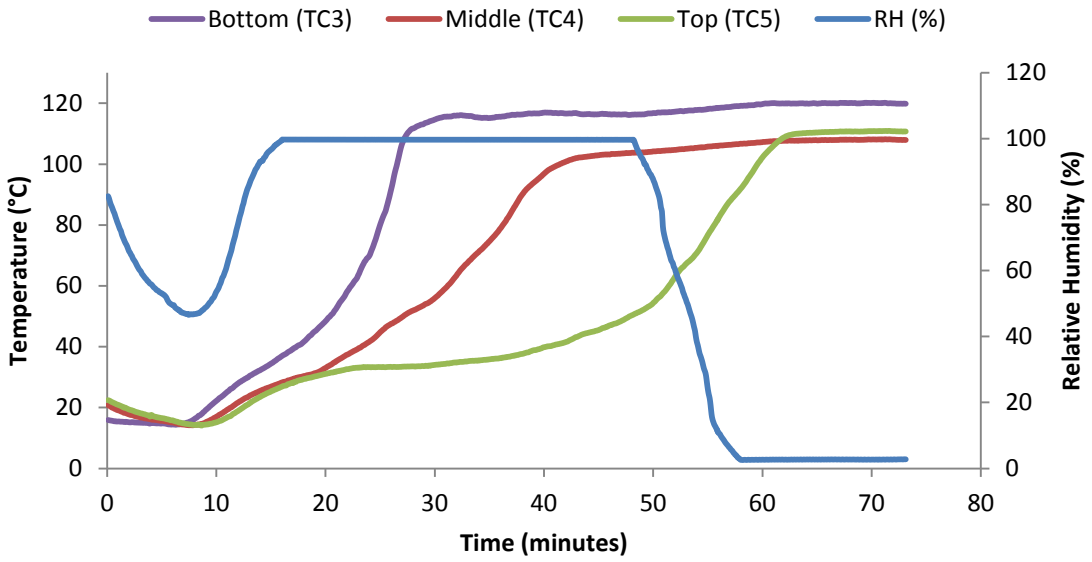


Figure 5-6: Breakthrough curves in drying experiment of verge grass (Air temperature: 130°C, flow rate: 90 Nl/min)

Records from thermocouple TC3, TC4 and TC5 also show the course of drying. After initial rise of temperatures, the bed temperature was kind of stabilized and increased relatively slowly from 30 °C to 40 °C, and then it went all the way up towards the inlet gas temperature (130 °C). This indicated a "constant drying rate period" at a temperature of around 30 °C, where a very high fraction of the heat transferred to the bed by the convective media was absorbed by the evaporating surface moisture as latent heat of vaporization, leading to a negligible sensible heating. As the bed dried up, the drying rate dropped (falling rate period) leading to the transferred heat resulting in a temperature rise. Eventually, the drying rate became relatively stable (close to zero) when biomass sample reached its EMC. This effect traveled upwards through the height of the bed, and finally reflected in the drop in relative humidity at the exit.

Table 5.4 shows the *drying time* at different process conditions (varying air temperatures and flow rates) for bed heights corresponding to the three in-bed thermocouples and the relative humidity detector. This drying time for the thermocouples is defined as the time duration for them to reach 95% of their respective equilibrium temperature. As for the relative humidity detector, it is defined as the time that relative humidity takes to reach its minimum value following the drying of the bed.

Table 5-4: Variation of drying time with process conditions

Case	Inlet Temperature (°C) TC2	Flow Rate (Nl/min)	Drying Time (min)			
			TC3	TC4	TC5	RH
1	90	30	50	69	119	146
2	90	90	56	60	91	80
3	130	90	28	54	61	58

Results show that both an increase in the flow rate and temperature have a positive effect on the drying rate of the bed. A comparison between case 1 and 2 shows that the increase in flow rate results in very significant shortening of the RH drying time. Also, the total duration of case 2 is much shorter than case 1, suggesting that higher flow rate results in faster drying and thus a smaller spread between drying times at different height. A comparison between case 2 and 3 shows the effect of increased inlet temperature, this results in a further reduction of drying time of all measuring points. TC5 has reached its equilibrium temperature around 33% faster than in case 2, and RH also shows about 25% reduction in its drying time.

5.4.2 Torrefaction experiments and results

Torrefaction experiments were carried out in August and September 2014, by Vidyut Mohan and Easwaran Krishnamurthy. These experiments were part of the assignment for their master course. For these experiments, grass samples were collected from location C.

The results of mass yield calculations are shown in table 5.5. In general, mass yield of verge grass after torrefaction becomes lower, as the torrefaction temperature goes up. Same conclusion can be drawn for the mass yield obtained at different residence times, mass yield goes down as the residence time increases. Also, since the temperature decreases with column height, top samples have larger mass yield than bottom samples. All of these phenomena can be explained with the fact that for the same retention time, devolatilisation and carbonization of biomass happen more extensively at higher temperature; if the temperature is constant, more volatiles will be removed as the retention time increases.

Samples from the torrefaction experiments will be further analyzed using HPLC for determination of carbohydrates contents. This will be presented in the next section.

Table 5-5: Calculated mass yields from torrefaction experiments.

Experiment	% Mass Yield			
	Bottom	Middle	Top	Total
230-15	82.00%	80.00%	91.00%	84.33%
230-30	88.00%	82.00%	88.00%	86.00%
230-45	72.00%	76.00%	92.00%	80.00%
250-15	79.00%	84.00%	85.00%	82.67%
250-30	78.00%	76.00%	83.00%	79.00%
250-45	72.00%	77.00%	81.00%	76.67%
270-15	69.00%	75.00%	79.00%	74.33%
270-30	59.00%	70.00%	74.00%	67.67%
270-45	69.00%	73.00%	76.00%	72.67%
290-15	57.00%	65.00%	70.00%	64.00%
290-30	54.00%	61.00%	65.00%	60.00%
290-45	52.00%	58.00%	61.00%	57.00%

5.4.3 Advantages and disadvantages of the torrefaction setup

In general, experiments were successfully carried out within the bench-top experimental torrefaction setup. The system was able to reach the required process conditions and maintained at these conditions without too large of fluctuations. Changing/mixing of the heat transfer gases was possible at the gas mixing station, which is (together with heater) controlled by LabVIEW through DAQ system. This system also collected readings from the installed temperature sensors, dP sensors and (for drying experiments) humidity sensor, these data were presented in LabVIEW for operators to monitor the entire process.

Despite all the advantages mentioned above, this setup had also some shortcomings which were mainly from the design perspective. The distance between the heater and the torrefaction reactor was too long, which caused a temperature drop of 20 °C even with additional heating from the tracing. This led to higher energy consumption and could be corrected in the future by shortening this distance. Another big problem of this setup was the assembly/disassembly of the torrefaction column, which was very inconvenient since it requires tightening and loosing 12 screws in top and bottom flange. These flanges must be perfectly aligned with other parts of the system to prevent damage on the screws; this was not an easy task to do, especially with the

perforated plates on both side of the column. For future setup with continuous system, this problem could easily be avoided.

Besides the design shortcomings mentioned above, there was another issue which must be taken care of when performing drying/torrefaction experiments. Some extractives / light volatiles such as waxes and fats in the flue gas were condensed in the pipelines after torrefaction column; this could clog the pipes and cause safety problems at certain moment. This seemed to be not a big problem for this setup, but it can become a big issue for future large scale torrefaction system.

5.5 High Performance Liquid Chromatography (HPLC) results

In this study, effects of mechanical fractionation and torrefaction on the carbohydrates content in verge grass were determined by measuring the sample's sugar concentration using HPLC. For these purposes, diverse samples including dried fresh grass (DFG), dried pressed solids (DPS), grass juice, EFG and torrefied grass were hydrolyzed and put through HPLC for quantifying cellulose and hemicellulose content. Notice that except for EFG samples, the carbohydrates content were referred as cellulose+ and hemicellulose+, since the measured sugar contents could be partially originating from the extractives. Samples for pressing experiments were collected from location C, whereas the samples for torrefaction were collected from location D.

In general, results in this section were given in weight percentage of structural carbohydrates on the basis of primary biomass sample (DFG). HPLC data were converted by following the steps mentioned in section 3.3.4. Content of acid insoluble lignin (AIL) was determined by subtracting ash from acid insoluble residues (AIR), and was not applicable for torrefied samples. This was because thermal treatment could change biomass's properties and causes devolatilisation and carbonization, which led to more acid insoluble matters. Considering the nature of HPLC experiment and small sample quantities, it was kept in mind that the results would contain a certain level of error. Large error could lead to an illogical result, which would be shown in this section.

It should be mentioned that considering the time constraint of this study and the number of experiments, the decision was made to not doing the extraction on torrefied grass. Because the

extractives contain in general only a small portion of the carbohydrates in a biomass, besides, by doing extraction, the total duration of one set of experiments will increase significantly.

Effect of pressing on carbohydrates and lignin content in biomass fuel

The reported effect of mechanical fractionation on biomass composition in the previous study [Joshi et.al, 2014] suggested that there was a partial transport of carbohydrates (especially hemicellulose) from the grass into the liquid phase during pressing. Unfortunately, the exact amount of removed sugar polymers was not determined since their employed method, TGA could not separate the cellulose and hemicellulose peak. However, this could be done by first break down the chemical bonds of carbohydrates by addition of acids (hydrolysis), this basically converted the polymeric sugars into monomeric sugars, which then can be measured using HPLC after neutralization, see paragraph 3.3.4 for the extensive procedure.

Table 5-6: Cellulose+, hemicellulose+, AIL and ash content in DPS, grass juice and DFG

Sample	Cellulose+	Hemicellulose+	AIL	Ash
DPS	16.2%	11.5%	13.0%	2.3%
Grass juice	1.6%	1.4%	3.3%	0.4%
Removal rate	9.1%	11.0%	20.3%	14.8%
Total	17.9%	12.9%	16.3%	2.7%
DFG	20.1%	12.8%	16.3%	3.3%
Std. Dev	1.6%	0.0%	0.0%	0.5%
CV%	8.5%	0.3%	0.1%	14.8%

Table 5.6 shows the cellulose+, hemicellulose+, acid insoluble lignin (AIL) and ash content in DPS and grass juice samples, corrected by the weight percentage of those in the primary sample, DFG. From the results it could be seen that only 9% of cellulose+ and 11% of hemicellulose+ were leached away during pressing, this corresponded to the previous research with TGA, where it was mentioned that only a small portion of carbohydrates were in the juice. The removal rate for AIL was slightly higher at 20.31%. The relative high AIL removal rate could be explained with the solids retained in the juice after mechanical fractionation. The ash removal rate however, was only at 15% and did not coincide with the ash removal rate in paragraph 5.3, which was on average close to 50%, this was because that the sample in this section was been hydrolyzed

whereby acid/water soluble inorganic matters were leached away. This was also the reason why the samples' ash content is much lower than the ash content in paragraph 5.1, which was measured before the hydrolysis.

Difference between the sum of DPS and grass juice and DFG was again analyzed by calculating the standard deviation and coefficient of variation. Both outcomes were at acceptable level, which suggested that these experiments were well performed and do not have significant losses.

Effect of torrefaction on carbohydrates content in biomass fuel

In this section, the cellulose+ and hemicellulose+ content of verge grass torrefied at various conditions are presented and compared. Torrefied grass was prepared from the verge grass sample collected around duck pond, then dried and torrefied with the test rig introduced in chapter 4. This series of experiments consisted of 8 experiments, each one started with the same amount of grass, experimental conditions varied across four different temperatures (230°C, 250 °C, 270 °C and 290 °C) and two different retention times (15 and 45 min). Experimental results regarding the torrefaction mass yield was given in table 5.5 in this chapter.

Following the same procedure mentioned earlier, HPLC results of the torrefied grass samples were converted into cellulose+ and hemicellulose+ content and together with the corrected AIR content, they are given below in table 5.7. This table also contains the carbohydrates and AIR content of the primary biomass (DFG), which is given as a reference. All results are given in weight percentage of DFG, on dry basis.

Table 5-7: Cellulose, hemicellulose and ash content in torrefied grass

Sample	Cellulose+		Hemicellulose+		AIR	
DFG	21.02%		12.71%		22.68%	
T	15min	45min	15min	45min	15min	45min
230°C	17.1%	13.1%	8.6%	5.2%	33.74%	35.5%
250°C	16.0%	13.7%	6.6%	4.2%	35.98%	37.7%
270°C	10.8%	8.7%	3.2%	2.5%	40.80%	43.4%
290°C	0.9%	1.0%	0.3%	0.2%	43.88%	46.1%

It can be seen from the results that both cellulose+ and hemicellulose+ content decreased during torrefaction. In general, the higher the temperature/ the longer the retention time was, the lower the carbohydrates content would be. The hemicellulose+ content was down to 50% at 250°C, as cellulose+ content was halved at 270°C. At 290°C, the torrefied grass contains a negligible amount of carbohydrates as both cellulose+ and hemicellulose+ content were lower than 1%. Notice that the underlined numbers were irregular results, which suggested that there were some uncommon biomass decomposition, or it might be just errors occurred during experiment or during data processing. The 250-45 cellulose content was higher than this of 230-45, and also, 290-45 contained more cellulose than 290-15. An explanation for these could be that the hemi-cellulose C6 side groups decomposing led to interpreted cellulose+ content. other possible reasons could be inaccurate mass yield, bad HPLC separation, imprecise integration etc.

AIR are the matters with remained solid after hydrolysis. These are the products created by torrefaction of verge grass, which are basically carbonized biomass or biochar. The given results show that the AIR content increases with the temperature and retention time. This means that biomass feedstock will have more char formation at higher temperature and/or longer retention time in the reactor.

Using the results in table 5.6, the percentage weight loss of hemicellulose and cellulose were calculated and depicted in figure 5.7. As it can be seen, each plot contains two sets of data as one for 15 min series and one for 45 min series. The horizontal axis shows both the temperatures of the experiments and exact value for each data point; the vertical axis is the weight percentage of the torrefied sample as compared to the primary, dried sample. The slope of the line thus corresponds to the increasing rate of the carbohydrates during torrefaction. For cellulose+ content, it is obvious that the decreasing rate is the highest after 270 °C, as the lines are more tilted. Hemicellulose+ plot shows its maximum slopes at temperatures higher than 250°C. Now compare these findings with results from literature; figure 2.3 in chapter 2 from Bergman's study shows that 250°C and 270°C are the transition temperatures from limited devolatilisation (D) to extensive devolatilisation (E) for hemicellulose and cellulose, respectively. Bergman's conclusion corresponds with the experimental result in this section, which proves that the experimental data was trustworthy.

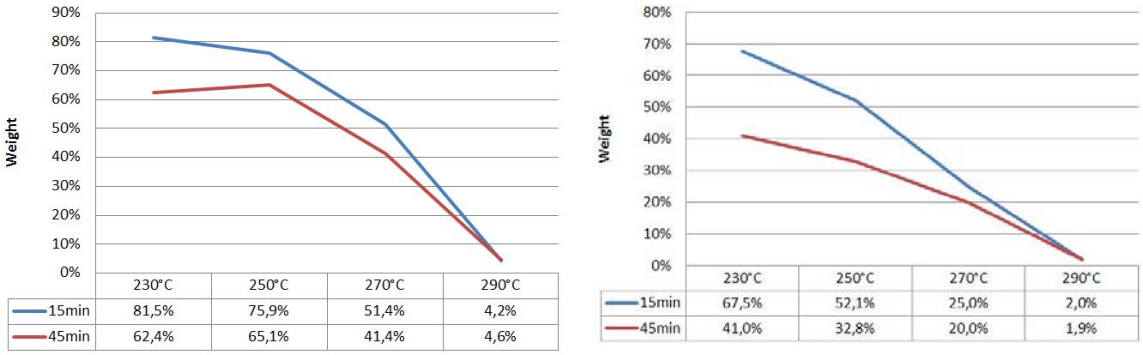


Figure 5-7: Weight decrease of cellulose+ (left) and hemicellulose+ (right) in torrefied grass

Composition of verge grass

Finally, in this section, the biochemical composition of verge grass collected from location C will be constructed; this will not only close the mass balance for biochemical analysis of verge grass, but also shows the effect of extraction on the biomass composition. In order to do that, the basic biomass properties such as moisture and ash content were first collected from table 5.1. Secondly, the amount of extractives and ash contents of DFG samples in table 5.2 were also taken. On top of that, HPLC experiments with the EFG samples were performed to determine the cellulose+, hemicellulose+ and AIL content. All of these data are summarized in table 5.8.

Table 5-8: Cellulose+, hemicellulose+, AIL and ash content of DFG, EFG and extractives samples

Sample	Percentage of sample	Cellulose+ (dry)	Hemicellulose+ (dry)	AIL (dry)	Ash (dry)
DFG	100%	20,1%	12,8%	16,3%	12.4%
EFG	58.8%	16,3%	10,8%	8,2%	2.4%
Extractives	41.2%	3,8%	2,0%	8,2%	9.9%

The amount of carbohydrates and AIL in extractives could be determined by calculating the difference between carbohydrates content in EFG samples and DFG sample. Notice that the carbohydrates in extractives were not only cellulose and hemicellulose, but could also be monosaccharides such as arabinose, galactose or other monomeric sugars. In this study, considering the small quantities of these water extractable carbohydrates, they have been categorized as cellulose+ and hemicellulose+ for the sake of simplicity. It can be seen from the

results that extraction has removed about 20% of the cellulose+ and 15% of the hemicellulose+ from the primary sample. These results are close to Thanmmasouk's results shown in section 2.1.2 [Thammasouk, 1997], where different kinds of herbaceous biomass were used.

The EFG sample contains about half of the AIL, which was much lower than the results (78%) from Thammasouk's study [Thammasouk et.al, 1997]. This could be explained by the different extraction durations between two studies. Thammasouk used a 3h extraction without mentioning the number of refluxes per hour; in this study, extraction was done for 24 hours with 4-6 siphon cycles per hour. Other possible reasons to explain this difference were measurement errors, different biomass species etc. Notice that all the contents in table 5.8 were calculated based on the dried weight of DFG samples in order to compare them directly. Finally, the ash content results show that extraction has removed about 80% of the inorganic contents; this is much higher that the removal rate of pressing, which is around 50%.

Figure 5.8 presents the biochemical composition of dried verge grass, with all the values expressed in weight percentage. The bigger pie shows the extractive free matters whereas the smaller pie shows the exact composition of the extractives. The part "Others" represents the missing portion which closes the full mass balance. This part could contain carbohydrates, pectin, fatty acids, waxes or other compounds which were not/inaccurate measured in this study.

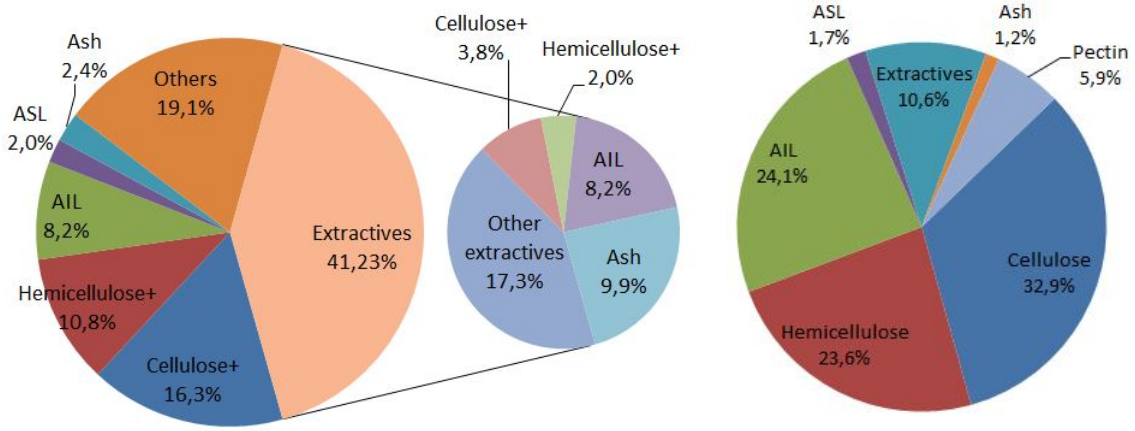


Figure 5-8: Biochemical composition of verge grass on dry basis, left chart shows the results from this study, right chart shows the results from Phillyis2 data base. [ECN Phillyis2 data base. Verge grass (#2541), 2012].

The biomass composition reported in ECN Phillyis2 data base are also given in this figure. Obviously, there is a large difference between the derived composition from this study and

ECN's result. Unfortunately, it is not clear what kind biomass species ECN had used and also the method for determining the biomass composition is unknown, these all makes explaining the difference very hard. By taking look at the two results, a conjecture will be that the extractives in ECN's result do not contain AIL, or probably even do not contain any carbohydrates. Also, ECN used an entirely different kind of grass than this study, which contains more carbohydrates and lignin.

5.6 Summary

This chapter started by presenting the properties of the prepared verge grass samples for this study. Biomass properties such as total solids content and moisture content were used to correct the experimental results in the next sections in order to make them directly comparable with each other. The obtained ash contents were used to calculate the removal rate of inorganic matters in biomass samples which underwent mechanical fractionation and extraction.

The second part of this chapter showed three DTG plots obtained from the TGA setup. The first plot depicted the rates of thermal decomposition of DPS, EFG and DFG samples during torrefaction, whereby the effect of extractives on torrefaction was shown. The second and third plots were both results from TGA analysis of torrefied samples. These plots illustrated the effects of different process conditions (temperature & retention time) on the carbohydrates and lignin content in biomass samples. These results had provided a reference for the expectations from the chemical analysis of these samples.

Although the removal rate of inorganic matters were determined through ashing, it was still not clear what components were exactly leached away during mechanical fractionation. This was especially important given that some inorganic compounds such as alkali metals would cause unfavorable ash deposition in energy production facilities. Part three of this chapter provided the answer to this question together with some discussions and comparison with results from ECN.

The fourth paragraph of this chapter presented the results obtained from the experiments carried out on the bench-top experimental setup. Results from the drying experiments were not linked with other results in this study per se, they were meant to be performed as try out sessions of the test rig and also for the operator to gain operational experience. Results from

the second part of this paragraph presented the mass yields of the torrefaction experiments. The torrefaction products were used for TGA and chemical analysis.

The last part of this chapter presented the results from the biochemical compositional analysis (hydrolysis + HPLC) on all the samples prepared in part 1 and part 4, including DFG, DPS, grass juice, EFG and torrefied grass. The comparison between the DFG, grass juice and DPS showed the effect of pressing on carbohydrates and lignin content in biomass samples, whereas the compositional changes of grass after torrefaction were depicted by comparing the DFG and torrefied samples. Finally, the biochemical composition of verge grass, including analysis on the extractives, was presented in the last part in order to show the effect of extraction on biomass composition.

6 Conclusions and Recommendations

This chapter contains the conclusions derived from the results in the previous chapter. Answers to the research questions are also provided with some explanations. Furthermore, suggestions upon work improvement as well as certain open issues to be elaborated on as future work are also provided.

6.1 Conclusion

In this study, research was done in the field of pretreatments of biomass fuel for co-firing. Verge grass was the selected feedstock and the main focus of this study was to analyze and quantify the losses of major components in biomass after mechanical fractionation or torrefaction. These results could be used in the future as a reference for biomass properties determination. This thesis provides some preliminary answers to the following research questions, which were defined in section 1.2:

1. What is the effect of extractives on the thermal reactivity of dried verge grass during torrefaction?

First of all, results have shown that extraction removed approximately 80% of the extractives whereas pressing "only" removed about half of them. This suggests that the comparison between the TGA plots of EFG and DFG would show clearer differences than comparing DFG with DPS. TGA results have shown that extractives have a catalytic effect on the thermal reactivity of biomass, which means that biomass became less reactive to thermal degradation (reacts at higher temperature) after the removal of the extractives. This effect is especially visible by comparing the DTG graphs of DFG and EFG samples.

2. How is the biochemical composition of verge grass going to change after pressing/extraction?

The main objective of pressing is to remove the moisture content in biomass, which is proven to be quite effective as the solids output underwent up to 30% moisture reduction on wet basis in

comparison to the primary feedstock. Results from HPLC have also shown that fractions of the organic matter, 10% of the carbohydrates and 20% of AIL, were also withdrawn upon screw pressing. In addition, pressing had also removed approximately 50% of the inorganic matter in biomass, in particular, results from XRF experiments have shown that the reduction in K_2O, Cl, CaO and MgO were more than 50%.

These findings all suggest that mechanical fractionation could be an easy and yet effective biomass fuel preparation procedure. Compared to pressing, extraction has an even higher inorganic matter removal rate of 80%, it has also removed approximately 18% of the carbohydrates and 50% of the AIL from the primary feedstock.

The presented answers to the first two research questions have shown the advantages of extraction over mechanical fractionation for chemical analysis. However, as extraction was initially meant to be employed as a pre-treatment prior to biomass hydrolysis as extractives will lead to an inaccurate estimation of carbohydrates and lignin content of a feedstock, it could not be considered as an alternative for biomass preparation on a large scale due to its high energy requirement and more complicated process.

3. How is the biochemical composition of verge grass going to change at different torrefaction conditions?

Dried verge grass underwent great alterations in its properties during torrefaction. In general, biomass will have more weight loss, lower carbohydrates content and more biochar formation at higher torrefaction temperature and / or longer retention time in the reactor.

Depending on the process conditions, biomass will suffer a 20% - 50% mass loss during torrefaction. This lost mass was caused by devolatilisation of light volatiles, extractives, hemicellulose etc, as it was converted into torrefaction gases such as CO, CO_2, CH_4, etc. during the process. At lower torrefaction temperatures (230°C and 250°C), solid phase torrefaction products generally contain 65%-80% cellulose+ and 35%-65% hemicellulose+ as compared to the carbohydrates contents in the primary sample, and for torrefaction at higher temperatures (270°C and 230°C), those numbers are 5%-50% for cellulose+ and 2%-25% for hemicellulose+. This showed that hemicellulose was more reactive to thermal treatments than cellulose; it started to devolatilize at 200°C and reached its maximum reaction rate at 250 °C. For cellulose,

those temperatures were 230°C and 270°C respectively. The missing fractions of cellulose+ and hemicellulose+ were partially devolatilized and another part of it was carbonized, which led to biochar formation. Since biochar is insoluble in acid, the amount of biochar could be reflected by the amount of AIR in the torrefied sample, which increased with the torrefaction temperature.

General conclusion

Analysis on the DPS samples and grass juice have shown that mechanical fractionation should be considered as an effective biomass pretreatment since it could remove up to 30% of the moisture and 50% of the inorganic matter present in the verge grass samples. This will significantly reduce the time and energy required for processing / drying of the feedstock and is (therefore) especially beneficial for high moist biomass feedstock. In addition, pressing also resulted in a better fuel quality, as lower ash content will lead to a higher heating value and less problems caused by molten ash. To be more specific, pressing has removed more than 50% of alkali, alkaline earth elements from biomass feedstock, the reactions between these compounds and other inorganic constituents such as sulfur, chlorine and silica, could result in unwanted deposits, slagging and corrosion in energy conversion facilities utilizing biomass fuels.

During torrefaction, dried biomass had lost up to 50% of its weight and was mostly converted into biochar, which had a higher energy density than the primary feedstock. The obtained products were dried and showed no signs of biological activity like rotting. All these factors led to a reduction in transport costs and made the biomass easier to store. Also, torrefaction has made the biomass feedstock more brittle and less fibrous, which would benefit the fuel preparation for cofiring. Furthermore, as it was observed during the experiments, the difference between different biomass feedstock was reduced through torrefaction since all the biomass samples were converted into biochar with similar fuel properties. Thus, while the quality of the delivered biomass supply might be variable, the obtained torrefaction products would have similar combustion characteristics and heating value.

To sum up, the results from this study suggest that both mechanical fractionation and torrefaction are very effective biomass pretreatment techniques. Mechanical fractionation is especially suitable for biomass with high moisture content, whilst torrefaction could greatly improve the biomass fuel quality and be applied for all kinds of biomass feedstock.

Another achievement of this study was commissioning and doing experiments with the bench-top torrefaction setup. During this period, operators gained experience from the rig and learned how to reach the operating conditions in an effective way with minimum heat losses. On the other hand, despite additional heating from the tracing, a lesson learned was that the distance between the heater and the reactor should be designed to be as short as possible in order to minimize the process heat loss. Another major issue was assembly / disassembly of the torrefaction column, which turned out to be very inconvenient and time consuming. In short, regarding the torrefaction setup, data obtained and experience gained from the test rig could serve as inputs to dynamic modelling and future scale-up studies. The obtained results could be used as inputs to dynamic modeling.

6.2 Recommendations

The accuracy issue of the HPLC results was a serious problem and it could not be solved by using the existing apparatus / method. The HPLC system in the P&E laboratory was built in the 90's and has regular ageing problems that often were reflected in the chromatograms. Problems such as an instable baseline, irregular/regular jumps in the chromatograms and bad components separation happen quite often. Although the accuracy level of the current HPLC system is accepted for this thesis, replacements of certain components of the system must be executed in case high accuracy is required for future work.

The bench-top torrefaction setup in this study was used to conduct a series of drying and torrefaction experiments with grass. It has provided valuable experimental data and operating experiences. However, its shortcomings are obvious: it is a batch reactor that requires a lot of time and labor for assembling and disassembling the reaction column. Also, control of the setup happens manually and thus can be inaccurate, which could affect the product quality. For future scale-up studies, a continuous reactor with an automatic control system should be considered.

For the determination of carbohydrates, some small and yet important adjustments for the NREL'S LAP procedure were developed. A pressure tube that contains biomass samples was put in an oil bath instead of autoclave as this was not available. Results have also shown that for neutralization of a low concentrated, hydrolyzed sample, barium hydroxide is a better

alternative than calcium carbonate. These adjustments can be quite useful and are worth recommending for future studies.

The obtained experimental data can be used for the modeling of the torrefaction setup in this study and provides good reference for building the model of other similar types of torrefaction reactors. Results from the chemical analysis can be useful for modeling the biochemical composition of (pre-treated) verge grass samples.

Finally, a future large-scale torrefaction setup should consider a continuous feeding system, such as moving bed. This generally has a larger production capacity than the fixed bed system and will also save the troubles of loading/unloading the reactor. The overall system heat loss could be reduced through better isolations, a shorter distance between heater and reactor and recycling the flue gas to pre-heat the feedstock.

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Appendix

Appendix A Soxhlet Extraction Setup

Description

A Sohexlet Extractor contains the following parts: A boiling flask which contains the extraction solvent; a reflux that circulates the solvent; a thimble which contains the solid to be laved; a siphon mechanism, which periodically empties the thimble and a condenser, which uses water flow as coolant.

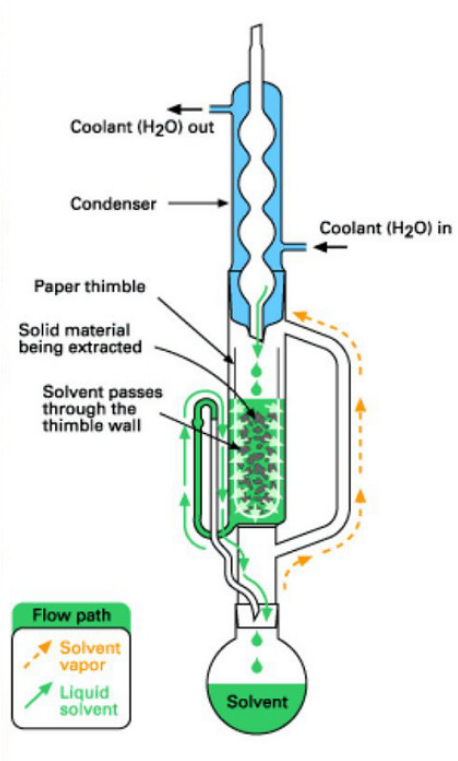

Figure A 1: Soxhlet extraction setup [Cremona tools, 2013]

Operation

Figure A1 shows the operating principles of the Soxhlet extraction setup. The solvent (green) in the boiling flask is heated to reflux. The solvent vapor (orange) then travels up a distillation arm, and floods into the extraction chamber. The condenser ensures that any solvent vapor cools and drips back down into the extraction chamber housing the thimble. The chamber will then be slowly filled up with warm solvent; some of the extractives will then dissolve in the solvent.

When the Soxhlet chamber is almost full, the chamber is empties by the siphon. The solvent is returned to the boiling flask. The thimble ensures that the rapid motion of the solvent does not transport any solid material to the still pot. The cycle may be allowed to repeat many times, over hours or days.

During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

Appendix B Calibration curves for HPLC analysis

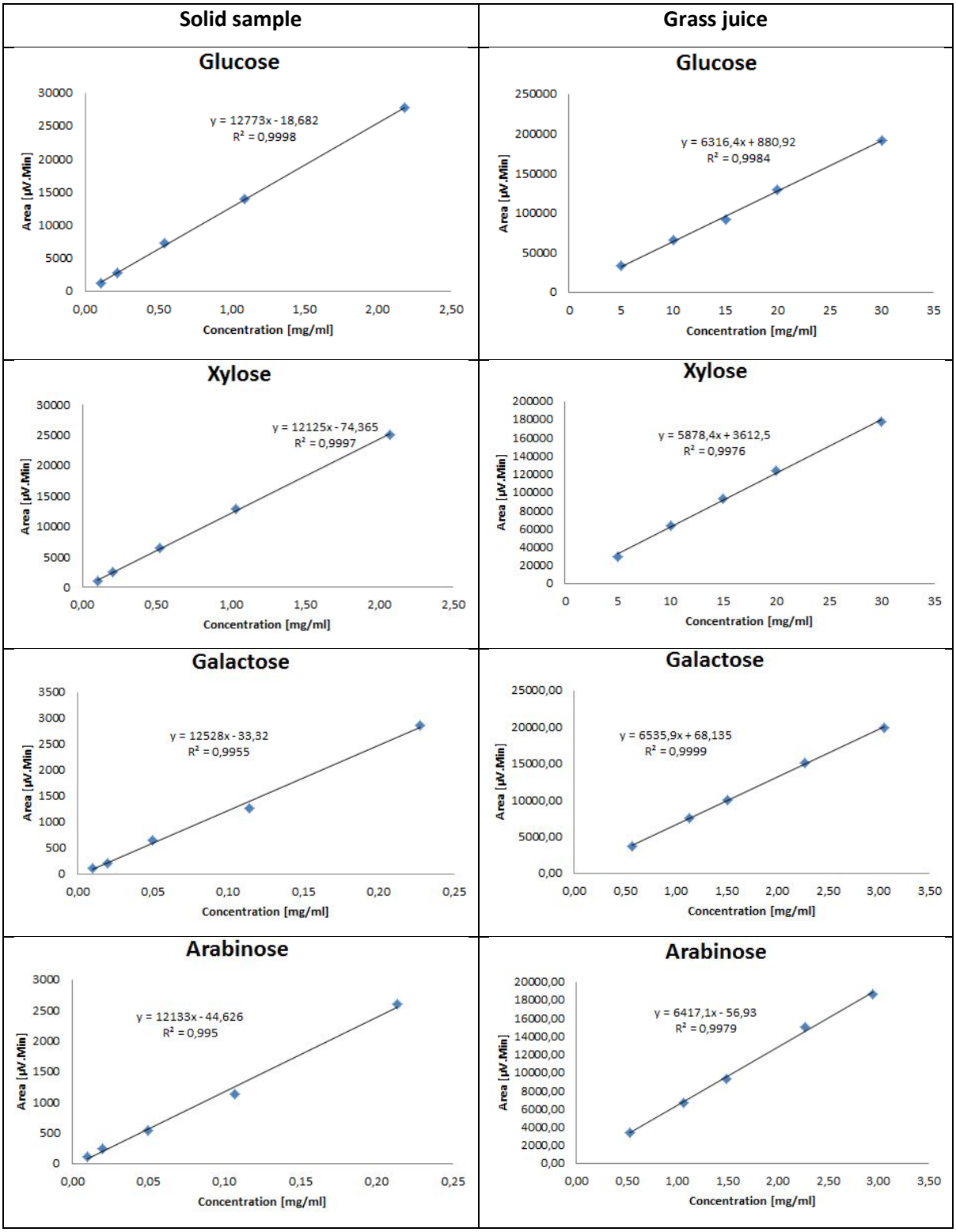

Figure B 1: Calibration curves for HPLC analysis of solid and grass juice samples

Appendix C Mineral content in DPS, grass juice and DFG

Table C 1: Mineral content in DPS, grass juice and DFG samples

Sample %	K_2O	SiO_2	P_2O_5	Cl	CaO	SO_3	MgO	Others
DPS	14.69	14.81	9.47	5.56	4.39	3.05	2.09	4.22
Grass Juice	15.80	1.59	5.27	7.96	5.44	2.20	2.70	0.75
Sum	30.48	16.40	14.75	13.52	9.83	5.25	4.79	4.97
DFG	32.52	16.67	14.94	13.97	10.09	6.08	3.95	1.79
Std. Dev	0.26	0.44	0.47	0.57	0.34	0.58	0.86	0.01
CV%	0.01	0.03	0.03	0.04	0.03	0.10	0.19	0.01

The standard deviation and coefficient of variation for a specific inorganic element were calculated based on the difference between 3rd row and 4th row in table C1. As it can be seen, most of the variation coefficients were below 4%, indicate that the errors of the XRF experiments were very small. Even for the elements with higher CVs (10% for SO_3 and 19% for MgO), their errors are still at an acceptable level. Notice that the mathematical procedure for calculating standard deviation and coefficient of variation can be found in appendix D.

Appendix D Standard deviation and coefficient of variation

Standard deviation

In statistics and probability theory, the standard deviation (SD) (represented by the Greek letter sigma, σ) measures the amount of variation or dispersion from the average. A low standard deviation indicates that the data points tend to be very close to the mean (also called expected value); a high standard deviation indicates that the data points are spread out over a large range of values.

Let X be a random variable with mean value μ:

$$E[X] = \mu \qquad \text{(Equation D1)}$$

Here the operator E denotes the average or expected value of X. Then the standard deviation of X is the quantity

$$\begin{aligned} \sigma &= \sqrt{E[(X-\mu)^2]} = \sqrt{E[X^2] + E[(-2\mu X)] + E[\mu^2]} \\ &= \sqrt{E[X^2] - 2\mu E[X] + \mu^2} = \sqrt{E[X^2] - 2\mu^2 + \mu^2} \\ &= \sqrt{E[X^2] - \mu^2} = \sqrt{E[X^2] - (E[X])^2} \end{aligned} \qquad \text{(Equation D2)}$$

In other words, the standard deviation σ is the square root of the variance of X; i.e., it is the square root of the average value of $(X-\mu)^2$.

Coefficient of variation

The coefficient of variation (CV) is a standardized measure of dispersion of a probability distribution or frequency distribution. It is defined as the ratio of the standard deviation σ to the mean μ. It is also known as unitized risk or the variation coefficient.

$$CV = \frac{\sigma}{\mu} \qquad \text{(Equation D3)}$$