CHEMICAL ENGINEERING TRANSACTIONS
VOL. 72, 2019

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216
DOI: 10.3303/CET1972014

Characteristics of Cellulose, Hemicellulose and Lignin of MD2 Pineapple Biomass

Adila Maisyarah Mansor[a], Jeng Shiun Lim[a,]*, Farid Nasir Ani[b] , Haslenda Hashim[a], Wai Shin Ho[a]

[a]Process Systems Engineering Centre (PROSPECT), Research Institute for Sustainable Environment, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.
[b]School of Mechanical Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.
jslim@cheme.utm.my

Three main lignocellulosic components (lignin, cellulose and hemicellulose) are major plant cell walls. Their content in biomass crops, for example, MD2 pineapple waste will affect the heating values (HHV) if uses as a feedstock for the solid biofuel (biocoke). The aim of this paper is to identify the amount of lignocellulosic content in the MD2 pineapple waste and its effect on heating value. The experiment and parameters setup were carried out by following the chemical composition determination of standard methods. The process involved the sample preparation and treatment process by using NaOH and sodium chlorite for bleaching purposes. The effect of a percent of the lignocellulosic content in the MD2 pineapple waste before and after bleaching process towards heating value was studied. From the result, lignocellulosic in leaves (Cellulose 30 wt%, Hemicellulose 37 wt% and Lignin 22 wt%) showed the similarities (slightly higher and lower) content compared to the stem (Cellulose 46 wt%, Hemicellulose 29 wt% and Lignin 17 wt%) and root (Cellulose 42 wt%, Hemicellulose 32 wt% and Lignin 19 wt%). The majority of the leaves for the whole non-woody plant will give the cumulative effects since the quantity of stem and root is only about 15 % of the total weight of the plant. The cellulose and hemicellulose produce different thermal stability due to their different chemical structure even though they are both polysaccharides. From the data, all parts of MD2 pineapple has high cellulose and hemicellulose content. The hemicellulose can indicate the ignition temperature and time to ignite of the biocoke product produce by MD2 pineapple waste same goes to the cellulose content. The decomposition of lignin from start to end of the burning process can be an indicator that the biocoke product produces from MD2 pineapple waste can withstand up until 900 °C or above with some additional reactor or chemical that can enhance its thermal properties.

1. Introduction

MD2 pineapple is a hybrid of pineapple (Ananascomosus) genus from a Bromeliaceae family that have high potential biomass productivity and could be used as a feedstock for renewable energy and bioproducts (Jin et al., 2017). The potentially as a sustainable bioenergy crop is due to the continuity of the plantation beside the availability and the quantity produced by every season. This variety of Ananas Comosus was produced by the research done with the collaboration of the Hawaii research institute and a few pineapple suppliers to suites the demanding all over the world. MD2 pineapple popularly planted in Pontian, Johor, Malaysia. MD2 pineapple is considered as a feedstock for solid biofuel because it can be converted into biohydrogen and biobutanol (Khedkar et al., 2017). In Malaysia, about 275,732 t of pineapple produced in 2013. It was estimated that 34.1 MJ/kg calorific value and 4,526 TJ of biocoke energy potential contributed from the pineapple waste (Mansor et al., 2018a).

Biomass or plant waste has 3 major components which are cellulose, hemicellulose and lignin besides the extractives and minerals (Di Blasi et al., 1999). The content of the cellulose, hemicellulose and lignin normally will be in range 40 - 60 wt%, 20 - 40 wt%, and 10 - 25 wt% of the biomass in dry basis (McKendry, 2002). Rowell et al. (2005) stated that major carbohydrate portion in woods is a combination of cellulose (40 - 45 %)

Paper Received: 30 March 2018; Revised: 01 August 2018; Accepted: 05 December 2018

Please cite this article as: Mansor A.M., Lim J.S., Ani F.N., Hashim H., Ho W.S., 2019, Characteristics of cellulose, hemicellulose and lignin of md2 pineapple biomass, Chemical Engineering Transactions, 72, 79-84 DOI:10.3303/CET1972014

and hemicelluloses (15 - 25 %) which so-called holocellulose and usually covered 65 - 70 % of dry basis biomass weight. Cellulose is a major part of polysaccharides that present in plants accompanied by hemicellulose (Browning, 1967). Cellulose is a glucan polymer of D-glucopyranose units that link together by β-(1 → 4)-glucosidic bonds (Dussan et al., 2014) and can be classified as a most abundant organic chemical of the earth (Rowell et al., 2005). Hemicellulose is a part of the wood fractions that consist of polysaccharide polymers with a lower degree of polymerisation (DP) compare that cellulose. It is containing mainly sugars D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid and D-galactopyranosyluronic acid with minor amounts of sugars (Rowell et al., 2005). Other minor of polysaccharides in softwood or hardwood in containing a small amount of pectins, starch, and proteins (Rowell et al., 2005). Lignin is defined as amorphous, polyphenolic materials that come from an enzyme-mediated dehydrogenative polymerisation of three phenylpropanoid monomers, coniferyl, sinapyl and p-coumaryl alcohols (Lin and Dence, 2012). It is typically in the range of 11 to 27 % for a lignin content in the non-woody fibre sources (Bagby et al., 1971). For a normal softwood, lignin contents vary in the range 24 to 33 % (Sarkanen and Ludwig, 1971). Extractive is a natural product in woods that are chemical can be extracted by using several solvents. Normally it can be classified as the way the solvents extraction process had been done onto them, for example, water-soluble extractives or ether soluble extractives (Rowell et al., 2005).

Zainuddin et al. (2014) estimated the physicochemical properties of pineapple from 3 varieties which is MD2, Moris and Josapine by using thermogravimetry analysis (TGA) data. The leaves and stem from the pineapple plant were chosen as a feedstock for the sample (Zainuddin et al., 2014). They found that every part of the pineapples plants showed the different percentage of the lignocellulosic content. However, they have not covered the root part and the value which is estimated from the TGA result might have some error.

Heating value is also known as calorific value or gross energy. This is a measurement of the amount of heat released by a specific quantity during the combustion process. The capabilities of the fuel to provide heat during the combustion process. Demirbas (2017) indicated that the lignin content of woody and non-woody plant give different heating value. They had divided the lignin from the different plant into three types which giving different amount of heating value for every each. From the results, they found that the increment of lignin content will increase the unsaturated carbon content and will result in a higher heating value. The lack of the information about the effect of cellulose and hemicelluloses towards heating value is a great challenge and interest to be studied in order to identify the whole lignocellulosic component affecting the thermal properties of the plant.

In this study, the untreated biomass waste from MD2 pineapple was used as a sample. The aim of this paper is to identify the amount of lignocellulosic content in the MD2 pineapple waste by experiment besides discussing its effect towards the heating value. Pineapple waste divided into three parts which are leaves, stem and root. The effect of the cellulose, hemicellulose and lignin in pineapple waste toward heating value from the Bomb Calorimeter result in an earlier study will be discussed.

2. Materials and experimental methods

This section describes the sample preparation process involved from the beginning. The details in chemical and equipment used for the experimental process also included.

2.1 Materials

MD2 pineapple waste was used as a biomass sample which representatives of highest production of local biomass. The pineapple waste was cut off into tiny pieces (range 3 - 5 mm in length) and (2 - 3 cm in wide). They have undergone the drying process by following the LAP-Preparation of the sample for compositional analysis (Hames et al., 2004). The biomass was placed under direct sun for three months before the size reduction process applied. By using laboratory blender with a single speed of 230 V by WARING/USA brand, the biomass was blend to a smaller size and passed the test sieve pan with size 35 meshes (500 microns).

2.2 Experimental methods

The amount three components of lignocellulosic (cellulose, hemicellulose and lignin) in MD2 pineapple waste was determined by the method proposed by Yang et al. (2006). For the experimental process, 4 types of the chemical will be used; (1) Acetone, (2) Sodium hydroxide (NaOH - 0.5 mol/L), (3) Sulphuric acid (98 %) and (4) Barium chloride solution.

2.2.1 To determine the amount of extractives in biomass solvent extraction

Figure 1 shows the flow process for determining the amount of extractives in biomass solvent extraction. 60 mL of Aceton added to 1 g pineapple waste (A). The temperature 90 °C controlled by using a hot plate for 2 h.

After 2 h, the sample dried in an oven at 105 – 110 °C until constant weight was obtained (B). By using Eq(1), the amount of extractives was identified.

$$(\mathrm{A}-\mathrm{B}) = \text{Amount of Extractives (g)} \tag{1}$$

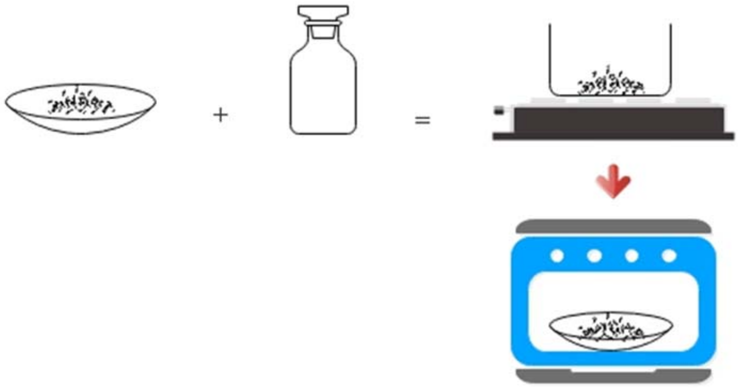

Figure 1: Flow diagram in the determination of extractives

2.2.2 To determine the amount of hemicellulose in biomass

Figure 2 shows the flow process for determining the amount of hemicellulose in biomass solvent extraction. 150 mL of Sodium Hydroxide (NaOH) solution (0.5 mol/L) was added to 1 g of pineapple waste with extractives free (B). The temperature 80 °C controlled by using a hot plate for 3.5 h. After that, the sample was washed with deionised water until it is free from Na^+. The Na^+ was detected by using pH paper and the reading should be closed to 7. The sample was dried in an oven at 105 – 110 °C until constant weight was obtained (C). By using Eq(2), the amount of hemicellulose was identified.

$$(\mathrm{B}-\mathrm{C}) = \text{Amount of Hemicellulose (g)} \tag{2}$$

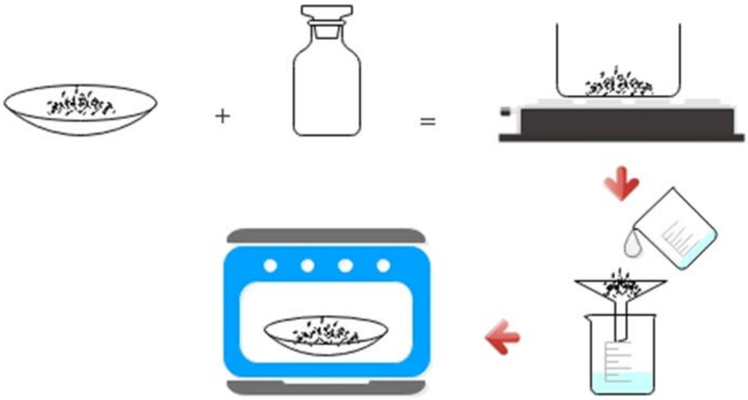

Figure 2: Flow diagram in the determination of hemicellulose

2.2.3 To determine the amount of lignin in biomass

Figure 3 shows the flow process for determining the amount of lignin in biomass solvent extraction. 30 mL of 98 % Sulphuric Acid added to 1 g pineapple waste with extractives free (B). The sample left at ambient temperature for 24 h before boiled at temperature 100 °C controlled by using a hot plate for 1 h. The mixture was filtered and the solid residue was washed by using deionised water until sulfate ion undetectable. Detection of sulfate ion was done via titration process with 10 % of Barium Chloride solution. The sample dried in an oven at 105 – 110 °C until constant weight was obtained (D). The final weight of residue is recorded as lignin content.

$$(\mathrm{D}) = \text{Amount of Lignin (g)} \tag{3}$$

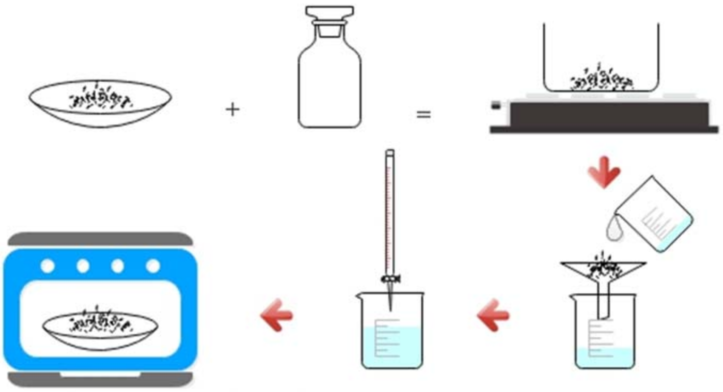

Figure 3: Flow diagram in the determination of lignin

2.2.4 To determine the amount of cellulose in biomass

Eq(4) is an assumption of the total lignocellulosic component inside the biomass. 1 g is referred to the total amount of biomass sample used in the experiment. By calculating the difference between the initial weight of the sample with the three others component weight calculated from the experimental process, the content of cellulose (E) will be identified.

$$(\mathrm{A} - \mathrm{B}) + (\mathrm{B} - \mathrm{C}) + \mathrm{D} + \mathrm{E} = 1\ \mathrm{g} \tag{4}$$

3. Results and discussion

This section will describe the data collected from the experimental procedure that had been done. The lignocellulosic content was determined by doing the experiment as above. The effect of the lignocellulosic component in the biomass towards its heating value will be discussed.

3.1 Content of the three components in MD2 pineapple waste

The proportion of three main components which is cellulose, hemicellulose and lignin also the extractives in the MD2 pineapple waste was identified. The result is given in Table 1.

Table 1: Content of extractives, hemicellulose, lignin and cellulose in MD2 pineapple waste (in wt%)

Nu.	Type	Extractives	Hemicellulose	Lignin	Cellulose
1.	Leaves	11	37	22	30
2.	Stem	9	34	20	37
3.	Root	7	32	19	42

The extractives, cellulose, hemicellulose and lignin in the pineapple waste observed based on the weight loss (%). Extractives are mainly a group of cell wall chemicals that contain fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acid, rosin, waxes and many other minor organic compounds. From the result, the leaves (11 wt%) have higher extractives compare to the stem (9 wt%) and root (7 wt%). The extractives are responsible towards colour, smell and durability of the biomass itself (Rowell, 2012). Hemicellulose of leaves (37 wt%) shows the highest content followed by the stem (34 wt%) and lastly root (32 wt%). Hemicellulose consists of several type of sugar unit and sometimes referred to by sugars they contain. Hemicellulose is associated with cellulose and contribute to the structural component of the plant (Rowell, 2012). Cellulose is a main structural component in a plant cell. From the result, root (42 wt%) claim the highest content of cellulose followed by the stem (37 wt%) and leaves (30 wt%). There are several types of cellulose in the plant: crystalline and noncrystalline, also accessible and non-accessible which is referred to the capability interact with water or microorganism and so on (Rowell, 2012). From the observation, it shows that the accessible cellulose content in the root is highest compared to the accessible cellulose in the stem and leaves. Lignins are highly cross-linked molecular complex with an amorphous structure and act as a glue between individual cells and between the fibrils that form the cell wall (Mohanty et al., 2000). Lignins can be defined in several ways but normally it is divided into their structural elements. For softwood lignin, it has a methoxyl content of 15 - 16 % and mainly is a polymerisation product of coniferyl alcohol and so-called guaiacol lignin (Rowell, 2012). From the data, leaves (22 wt%) showed the highest content of lignin followed by the stem (20 wt%) and root (19 wt%). The high lignins in leaves can increase the hardness of the compacted biomass product example biocoke due to its function as glue (binder). It also helps in increasing of stability biocoke product without fracture after the compaction.

3.2 Effect of three components towards heating value (HHV)

The cellulose, hemicellulose and lignin will give impact towards the capability of biomass to supply heat and to be heated. Most of the biomass consists cellulose, hemicellulose and lignin in their secondary cell wall as a structural compound (Pandey et al., 2015). The cellulose and hemicellulose exhibit different thermal stability due to inherent differences chemical structure even though they are polysaccharides (Pandey et al., 2015). The hydrogen bonds and van der Waal’s forces between glucose subunits of adjacent cellulose polymers causing the parallel aligned of multiple polymer chains (Pandey et al., 2015).

Cellulose polymers are aggregated into crystalline, fibrous structures known as microfibrils (Vanholme et al., 2013) to which cellulose owes its thermal stability (Pandey et al., 2015). Saha (2003) indicated that the hemicellulose is short and it branched of heteropolysaccharides that built up from various C5 (pentose, such as xylose and arabinose) and C6 (hexoses, such as glucose, galactose and mannose) sugars with some amount of uronic acids.

Hemicellulose is an amorphous and having lack of crystallinity that causing low thermal stability besides the low degree of polymerisation in the order of a few 100 (Pandey et al., 2015). Previous study showed that the hemicellulose is the first biomass constituent to decompose during heating by referring the TGA-DTG graph at temperature interval 200 °C and 300 °C. The decomposition of stable cellulose started at around 300 °C. Lignin is characterised as slow decomposition process, spanning over an entire temperature range between 120 °C and 900 °C (Mansor et al., 2018b).

From the data, all part of MD2 pineapple has high cellulose and hemicellulose content. The hemicellulose can indicate the ignition temperature and time to ignite of the biocoke product produce by MD2 pineapple waste. This is because the first pyrolysis process or burning process involved the removing of moisture content in the biomass followed by decomposition of hemicellulose content. Higher content of hemicellulose meaning that long time required for hemicellulose to decompose and at the same time increase capability of biocoke product to be burned. The high content of cellulose also can be as a measurement for how long the biocoke can burn before it becomes an ash. The continuity of lignin from start to end of the burning process can be an indicator that the biocoke product produces from MD2 pineapple waste can be last until 900 °C or above with some additional reactor or chemical that can enhance its thermal properties.

Table 2 showed the higher heating value of MD2 pineapple waste. (Demirbaş, 2001) in their research stated that the lignin content affects the heating value of biomass. From the lignin content value, the leaves showed the highest content followed by the stem and lastly the root. As compared with the HHV result, it proves that the lignin content contributes towards HHV value.

Table 2: Higher heating value (HHV) of MD2 pineapple waste (in wt%) (Mansor et al., 2018b)

Nu.	Type	HHV
1.	Leaves	18.7508
2.	Stem	18.0187
3.	Root	16.8266

4. Conclusion

The conclusion can be made that from the present study, the cellulose, hemicellulose and lignin content of the MD2 pineapple biomass including root, leaves and stem are in the range of the content main lignocellulosic component for softwood biomass. Based on the high cellulose, hemicellulose and lignin content, it will ensure the potential to become a feedstock for alternative solid biofuels in term of their heating value and long lifespan. The value of the lignocellulosic analysis is dependent on the sample collected from the similar field and might be slightly different with the previous studies and others biomass due to the other factors affecting for example during sample preparation and the conducting process of the analysis.

Acknowledgements

We would like to express our gratitude to the Malaysian Pineapple Industry Board (MPIB) for giving us the opportunity to obtain samples of MD2 pineapple and Universiti Teknologi Malaysia for a financial support under grant Optimal Design and Planning for Bio-refinery;Q.J130000.2446.03G62.

References

Bagby M., Nelson G., Helman E., Clark T., 1971, Determination of lignin in non-wood plant fiber sources, Tappi Journal, 54(11), 1876-1878.

Browning B.L., 1967, Methods of wood chemistry, Volumes I & II, John Wiley & Sons, Inc., New York, USA.

Demirbaş A., 2001, Relationships between lignin contents and heating values of biomass, Energy Conversion and Management, 42(2), 183-188.

Demirbas A., 2017, Higher heating values of lignin types from wood and non-wood lignocellulosic biomasses, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39(6), 592-598.

Di Blasi C., Signorelli G., Di Russo C., Rea G., 1999, Product distribution from pyrolysis of wood and agricultural residues, Industrial & Engineering Chemistry Research, 38(6), 2216-2224.

Dussan K.J., Silva D., Moraes E., Arruda P.V., Felipe M., 2014, Diluted-Acid Hydrolysis of Cellulose To Glucose from Sugarcane Bagasse, Chemical Engineering Transactions, 38, 433-438.

Hames B., Ruiz R., Scarlata C., Sluiter A., Sluiter J., Templeton D., 2004, Preparation of samples for compositional analysis biomass, Vol 1617, Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory, Colorado, USA.

Jin X., Chen X., Shi C., Li M., Guan Y., Yu C. Y., Peng J., 2017, Determination of hemicellulose, cellulose and lignin content using visible and near infrared spectroscopy in Miscanthus sinensis, Bioresource Technology, 241, 603-609.

Khedkar M.A., Nimbalkar P.R., Gaikwad S.G., Chavan P.V., Bankar S.B., 2017, Sustainable biobutanol production from pineapple waste by using Clostridium acetobutylicum B 527: drying kinetics study, Bioresource Technology, 225, 359-366.

Lin S.Y., Dence C.W., 2012, Methods in lignin chemistry, Springer-Verlag, New York, USA.

Mansor A.M., Theo W.L., Lim J.S., Ani F.N., Hashim H., Ho W.S., 2018a, Potential Commercialisation of Biocoke Production in Malaysia – A Best Evidence Review, Renewable and Sustainable Energy Reviews, 90, 636-649.

Mansor A.M., Theo W.L., Lim J.S., Ani F.N., Hashim H., Ho W.S., 2018b, Ultimate and Proximate Analysis of Malaysia Pineapple Biomass from MD2 Cultivar for Biofuel Application, Chemical Engineering Transactions, 63, 127-132.

McKendry P., 2002, Energy production from biomass (part 1): overview of biomass, Bioresource Technology, 83(1), 37-46.

Mohanty A., Misra M.A., Hinrichsen G., 2000, Biofibres, biodegradable polymers and biocomposites: an overview, Macromolecular materials and Engineering, 276(1), 1-24.

Pandey A., Bashkar T., Stocker M., Sukumaran R.K., 2015, Recent Advances in Thermomechanical Conversion of Biomass, Elsevier, Amsterdam, Netherlands.

Rowell R.M., 2012, Handbook of wood chemistry and wood composites, CRC press, Boca Raton, Florida, USA.

Rowell R.M., Pettersen R., Han J.S., Rowell J.S., Tshabalala M.A., 2005, Cell wall chemistry, Handbook of wood chemistry and wood composites, CRC Press, Florida, USA, 35-74.

Saha B.C., 2003, Hemicellulose bioconversion, Journal of Industrial Microbiology and Biotechnology, 30(5), 279-291.

Sarkanen K.V., Ludwig C.H., 1971, Liguins, Occurrence, formation, structure, and reactions, Wiley-Interscience, New York, USA.

Vanholme B., Desmet T., Ronsse F., Rabaey K., Van Breusegem F., De Mey M., Boerjan W., 2013, Towards a carbon-negative sustainable bio-based economy, Frontiers in plant Science, 4, 174.

Yang H., Yan R., Chen H., Zheng C., Lee D.H., Liang D.T., 2006, In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin, Energy & Fuels, 20(1), 388-393.

Zainuddin M.F., Shamsudin R., Mokhtar M.N., Ismail D., 2014, Physicochemical properties of pineapple plant waste fibers from the leaves and stems of different varieties, BioResources, 9(3), 5311-5324.