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EFFECT OF STORED OIL PALM TRUNK SAP TOWARDS METHYL ESTER SYNTHESIS

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ABSTRACT

Oil palm trunk (OPT) has highest content of sap, 80% of the overall weight. OPT sap contains free sugars which can be converted into valuable compounds such as ester. The objective of this study is to determine the changes of free sugars at different storage time and the effect on methyl ester synthesis. The sap was extracted and stored at different durations time (1, 7, 14, 21 and 28 days). 10ml of dried sap was added with 100mg $Fe_2(SO_4)_3$ EFB and 15ml of methanol. The mixture was put into the autoclave to be heated at 160 ^oC for 150 minutes. Free sugars found in OPT sap were glucose, fructose and sucrose. The free sugars vary upon the storage time and highest concentration of glucose and fructose achieved at day 21. This is due to hydrolysis of sucrose. The GC-MS analysis identified and quantified several methyl ester such as methyl pyruvate, methyl levulinate, methyl-9-oxononanoate and methyl palmitate. These findings confirmed that the free sugars from OPT sap were possible to be an alternative carbon in ester synthesis.

Keywords: *glucose; $Fe_2(SO_4)_3$; GC-MS; methanolysis; methyl levulinate; methyl-3-acetoxy-3-hydroxypropanoate; 5-hydroxymethylfurfural*

1. INTRODUCTION

In consideration of fossil resources depletion, many recent researches have focused on converting renewable biomass to fuels, polymer and resin (Hu et al., 2010). For example, polyester is widely use in structural composites, fabric and toner. Polyester shows a good tenacity and durability properties. However, the price for the raw materials are highly costly (Braunegg et al.; 2002). Every year, there is almost 8.6 million tonnes of oil palm trunk (OPT) waste were produced. OPT has an average productive life span between 25 to 30 years and need to replanted. Utilization of OPT is limited as it has low mechanical properties due to high water and sap content. Specifically, OPT sap is known to be rich in various metabolites especially free sugars which can be use as raw materials in synthesis applications.

Effect of using different alcohols as solvents in methyl ester synthesis has received increased attention. Different type of alcohols may have different availability to suppress humin formation, dark brown insoluble substance (Li et al., 2013) during synthesis reaction. Besides, the amount of solvent can affect the yield of synthesis as esterification is a reversible reaction. Low amount of solvent caused the reaction undergone dehydration reaction. Methanol is a

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good solvent for the products from cellulose with relatively high molecular weight as well as methylating agent in chemical reactions.

Nowadays, solid acid catalysts (SAC) become more demanding due to the unique combination of properties such as hydrothermal stability, well defined micro porosity and acidity (Nandiwale et al., 2013). $AlCl_3$ catalyst is effective in converting glucose to high selectivity for methyl levulinate under reasonably mild conditions (Yang et al., 2012). Zeolite also indicated a good catalyst in this reaction. However, the leaching of SAC may happened due to severe reaction system. SAC of $Fe_2(SO_4)_3$ EFB exhibited good catalytic activity because of the high density of $–SO_3H$ in the catalyst (Krishnan et al. 2016). The encapsulation of SAC with natural fiber such as empty fruit bunch (EFB) was used to overcome leaching.

In this paper, sap from OPT waste was extracted and stored at different duration time and the sap was continued with methyl ester synthesis with addition of $Fe_2(SO_4)_3$ EFB as catalyst. The identification and quantification of free sugars were analysed with HPLC and the synthesized methyl ester was analysed with GC-MS. The results of this study offer a new approach in methyl ester synthesis from biomass waste.

2. EXPERIMENTAL

2.1 Sample Preparation

The OPT sap was extracted with laboratory press machine. Then the extracted sap was filtered with Whatmann filter paper and stored at 10 ^oC at different storage time (1, 7, 14, 21 and 28 days) before continue to the next step.

2.2 Reaction of Methanolysis

The experiment was carried out in 30 mL cylindrical stainless steel autoclave. A mixture of water and methanol (1:1) was used as the reaction medium. For each experiment, 10ml of dried sap, 100mg $Fe_2(SO_4)_3$ EFB and 15ml of methanol: water was charged into the autoclave. The autoclave was heated in an oil bath at 160^oC for 150 min. After the reaction completed, the autoclave was quenched in an ice bath to terminate the reaction. Later, the sample was filtered and vacuumed concentrate to remove excess methanol and water. The fraction was collected for further analysis.

2.3 Analysis

Free sugars that contained in the stored sap was determined by HPLC with a ZORBAX carbohydrate capillary column (7.7 mm x 300mm, Agilent 1260) at 30^oC, equipped with a refractive index (RI) detector. The system was run with 1.4mL of acetonitrile:water (75%:25%) as mobile phase. The free sugars were identified by comparing their retention time with those of authentic standards under analytical conditions and quantified by the external standard method. Quantitative analysis of 5-hydroxymethylfurfural (5-HMF) compound was analyzed using HPLC using Hplex column (Agilent) and UV detector. 0.005M H_2SO_4 solution was used as the mobile phase at a flow rate of 0.6 ml/min, and the column temperature was maintained at 60^oC. The amount of ester and its derivatizations were determined by GC-MS with a dimension of length 30m x diameter 0.25mm x film thickness

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0.25 µm. The capillary column HP-INNO-Wax was used for analysis. 1µl of sample was injected into the injection sample port set at 250^{o}C. Using 3.0 ml/min helium as a carrier gas, the column as operated in a constant flow mode at temperature initially maintained at 40^{o}C for 3 min before increasing to 260^{o}C at a heating rate of 15^{o}C/min. Methyl levulinate was used as external standard. The data were analysed by the MSD Chemstation. A library search was carried out for all the peaks using the NIST/EPA/NIH version 2.0.

3. RESULTS AND DISCUSSION

3.1 Sugar Quantification

From the HPLC study, the dominant free sugar that identified in the OPT sap were glucose, fructose and sucrose (Figure 1). This finding is also compliment with Jung et al (2011). It was also found that the free sugars concentrations changed upon the storage time from day 1 to 28. For glucose and fructose, the highest concentrations found at day 21 of storage, which value of 26.04g/l and 6.99 g/l respectively. This is due to the hydrolysis of sucrose (disaccharide) to its monosaccharides prior to the storage effect. Up to 21 day of storage, these sugars concentration became less because of degradation happened (Eggleston & Vercellotti 2000). Consequently, the amount of sucrose decreased as the sap was further stored due to microorganism activity (Ogbulie et al., 2007) that presence naturally in the sap instead of degradation activity.

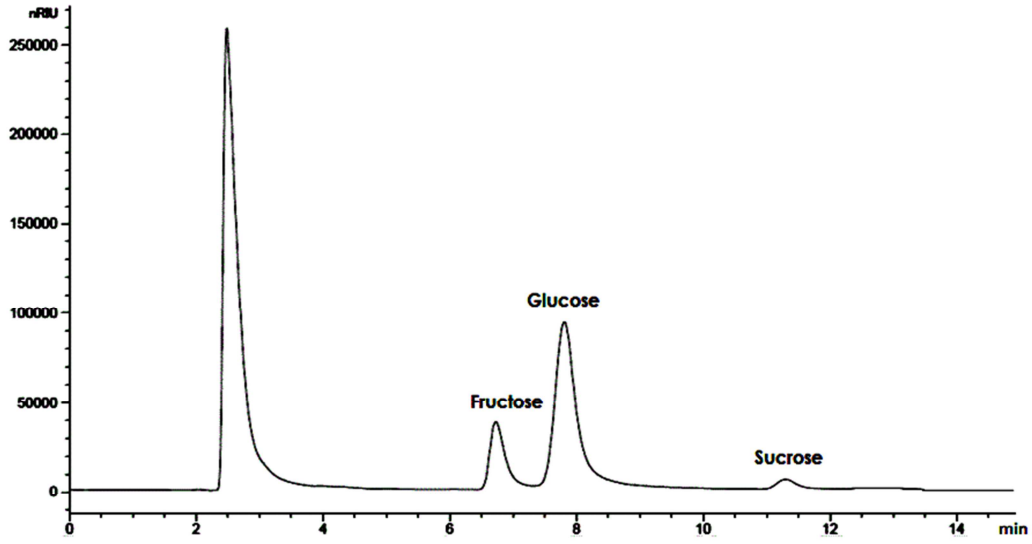

Figure 1: HPLC chromatogram of free sugar from OPT sap at day 21

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Table 1: Effect of storage time on the amount of glucose, fructose and sucrose in sap

Free Sugars	Concentration (g/L)				
	1 day	7 day	14 day	21 day	28 day
Glucose	25.29	24.18	22.63	26.04	24.25
Fructose	6.28	5.46	6.09	6.87	6.69
Sucrose	2.44	1.53	1.25	1.06	0.76

3.2 Synthesis of Methyl Ester

Effect of different free sugars concentrations on methanolysis were studied with GC-MS. From the reaction, there were several methyl esters produced such as methyl pyruvate, methyl levulinate, methyl-3-acetoxy-3-hydroxypropanoate, methyl-9-oxononanoate and methyl palmitate (Table 2). The highest ester compound found in all samples was methyl-3-acetoxy-3-hydroxypropanoate. This compound is often found in methanol extraction of biomass (Shi et al., 2015) and potential to be used further for biodegradable polyester synthesis. Methyl pyruvate was derived from the glycolysis. Methyl levulinate can be used as detergent and biodiesel. The results proved that the initial concentration of glucose, fructose and sucrose influenced the formation of difference ester compounds.

Table 2: Effect of different stored OPT sap on yield of methyl ester synthesis

	Yield (mol%)		
Compounds	1 day	14 day	28 day
Methyl pyruvate	0.82	0.85	0.83
Methyl levulinate	1.23	0.59	1.25
Methyl-3-acetoxy-3-hydroxypropanoate	54.41	38.42	55.12
Methyl-9-oxononanoate	2.09	-	2.12
Methyl palmitate	-	1.85	-

Other than methyl ester, 5-hydroxymethylfurfural (5-HMF) was also obtained in the methanolysis reaction. This is due to the dehydration of free sugars at high temperature. Methanolysis of day 14 sap, gave the highest yield of 5-HMF (55%) followed by 28 day (42%) and day 1 (39%). 5-HMF can serve as a platform chemical for liquid fuels, renewable polyesters (Peng et al., 2012) and inhibitor.

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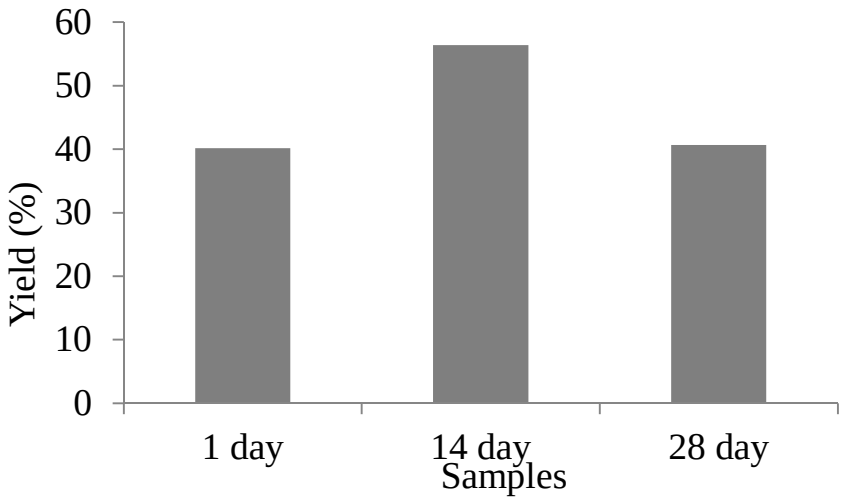

Figure 2: Yield of 5-HMF at different stored time of OPT sap

4. CONCLUSION

In conclusion, free sugars e.g. glucose, fructose and sucrose could be find in OPT sap in different concentrations. The storage time affect the amount of free sugars thus influence the methanolysis reaction of methyl ester synthesis. The type and amount of methyl pyruvate, methyl levulinate, methyl-3-acetoxy-3-hydroxypropanoate, methyl-9-oxononanoate and methyl palmitate varied depending on the initial free sugars concentrations. On the other hand, dehydration also happened during the methanolysis and caused the formation of 5-HMF.

5. ACKNOWLEDGEMENT

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REFERENCES

Braunegg, G., Bona, R., Schellauf, F., & Wallner, E. (2002). Polyhydroxyalkanoates (PHAs):sustainable biopolyester production. *Polymer*, 47,479-484.

Eggleston, G., & Vercellotti, J.R. (2000). Degradation of sucrose, glucose and fructose in concentrated aqueous solutions under constant pH conditions at elevated temperature. *Journal of Carbohydrate Chemistry*, 19, 1305-1318.

Hu, R., Lin, L., Liu, T. & Liu, S. (2010). Dilute sulfuric acid hydrolysis of sugar maple wood extract at atmospheric pressure. *Bioresource Technology*, 101, 3586-3594.

p-ISSN 1675-7939; e-ISSN 2289-4934
© 2017 Universiti Teknologi MARA Cawangan Pulau Pinang

Jung, Y. H., Kim, I. J. Kim, J. J., Oh, K. K. Han, J. I., Choi, I. G., & Kim, K. H. (2011). Ethanol production from oil palm trunks treated with aqueous ammonia and cellulase. *Bioresource Technology*, 102, 7307-7312.

Krishnan, S.G., Pua, F.L., Palanisamy, K., & Syed, S.N.S. (2016). Preparation of oil palm EFB derived solid acid catalyst for esterification reaction:effect of calcination temperature. *Key Engineering Materials*, 701, 117-121.

Li, H., Peng, L., Lin, L., Chen, K. & Zhang, H. (2013). Synthesis, isolation and characterization of methyl levulinate from cellulose catalyzed by extremely low concentration acid. *Journal of Energy Chemistry*, 22, 895-901.

Nandiwale, K. Y., Sonar, S. K., Niphadkar, P. S., Joshi, P. N., Deshpande, S. S., Patil, V. S & Bokade, V. V. (2013). Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst. *Applied Catalysis A: General*, 460, 90-98.

Ogbulie, T. E., Ogbulie, J. N. & Njoku, H. O. (2007). Comprative study on the microbiology and shelf life stability of palm wine from Elaeis guineensis and Raphia hookeri obtained from Okigwe, Nigeria. *African Journal of Biotechnology*, 6, 914-922.

Peng, L. C., Lin, L. & Li, H. (2012). Extremely low sulfuric acid catalyst system for synthesis of methyl levulinate from glucose. *Industrial Crops and Products*, 40, 136-144.

Shi, J., Li, F. F., Ma, H., Li, Z. Y. & Xu, J. Z. (2015). Efects of different dwarfing interstocks on key enzyme activities and the expression of genes related to mallic acid metabolism in red fuji apples. *Genetics and Molecular Research*, 14, 17673-17683.

Yang, Y., Hu, C. & Omar, M. M. A. (2012). Conversion of glucose into furans in the presence of AlCl3 in an ethanol–water solvent system. *Bioresource Technology*, 116, 190-194.

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