Direct Conversion of Glucose to 5-Hydroxymethylfurfural over $H_3PW_{12}O_{40}/TEOS$ Heterogeneous Catalyst

(Penukaran Terus Glukosa kepada 5-Hidroksimetilfurfural Menggunakan Mangkin Heterogen $H_3PW_{12}O_{40}/TEOS$)

Afeeq Asyraf^a, Siti Aishah Anuar^a, Wan Nor Roslam Wan Isahak^{a,b,*}

^aResearch Centre for Sustainable Process Technology,

^bChemical Engineering Programme,

Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia

ABSTRACT

5-Hydroxymethylfurfural (5-HMF) is a valuable bio-based intermediate designed from carbohydrate resources such as glucose (hexose) or fructose. In this work, direct conversion of glucose into 5-HMF was studied by analysing the activity of solid acid catalyst namely silica-supported phosphotungstic acid ($H_3PW_{12}O_{40}/TEOS$) as a heterogeneous catalyst. The reactions were conducted in a three-neck conical flask using dimethyl sulfoxide (DMSO) as reaction solvent under different reaction time (1, 3 and 5 hours) and temperature (100, 115 and 130°C). The effect of phosphotungstic acid loading was also studied in this literature (5, 12.5 and 20% $H_3PW_{12}O_{40}$). Thus, this paper aims to study the optimum reaction time, temperature and $H_3PW_{12}O_{40}$ loading to give the maximum yield of 5-HMF via direct catalytic dehydration process. The prepared catalyst 20% $H_3PW_{12}O_{40}/TEOS$ shows promising results by displaying a yield of 5-HMF as high as 62% after 3 hours at 130°C reaction temperature in the presence of DMSO solvent. Since heteropoly acid is highly soluble in DMSO, thus $H_3PW_{12}O_{40}$ supported in TEOS ($H_3PW_{12}O_{40}/TEOS$) is a promising solid catalyst for the conversion of glucose into 5-HMF. The prepared catalyst can also be recovered and recycled easily without significant loss of performance.

Keywords: 5-HMF; solid acid catalyst; supported silica catalyst; one step dehydration; selective conversion

ABSTRAK

5-Hidroksimetilfurfural (5-HMF) merupakan sumber-bio perantaraan yang terbentuk daripada karbohidrat seperti glukosa (heksosa) atau fruktosa. Dalam kajian ini, penukaran glukosa kepada 5-HMF dikaji melalui analisis aktiviti asid mangkin pepejal fosfotungstik asid berpenyokong ikatan silika berstruktur daripada TEOS ($H_3PW_{12}O_{40}/TEOS$). Tindak balas dijalankan di dalam sebuah kelalang berkepala tiga dengan menggunakan dimetil sulfoksida (DMSO) sebagai pelarut mengikut kadar perubahan masa (1, 3 dan 5 jam) dan suhu (100, 115 dan 130°C). Kesan penambahan fosfotungstik asid juga telah dikaji (5, 12.5 dan 20% $H_3PW_{12}O_{40}/TEOS$). Oleh itu, kajian ini dijalankan bagi mengkaji masa dan suhu tindak balas serta beban yang optimum untuk memberikan hasil maksimum 5-HMF melalui proses dehidrasi bermangkin. Sampel mangkin 20% $H_3PW_{12}O_{40}$ menunjukkan keputusan yang memberangsangkan dengan 62% hasil 5-HMF, selepas 3 jam tindak balas pada 130°C dengan kehadiran DMSO. Oleh kerana asid heteropoli sangat terlarut di dalam larutan DMSO, $H_3PW_{12}O_{40}$ berpenyokong TEOS ($H_3PW_{12}O_{40}/TEOS$) merupakan mangkin pepejal yang baik bagi penukaran glukosa kepada 5-HMF. Mangkin yang disediakan juga boleh dibaik pulih dan dikitar semula dengan mudah tanpa penurunan kadar tindak balas.

Kata kunci: 5-HMF; mangkin asid pepejal; bahan penyokong silika; pengdehidratan terus; penukaran terpilih

INTRODUCTION

The process of acid-catalyzed dehydration of dissimilar carbohydrates such as fructose, glucose, sucrose, cellulose or inulin are usually done in order to produce 5-Hydroxymethylfurfural (5-HMF). Although 5-HMF is popularly known as an intermediate element, it is yet produced in large industrial scale due to their high production cost. Luckily, glucose carbohydrate which is the most abundant and the cheapest monosaccharide are easily available although they give a low yield of 5-HMF, which is credited to their stable pyranoside ring glucose structure (Gomes et al. 2015).

Recently, biomass is treated as a way to substitute fossil fuel in the production of chemical substances. However people are currently focusing on the production of furan derivatives from biomass, a valuable platform chemical for the production of other series of chemicals. Thus, less development is directed towards the production of 5-HMF from biomass. If biomass can be utilized into 5-HMF, it can be the key intermediate in the development of biomass-based products such as organic acids, polymer precursors and also biofuels.

A catalyst is generally defined as a substance that can accelerate the rate of a chemical reaction to achieve balance

without having to undergo any change after the reaction. (de Souza et al. 2012, Gomes et al. 2017). Since the synthesis of 5-HMF is very complex and less stable depending on the reaction conditions, 5-HMF may be converted to levulinic

and formic acid during the dehydration process resulting in loss of yield. Thus, solid acid catalyst is used to lead a huge influence to the yield of 5-HMF during the dehydration of glucose carbohydrate.

FIGURE 1. Mechanism of dehydration of glucose to 5-HMF and its parallel reactions (Gomes et al. 2015)

In this study, the dehydration reaction was carried out in the presence of solid acid catalyst phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) supported on silica, which is derived from tetraethoxysilane (TEOS) and dimethylsulfoxide (DMSO) as a reaction solvent to further enhance the reaction. Heteropoly acid catalyst synthesis was first done before glucose dehydration reaction by producing heteropoly acid catalyst in different catalyst-to-support percentage ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$). DMSO was used as the reaction solvent since biphasic and organic media have higher advantages for 5-HMF production over aqueous medium. Among a lot of solvents used in the literature, compound with four carbon interaction have been identified to produce better yield of 5-HMF (Huang et al. 2014, Jimenez-Morales et al. 2014, Safri et al. 2017). In this study, DMSO showed similar results to solvents with four carbon by reducing the parallel reaction and oxidation possibility of 5-HMF in the same medium. However, the acid strength of the catalyst can also give a huge influence to the selectivity of 5-HMF. The use of heterogeneous catalysts require a longer residence time for glucose conversion, where it can increase the polymerization reaction of both substrates and products.

METHODOLOGY

SYNTHESIS OF THE CATALYST

According to Izumi et al. (2009), the catalyst can be produced through various methods. In this study, 0.72 g of water, 2.96 g of 1-butanol and 0.48 g of phosphotungstic acid was added into 8.3 g of tetraethyl orthosilicate (TEOS), before they were agitated at 80°C for 3 hours. The solution was stirred for another 1.5 hours before the dehydrated hydrogel form can be seen. The resulting sample was dried at 100°C for 3 hours in an oven and labeled as 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$. The experiment was then repeated with different reaction time and catalyst to support loading to produce 5% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ and 12.5% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ as in Table 2.

TABLE 1. Mass percentage for the synthesis of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$

Solution	$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$		
	5%	12.5%	20%
Water	0.72 g	0.72 g	0.72 g
1-butanol	2.96 g	2.96 g	2.96 g
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	0.12 g	0.48 g	0.48 g
TEOS	8.3 g	8.3 g	8.3 g

DEHYDRATION OF GLUCOSE TO 5-HMF

All dehydration reaction experiments were conducted in a 1 liter round bottom flask equipped with a magnetic stirrer and condenser. A usual step of glucose dehydration process were done as follows, a solution of glucose (3 g), solid acid catalyst (0.3 g) and DMSO (30 g, 27.7 mL) were channeled into a round bottom flask. Under stirring, the flask was heated to variable temperature (100°C, 115°C and 130°C) and time (1 h, 3 h and 5 h) in nitrogenous atmosphere. The products yielded after dehydration reaction of glucose was filtered for the remaining catalyst to obtain the desired 5-HMF liquid.

CATALYST AND PRODUCT ANALYSIS

The catalytic sample $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ obtained was analyzed by using Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) methods. The desired 5-HMF liquid was analysed with FTIR and high-performance liquid chromatography (HPLC) in a Agilent 1100 Series system, equipped with ultra violet (UV) and refractive index (RID) detectors and a Jones Chromatography Genesis C18 column, using 20 mM H_2SO_4 and 5% acetonitrile as the mobile phase. The column temperature was maintained at 40°C.

RESULTS AND DISCUSSION

FTIR ANALYSIS OF CATALYST

The typical FTIR spectrum of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ achieved at 1100 cm^{-1} with bonding of Si-O-Si, 968 cm^{-1} bonding of W-O_4 terminal, W-O_b -W edge shared at 903 cm^{-1} and $(\text{W-O}_c\text{-W})$ corner shared at 719 cm^{-1} related to the primary structure $(\text{PW}_{12}\text{O}_{40})^{4-}$ of the catalyst as shown in Figure 1. As seen in 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ catalyst spectrum, the Si-O-Si bond spotted at 1100 cm^{-1} has bigger and wider peak than others catalyst. It obviously showed the bend of Si-O-Si with higher composition in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ affected Si and O from TEOS was chemically bonded with each other (Isahak et al. 2011).

FIGURE 2. FTIR spectrum of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ catalyst

CATALYSTS CRYSTALLINITY BY XRD

According to the XRD analysis, the presence of silica compound gave the amorphous state of the catalyst that is produced by sol-gel technique. From XRD pattern in Figure 3, a broader peak displayed at diffraction peak around 28° has represented the Si-O-Si bond as the major component in $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ catalyst while the element of tungsten can be obtained at diffraction angle of 41° and 54° (Firoozi et al. 2014). Since the intensity of silica is higher than tungsten in the spectrum, it can be concluded that the sample is mainly in amorphous state.

FTIR ANALYSIS OF 5-HMF

Figure 3 below clearly demonstrated the almost similar shape of FTIR spectrum for all samples of 5-HMF regardless of the catalyst to support loading. The major analysis excluded on the bonding of conjugate ketone ($\text{C}=\text{O}$) bond which has the physical characteristic of the molecular structure of 5-HMF.

Among the 5-HMF spectrum, sample 1, 11 and 13 have been selected as the best sample for this analysis due to their highest peak of $\text{C}=\text{O}$ bond detected at 1662.5 cm^{-1} , which is bigger and wider than other samples. It was indicated that the higher composition of $\text{C}=\text{O}$ bond was due to reaction of C and O molecules in glucose (Nybacka 2016).

FIGURE 3. XRD diffractogram of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$

FIGURE 4. FTIR spectrum of 5-HMF

CATALYTIC TESTS OF GLUCOSE DEHYDRATION

Performance of dehydration reaction of glucose into 5-HMF by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ catalysts was evaluated in dimethyl sulfoxide (DMSO) as an aprotic solvent. According to the literature by Shimizu et al. (2009) and van Putten et al. (2013), DMSO is a good solvent that would defeat unwanted side reactions in hexose dehydration. However, for the formation of 5-HMF, the main byproducts reported in hexose dehydration are humins, soluble polymers, furfural, levulinic acid and formic acids, where these compounds are products from a few of reaction which is cross-polymerization, condensation and rehydration reactions.

The use of 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ catalyst has resulted in maximum yield of 62% 5-HMF with reaction time and temperature of 3 hours and 130°C . This result is comparable to Fan et al. (2011) who used heteropolyacid catalyst $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ which results in 5-HMF yield of 70-78% with water/MIBK biphasic solvent system at 120°C in 60-120 min. The yield is also identified to be effected by initial feedstock concentration and temperature. This is proven though Figure 5(a) and 5(b), where dehydration yield is directly proportional to catalyst ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) loading and dehydration temperature. The sample with 20 % catalyst loading perform better than other sample. For reacting temperature, it was observed that the yield was the highest at 130°C reacting temperature, regardless of catalyst loading. From the relationship of temperature and 5-HMF yield, we can also see the significant effect of time where 3 h is the optimum dehydration time for all sample.

Based on overall experiment data, it is difficult to confirms the effect of 5-HMF yield changes unless it is at

the optimum reaction time and temperature. Furthermore, the increase in temperature gives less obvious impression on the 5-HMF results (van Der Vis et al. 1993, Tong et al. 2011, Tao et al. 2014, Toftgaard et al. 2015). Therefore we prepare Figure 5(c) to prove that the effect of temperature and time was only significant at their optimum state which is at 103°C and 3 h. Given the optimum temperature as seen in figure, the yield of 5-HMF was perpendicular to the time regardless of catalyst loading, however until at 3h. Beyond that, the yield decreases. According to Kuster et al., 5-HMF formation increases with increasing enolization levels as well as increased levels of acyclic and fructose furanose forms at higher temperatures, which it may be disclosed that rising temperatures play a positive role to 5-HMF results. However, this attention is only used in case of less than 10 min of follow-up. After 20 min, there is almost no change to apply to 5-HMF results with rising temperatures. Therefore, it can be concluded that 5-HMF yield is directly proportional to the function of optimum time and temperature.

Previous studies also concluded the maximum yield of 5-HMF obtained at the optimum condition was 62% at 130°C for 3 hours (Tahvildari et al. 2011, Wang et al. 2014, Su et al. 2016). Meanwhile, Zhao et al. (2009) figured out about the effect of reaction time, aqueous to organic solvents ratio and catalyst loading. They concluded that higher yields can be obtained at longer reaction time, greater amounts of DMSO and lower catalyst loadings.

TABLE 2. Result of glucose dehydration in DMSO under different reaction conditions

Sample	H ₃ PW ₁₂ O ₄₀ /TEOS (wt.%)	Temperature (°C)	Time (h)	Yield of 5-HMF (%)
1	12.50	100	1	2.0
2	20.00	115	1	2.7
3	5.00	115	1	5.0
4	12.50	130	1	24.0
5	20.00	130	3	62.0
6	5.00	130	3	1.3
7	12.50	115	3	7.2
8	12.50	115	3	0.2
9	20.00	100	3	6.8
10	5.00	100	3	2.1
11	12.50	115	3	10.1
12	12.50	130	5	3.5
13	20.00	115	5	1.9

As shown in Figure 5, the reaction temperature plays an important role on the outcome of 5-HMF. At higher reaction temperature, the 5-HMF also have increased rate of reaction as well as 5-HMF yield. 5-HMF yield increase from 6.8% at 100°C to 62% at 130°C after 3 hours of reaction. Shimizu et al. was reported the removal of water is a mild evacuation suppresses into two side reactions which are the hydrolysis of 5-HMF to levulinic acid and the partially reaction of dehydrated intermediates to condensation products. The effect of phosphotungstic acid (PA) content also showed a significant improvement of the catalytic performance where

5% PA content only gives 5% of 5-HMF, but when PA content increases to 20%, it gives higher product yield of 62%. For the effect of reaction time, the highest yield of 5-HMF was obtained at 3 hours of reaction, however the yield decrease into 3.5% after 5 h reaction time. It was noted that excessive reaction time promoted the decomposition of 5-HMF into smaller molecules such as formic acid and levulinic acid which subsequently decrease the yield of 5-HMF (Pagan-Torres et al. 2012; Rosatella et al. 2011).

FIGURE 5. Effect of parameters on highest 5-HMF yield, (a) phosphotungstic acid loading, L (wt.%), (b) dehydration temperature, T (°C) at 3 h and (c) dehydration time, t (h)

POSSIBLE MECHANISTIC CONSIDERATION

Normally, the mechanism reaction was more a cyclic cycle of dehydration of fructose. Figure 6 explains the molecular mass of 145 gmol⁻¹ was the result of dehydration of fructose, which is a molecule (4R, 5R) -4-hydroxy-5-hydroxymethyl-4

or 5-dihydrofuran-2-carbaldehyde known as intermediates for the dehydration of fructose to 5-HMF in a solvent DMSO (Yue et al. 2016). The molecular mass of 163 gmol^{-1} showed that it was the product dehydrogenated of compound 1, namely 2,5-anhydro-hexose involved in the dehydration of fructose (Yan et al. 2009; Yue et al. 2014). This dehydrogenated product is a byproduct related to the stoichiometric oxidation of the alcohol group of tungsten oxide catalyst into the by-product dehydrogenated stable and sturdy. 5-HMF can be obtained where the presence of two compounds with a molecular masses of 145 gmol^{-1} (compound 2) and 163 gmol^{-1} (compound 3) shows the unconverted sugar as monomer and oligomer. Figure 7 shows the reaction scheme of intermediates in the dehydration of glucose to 5-HMF.

FIGURE 6. LC-MS spectrum of molecular mass for intermediate compounds and the target product of 5-HMF

FIGURE 7. Reaction scheme of intermediates in the dehydration of glucose to 5-HMF (Yue et al. 2016)

CONCLUSION

Conversion of carbohydrates-rich biomass into chemicals that may be used as direct substitutes for non-renewable source compounds was done. The study evaluated the synthesis of 5-HMF (5-Hydroxymethylfurfural) by dehydration of glucose in the presence of aprotic solvent, DMSO. The prepared sample 20% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TEOS}$ gives the highest yield of 5-HMF production (62% of 5-HMF yield at 130°C in 3 h). The synthesized solid acid catalyst, set by sol-gel procedures also displayed good physical and catalytic properties, since the heteropoly acid has turned into insoluble compound by substituting a fraction of their proton apart from being supported on TEOS.

ACKNOWLEDGEMENT

The authors wish to thank Universiti Kebangsaan Malaysia (UKM) and Ministry of Higher Education of Malaysia for funding this project under research grant, DIP-2016-010 and GUP-2016-057, respectively. The authors also wish to thank the Centre of Research and Innovation Management (CRIM), UKM for the use of their instrumentation.

REFERENCES

- Fan, C., Guan, H., Zhang, H., Wang, J., Wang, S. & Wang, X. 2011. Conversion of fructose and glucose into 5-hydroxymethylfurfural catalyzed by a solid heteropolyacid salt. *Biomass Bioenergy* 35: 2659-2665.
- Firoozi, A.A., Taha, M.R., Firoozi, A.A. & Khan, T.A. 2014. Evaluation of physical properties of clays mixed with silica sand. *Jurnal Kejuruteraan* 26: 77-81.
- De Souza, R. L., Yu, H., Rataboul, F. & Essayem, N. 2012. 5-Hydroxymethylfurfural (5-HMF) production from hexoses: limits of heterogeneous catalysis in hydrothermal conditions and potential of concentrated aqueous organic acids as reactive solvent system. *Challenges* 3: 212-232.
- Gomes, F. N. D. C., Mendes, F. M. T. & Souza, M. M. V. 2017. Synthesis of 5-hydroxymethylfurfural from fructose catalyzed by phosphotungstic acid. *Catalysis Today* 279: 296-304.
- Gomes, F. N. D. C., Pereira, L. R., Ribeiro, N. F. P. & Souza, M. M. V. 2015. Production of 5-Hydroxymethylfurfural (HMF) via fructose dehydration: effect of solvent and salting-out. *Brazilian Journal of Chemical Engineering* 32(1): 119-126.
- Hsu, Y., Hsu, Y., Hsu, H. & Yang, C. 2007. Facile synthesis of mesoporous silica SBA-15 with additional intra-particle porosities. *Chemistry of Materials* 28: 1120-1126.
- Huang, H., Denard, C. A., Alamillo, R., Crisci, A. J., Miao, Y., Dumesic, J. A., Scott, S. L. & Zhao, H. 2014. Tandem catalytic conversion of glucose to 5-Hydroxymethylfurfural with an immobilized enzyme and a solid acid. *ACS Catalysis* 4: 2165-2168.
- Isahak, W. N. R. W., Ismail, M., Nordin, N. M., Jahim, J. M. & Yarmo, M. A. 2011. Synthesis, characterization and catalytic performance of $\text{H}_3\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ prepared by sol-gel technique. *Journal of Nanotechnology*, 1-6.
- Jimenez-Morales, I., Teckchandani-Ortiz, A., Santamaria-Gonzalez, J., Maireles-Torres, P. & Jimenez-Lopez, A. 2014. Selective dehydration of glucose to 5-hydroxymethylfurfural on acidic mesoporous tantalum phosphate. *Applied Catalysis B, Environmental* 144: 22-28.
- Kuster, B.F.M. 1990. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch* 42: 314-321.
- Nybacka, L. 2016. FTIR spectroscopy of glucose. Uppsala Universitet, Sweden.

- Pagán-Torres, Y. J., Wang, T., Gallo, J. M. R., Shanks, B. H. & Dumesic, J. A. 2012. Production of 5-hydroxymethylfurfural from glucose using a combination of lewis and bronsted acid catalysts in water in a biphasic reactor with an alkylphenol solvent. *ACS Catalysis* 2(6): 930-934.
- Rosatella, A. A., Simeonov, S. P., Frade, R. F. M. & Afonso, C. A. M. 2011. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chemistry* 13(4): 754-793.
- Safri, N.A., Jalil, R. & Kalil, M.S. 2017. Fermentable sugars from agrowastes using cellulase enzymes from local white rot fungi *pycnoporus sanguineus*. *Jurnal Kejuruteraan* 29: 105-111.
- Shimizu, K.I., Uozumi, R. & Satsuma, A. 2009. Enhanced production of hydroxymethylfurfural from fructose with solid acid catalysts by simple water removal methods. *Catalysis Communications* 10: 1849-1853.
- Su, Y., Chang, G., Zhang, Z., Xing, H., Su, B., Yang, Q., Ren, Q., Yang, Y. & Bao, Z. 2016. Catalytic dehydration of glucose to 5-hydroxymethylfurfural with a bifunctional metal-organic framework. *AIChE Journal* 62: 4403-4417.
- Tahvildari, K., Taghvaei, S. & Nozari, M. 2011. The study of hydroxymethylfurfural as a basic reagent for liquid alkanes fuel manufacture from agricultural wastes. *International Journal of Chemical & Environmental Engineering* 2: 1-7.
- Tao, F., Zhuang, C., Cui, Y. & Xu, J. 2014. Dehydration of glucose into 5-hydroxymethylfurfural in SO_3H -functionalized ionic liquids. *Chinese Chemical Letters*, 25: 757-761.
- Toftgaard, A., Ringborg, R., Grotkjær, T., Pedersen, S. & Woodley, J. M. 2015. Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose – fructose mixtures. *Chemical Engineering Journal* 273: 455-464.
- Tong, X., Li, M., Yan, N., Ma, Y., Dyson, P. J. & Li, Y. 2011. Defunctionalization of fructose and sucrose: Iron-catalyzed production of 5-hydroxymethylfurfural from fructose and sucrose. *Catalysis Today*, 175(1): 524-527.
- Van Der Vis, M. G. M., Cordfunke, E. H. P. & Konings, R. J. M. 1993. The thermodynamic properties of tetraethoxysilane (TEOS) and an infrared study of its thermal decomposition. *Le Journal de Physique IV* 3(C3): C3-75-C3-82.
- Van Putten, R. J., Soetedjo, J. N., Pidko, E. A., van der Waal, J. C., Hensen, E. J., de Jong, E. & Heeres, H. J. 2013. Dehydration of different ketoses and aldoses to 5-hydroxymethylfurfural. *ChemSusChem* 6: 1681-1687.
- Wang, T. 2014. Catalytic conversion of glucose to 5-hydroxymethylfurfural as a potential biorenewable platform chemical. PhD Thesis, Iowa State University, USA.
- Yan, H., Yang, Y., Tong, D., Xiang, X. & Hu, C. 2009. Catalytic conversion of glucose to 5-hydroxymethylfurfural over $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ solid acid catalysts. *Catalysis Communications* 10: 1558-1563.
- Yue, C., Rigutto, M. S. & Hensen, E. J. M. 2014. Glucose dehydration to 5-hydroxymethylfurfural by a combination of a basic zirconosilicate and a solid acid. *Catalysis Letters* 144: 2121-2128.
- Yue, C., Li, G., Pidko, E.A., Wiesfeld, J.J., Rigutto, M. & Hensen, E.J.M. 2016. Dehydration of Glucose to 5-Hydroxymethylfurfural using Nb-doped Tungstite. *ChemSusChem* 9: 2421-2429.
- Zhao, X., Peng, F., Cheng, K. & Liu, D. 2009. Enhancement of the enzymatic digestibility of sugarcane bagasse by alkali-peracetic acid pretreatment. *Enzyme and Microbial Technology* 44: 17-23.

*Afeeq Asyraf
Chemical Engineering Programme,
Faculty of Engineering & Built Environment,
Universiti Kebangsaan Malaysia, Malaysia.

*Wan Nor Roslam Wan Isahak
Chemical Engineering Programme,
Research Center for Sustainable Process and Technology,
Faculty of Engineering & Built Environment,
Universiti Kebangsaan Malaysia, Malaysia.

*Corresponding author;
email: wannorroslam@ukm.edu.my

Received date: 19th April 2018
Accepted date: 23rd July 2018
Online First date: 1st October 2018
Published date: 30th November 2018