

REFERENCES

- Aida, T.M., Tajima, K., Watanabe, M., Saito, Y., Kuroda, K., Nonaka, T., Hattori, H., Smith, R.L., Arai, K. Reactions of d-fructose in water at temperatures up to 400 C and pressures up to 100 MPa. *J. of Supercritical Fluids* 42(2007):110–119
- Albrecht, T. Conversion of Lignocellulosic Material and Model Compounds in Sub- and Supercritical Water. Shaker Verlag. Aachen (2007)
- Ananda, S.A., LaToya, D.W., Chidinma, C.E. Mechanism of the dehydration of D-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 °C: an NMR study. *Carbohydrate Research* 343 (2008):3021–3024
- Ando, H., Sakaki T., Kokusho, T., Shibata, M., Uemura, Y., and Hatate, Y. Decomposition Behavior of Plant Biomass in Hot-Compressed Water. *Ind Eng Chem Res.* 39 (2000):3688-3693
- Antal, M. J., Mok, W. S. L.; Richards, G. N. Kinetic studies of reactions of ketoses and aldoses in water at high temperature. 1. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose, *Carbohydrate Research* 199 (1990):91.
- Asghari, F.S., Yoshida, H. Acid-catalyzed production of 5-hydroxymethylfurfural from D-fructose in subcritical water. *Ind. Eng. Chem. Res.* 45 (2006):2163-2173
- Barrett C.J., Chheda J.N., Huber G.W., Dumesic J.A., Single-reactor process for sequential aldol-condensation and hydrogenation of biomass-derived compounds in water. *Environmental* 66 (2006):111–118.
- Bicker, M., Kaiser, D., Ott, L., Vogel, H., Dehydration of d-fructose to hydroxymethylfurfural in sub- and supercritical fluids, *J. of Supercritical Fluids* 36 (2005) :118–126
- Chareonlimkul, A., Champreda, V., Shotipruk, A., Laosiripojana, N. Reactions of C₅ and C₆ -sugars, cellulose, and lignocellulose under hot compressed water (HCW) in the presence of heterogeneous acid catalysts. *Fuel* xxx(2012a)xxx
- Chareonlimkul, A., Champreda, V., Shotipruk, A., Laosiripojana, N. Catalytic conversion of sugarcane bagasse, rice husk and corncob in the presence of TiO₂, ZrO₂ and mixed-oxide TiO₂-ZrO₂ under hot compressed water (HCW) condition. *Bioresource Technology* 101(2010b): 4179-4186
- Chernik, S., Bridgwater, A.V. Overview of Applications of biomass Fast Pyrolysis Oil, *Energy and Fuels* 18(2004):590-598

- Chheda, J.N., Dumesic, J.A. An overview of dehydration, aldol-condensation and hydrogenation processes for production of liquid alkanes from biomass-derived carbohydrates. *Catalysis Today* 123 (2007):59-70
- Cottier, L.; Descotes, G. Trend. Heterocycl. 5-Hydroxymethylfurfural, syntheses and chemical transformations, *Chem.* 2 (1991): 233-248
- Dry, M.E. High quality diesel via the FS process - a review, *Journal of Chemical Technology and Biotechnology*, 77(2001):43-50.
- Huber, G.W., Chheda, J.N., Barrett, C.J., Dumesic, J.A. Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates, *Science* 308 (2005):1446-1449.
- Lewkowski, J. Synthesis Chemistry and Applications of 5-Hydroxymethyl-furfural And Its Derivatives, Department of Organic Chemistry, *University of POLAND*:17-54.
- Qi, X, Watanabe, M., Aida, T.M., Richard, L., Smith, Jr., Sulfated zirconia as a solid acid catalyst for the dehydration of fructose to 5-hydroxymethylfurfural Catalysis, *Communications* 10 (2009):1771–1775.
- Kabyemela, B. M.; Adschiri, T.; Malaluan, R. M.; Arai, K. Glucose and fructose decomposition in subcritical and supercritical water: Detailed reaction pathway, mechanisms, and kinetics, *Ind. Eng. Chem. Res.*38 (1999):2888.
- Kruse, A., Dinjus, E. Hotcompresses water as reaction medium and reactant: properties and synthesis reaction, *Journal of Supercritical Fluids* 62 (2006) :46-55.
- Lichtenthaler, F.W., Ronninger, S. α -o-Glucopyranosyl-D-f ructoses: Distribution of Furanoid and Pyranoid Tautomers in Water, Dimethyl Sulphoxide, and Pyridine. Studies on Ketoses, *Organische Chemie, Technische Hochschule Darmstadt, Petersenstrabe* 22 (1999) :1489-1497.
- Moreau, C., Finiels, A., Vanoye, L. Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst, *Journal of Molecular Catalysis A: Chemical* 253 (2006):165–169.
- Qi, X., Watanabe, M., Aida, T.M., Smith, R.L. Selective Conversion of D-Fructose to 5-Hydroxymethylfurfural by Ion-Exchange Resin in Acetone/Dimethyl sulfoxide Solvent Mixtures. *Ind. Eng. Chem. Res.* 47 (2008):9234–9239.
- Qi, X., Watanabe, M., Taku, M. Aidaa and Richard Lee Smith, Jr. Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating, *Green Chem.*10 (2008):799–805.

- Richard, M. Musau and Raphael M. Munavu., The Preparation of 5-Hydroxymethyl-2-Furaldehyde (HMF) from D-Fructose in the Presence of DMSO. *Biomass* 13(1987):67-74
- Roman-Leshkov, Y., Chheda, J.N. Dumesic, J.A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* 312(2006):1933-1938.
- Sievers, C., Mariefel, B. Olarte, V., Marzialetti, T., Musin, I., Agrawal, P.K., and Jones, C.W. Ionic-Liquid-Phase Hydrolysis of Pine Wood. *Ind. Eng. Chem. Res.* 48 (2009) :1277–1286.
- Srinorakutara, T., Suesat, C., Pitiyont, B., Kitpreechavanit, W., Cattithammanit, S. Utilization of Waste from Cassava Starch Plant for Ethanol Production. The Joint International Conference on “Sustainable Energy and Environment (SEE)” 1-3 December 2004, Hua Hin, Thailand
- Sriroth, K., Chollakup, R., Chotineerarat, S., Piyachomkwan, K., Oates, CG., Processing of cassava waste for improved biomass utilization. *Bioresource Technology* 71(2000): 63-69
- Su, Y., Brown, H.M., Huang, X., Zhou, X.d, Amonette, J.E., Zhang, Z.C. Single-Step Conversion of Cellulose to 5-Hydroxymethylfurfural (HMF), a Versatile Platform Chemical Pacific, *Northwest National Laboratory Institute for Interfacial Catalysis*, P. O. Box 999, Richland, WA 99352.
- Vessia, Q. Biofuels from lignocellulosic material, NTNU, *Norwegian University of Science and Technology Faculty of information technology, mathematics and electrical engineering Department of electrical engineering* (2005)
- Watanabe, M., Aizawa, Y., Iida, T., Aida, T.M., Levy, C., Sue, K., and Inomata, H. Glucose reactions with acid and base catalysts in hot compressed water at 473 K. *Carbohydrate Research* 340 (2005a):1925–1930.
- Watanabe, M., Aizawa, Y., Iida, T., Levy, C., Taku, M. Aida and Inomata H. Glucose reactions within the heating period and the effect of heating rate on the reactions in hot compressed water. *Carbohydrate Research* 340 (2005b): 1931–1939
- Watanabe, M., Aizawa, Y., Iida, T., Nishimura, R., Inomata, H. Catalytic glucose and fructose conversions with TiO₂ and ZrO₂ in water at 473 K: Relationship between reactivity and acid–base property determined by TPD measurement. *Applied Catalysis A: General* 295 (2005):150–156.
- Yoshida, T., Yanachi, S., Matsumaru, Y., Glucose Decomposition in Water under Supercritical Pressure at 448-498 K. *J.Jpn.Inst Energy* 86(2007): 700-707

APPENDICES

APPENDIX A

EXPERIMENTAL DATA FOR ANALYSIS

A-1 Standard calibration curve for HPLC analysis of HMF and furfural

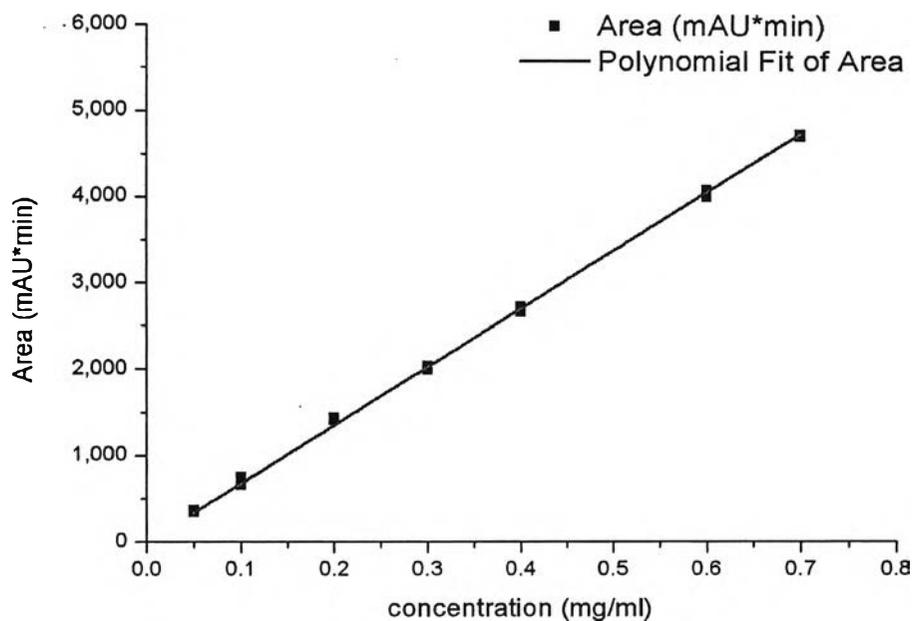


Figure A-1.1 Standard curve of HMF

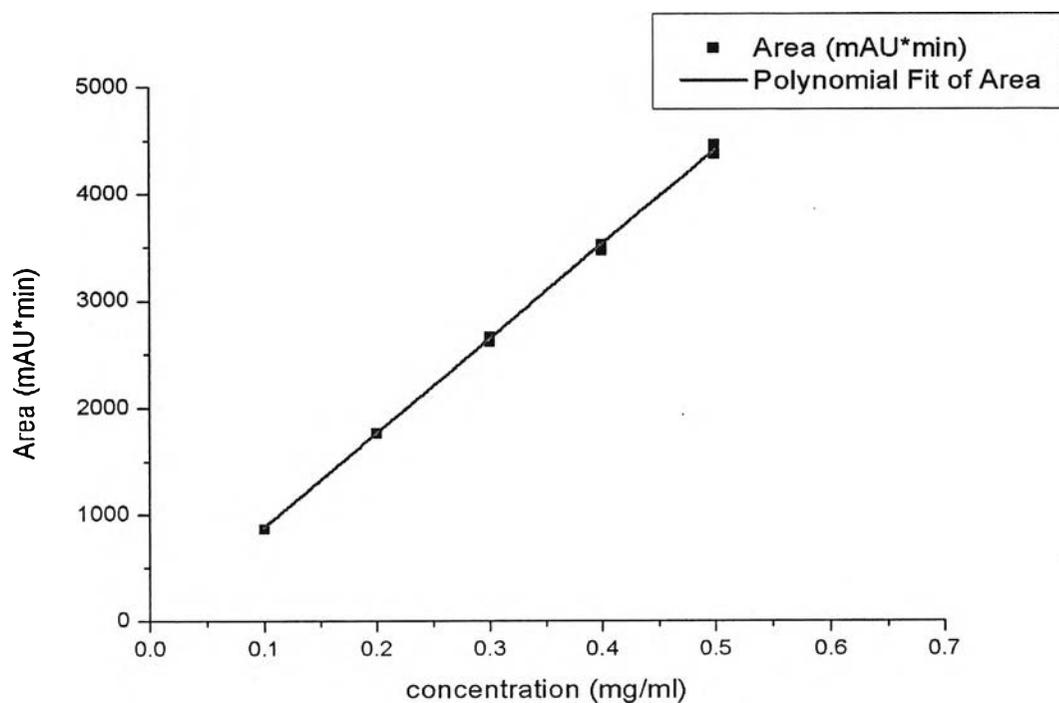


Figure A 1.2 Standard curve of furfural

A-2 Standard calibration curve for HPLC analysis of glucose fructose xylose and AHG

Table A-2.1 Standard calibration curve data for glucose

Peak area (UV detector at 270 nm)	Concentration of glucose (mg/ml)
109	0.1
508	0.3
987	0.5
1570	0.7
2128	1.0

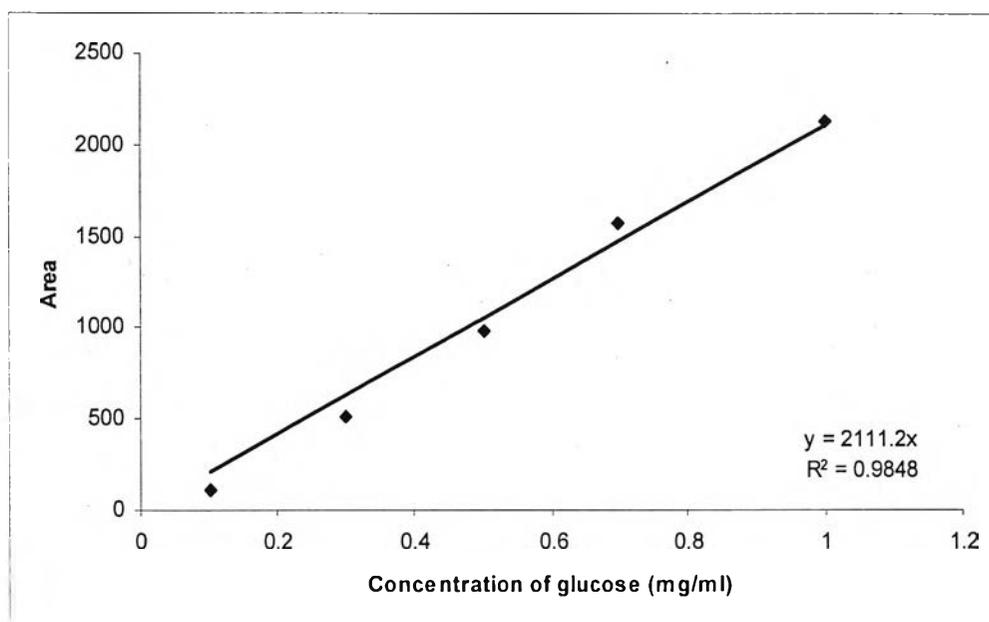


Figure A 2.1 Standard curve of glucose

Table A-2.2 Standard calibration curve data for fructose

Peak area (UV detector at 270 nm)	Concentration of fructose (mg/ml)
83.36	0.1
457.332	0.3
945.716	0.5
1457.735	0.7
2212.2	1.0

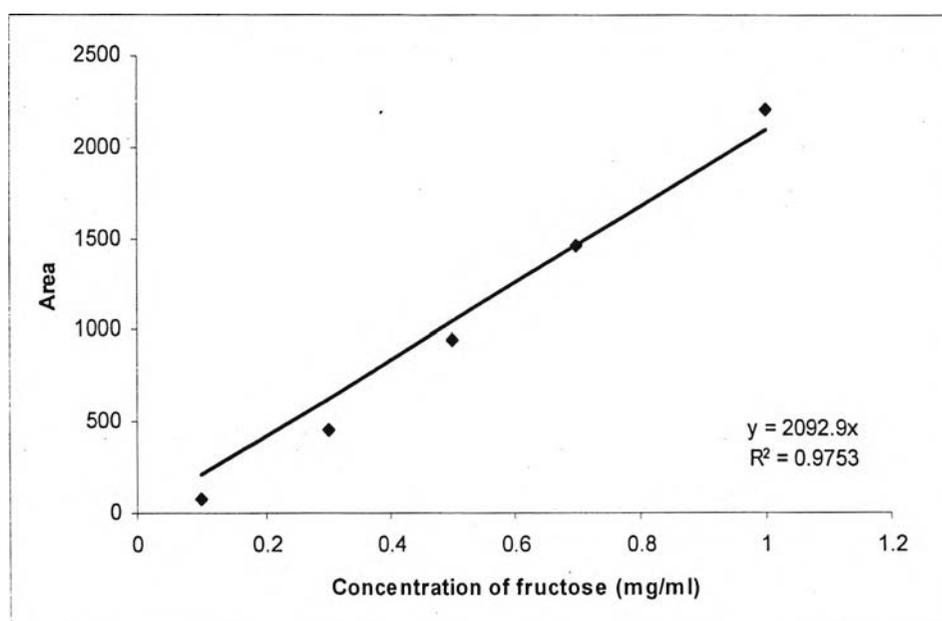
**Figure A 2.2** Standard curve of fructose

Table A-2.3 Standard calibration curve data for xylose

Peak area (UV detector at 270 nm)	Concentration of xylose (mg/ml)
89.177	0.1
231.71	0.3
411.40	0.5
668.51	0.7
1001.57	1.0

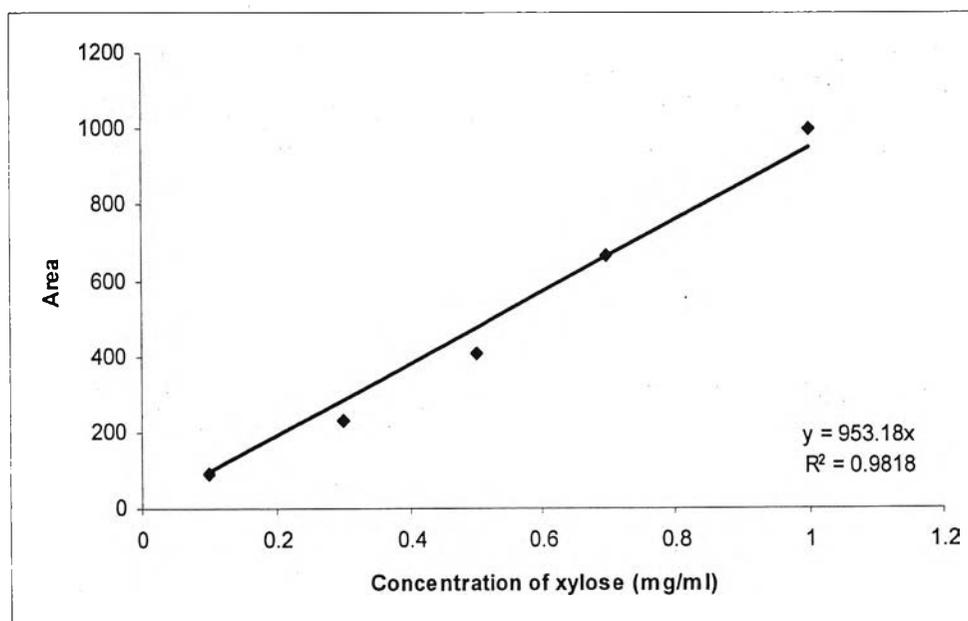
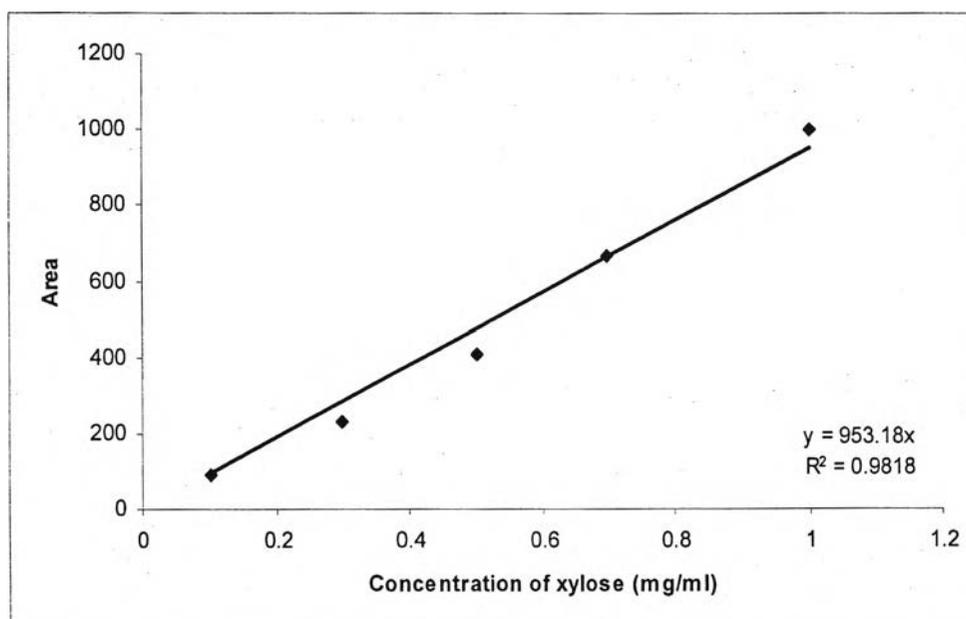
**Figure A 2.2** Standard curve of xylose

Table A-2.3 Standard calibration curve data for 1,6 anhydroglucose (AHG)

Peak area	Concentration of AHG (mg/ml)
89.177	0.1
231.71	0.3
411.40	0.5
668.51	0.7
1001.57	1.0

**Figure A 2.2** Standard curve of xylose

APPENDIX B

EXPERIMENTAL DATA

B-1 Calculation of %conversion and concentration of 1,3-PDO and 2-MD

$$\text{Product yield (\%)} = \frac{\text{gram of HMF or furfural in product} \times 100}{\text{gram of feedstock}}$$

$$\text{Conversion of sugar (\%)} = \frac{(\text{initial sugar mass} - \text{last sugar mass}) \times 100}{\text{initial sugar mass}}$$

B-2 Experimental data of HMF and furfural from biomass.

Table B-1 Effect of the composition of medium (Acetone/DMSO (70/30 %w/w) to water) on HMF and furfural yield at 250°C

Composition of medium (Acetone:DMSO) / water	Yield (%)	
	HMF	Furfural
100/0	0.07	0
90/10	0.13	0
80/20	0.08	0
70/30	0.06	0
60/40	0.06	0
50/50	0.1	0
40/60	0.1	0
30/70	0.6	0.1
20/80	1.4	0.2
10/90	2.8	0.3
0/100	4.6	0.32

Table B-2 Effect of the composition of medium (Acetone/DMSO (70/30 %w/w) to water) on HMF and furfural yield at 250°C with carbon based catalyst

Composition of medium (Acetone:DMSO) / water	Yield (%)					
	HMF			Furfural		
	Exp 1	Exp 2	Sd	Exp 1	Exp 2	Sd
100/0	9.5	9.6	0.0565	1.8	1.6	0
90/10	10.8	10.3	0.0707	2.1	1.9	0.0707
80/20	10.3	10	0.2121	1.9	1.8	0.0707
70/30	10.2	10.7	0.0707	2	1.9	0.1414
60/40	9.68	8.6	0.6363	1.6	1.6	0.1414

Table B-3 Effect of temperature on HMF and furfural yield at 10/90 (Acetone/DMSO (70/30 %w/w) to water) with carbon based catalyst

Temperature (°C)	Yield (%)					
	HMF			Furfural		
	Exp 1	Exp 2	Sd	Exp 1	Exp 2	Sd
220	3.21	3.55	0.2404	0.5	0.7	0.1414
230	6.44	6.32	0.0848	1	0.98	0.0141
240	9	9.1	0.0707	1.4	1.4	0
250	10.8	10.7	0.2645	2.1	1.9	0.1527
260	10	9.8	0.1414	2.1	1.8	0.2121
270	8.26	8.11	0.1060	1.3	1.2	0.0707

Table B-4 Effect of time on HMF and furfural yield at 10/90 (Acetone/DMSO (70/30 %w/w) to water), reaction temperature 250°C with carbon based catalyst

Time (min)	Yield (%)					
	HMF			Furfural		
	Exp 1	Exp 2	Sd	Exp 1	Exp 2	Sd
0	10.8	10.7	0.0707	2.1	1.9	0.1414
1	11.2	11	0.1414	2.2	2	0.1414
2	10.2	10.3	0.0707	2.2	2.1	0.0707
5	8.48	8	0.3394	2.2	2	0.1414
7	5.91	5.87	0.0282	2.3	2	0.1414
10	3.56	4	0.3111	1.8	1.9	0.0707

Table B-5 Effect of dose of catalyst on HMF and furfural yield at 250°C, 1 min and 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium.

Dose of carbon based catalyst (g)	Yield (%)					
	HMF			Furfural		
	Exp 1	Exp 2	Sd	Exp 1	Exp 2	Sd
0.05	12.1	11.4	0.4949	2	1.6	0.2828
0.1	11	11.2	0.1154	2	2.2	0.1414
0.15	9.8	11	0.4242	2.1	2.2	0.0707

Table B-6 Production yield from fructose at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without carbon based catalyst, range of time at 0 to 12 minute.

Time (min)	% conversion of fructose		% Yield					
			Without catalyst			With catalyst		
	Without cat	With cat	Glucose	HMF	furfural	Glucose	HMF	furfural
0	10	78	0	4.8	0.1	0	22.5	0.6
2	30	87	0	7.2	0.3	0	23	0.6
5	50	93	0	14	0.4	0.1	26.6	0.8
7	63	94	0	16.7	0.5	1.25	27.5	0.9
10	72	94.7	0	20.2	0.7	0.9	28.5	0.9
12	82	95	0	26.2	1	0	28.5	1

Table B-7 Production yield from glucose at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without catalyst, range of time at 0 to 12 minute.

Time (min)	% conversion of glucose		% Yield							
			Without catalyst				With catalyst			
	Without cat	With cat	Fructose	AHG	HMF	furfural	Fructose	AHG	HMF	furfural
0	5	15	1	2.3	1.3	0	0	0	0.8	0
2	10	15	2	4	2.1	0	0	0	1.8	0.1
5	12	16	4	0	3.3	0.1	0	0	2.5	0.1
7	22	19	5	0	4	0.1	0	0	3.3	0.1
10	29	27	6	0	5.1	0.1	0	0	3.6	0.1
12	33	30	4	0	5.8	0.2	0	0	4	0.2

Table B-8 Production yield from xylose at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without catalyst, range of time at 0 to 12 minute.

Time (min)	% conversion of glucose		% yield furfural	
	Without catalyst	With catalyst	Without catalyst	With catalyst
0	5.7	13	2.4	2.4
2	7.2	18	3.1	3.9
5	10	22	5	7
7	28	35	5.7	7.6
10	30	45	7.1	9.4
12	35	45	7.7	11.7

Table B-9 Production yield from cellulose at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without catalyst, range of time at 0 to 12 minute.

Time (min)	% Yield									
	Without catalyst					With catalyst				
	glucose	xylose	AHG	HMF	furfural	glucose	xylose	AHG	HMF	furfural
0	3.75	0	0	0.3	0.1	17	0.45	0	1.2	0.3
2	6.5	0.5	0	0.7	0.2	23	0.4	0	2	0.3
5	7	0.4	0	1.1	0.2	25	0.1	10	3.9	0.5
7	7.2	0	0	1.2	0.2	43	0.08	15	5.9	0.8
10	10	0	4	2	0.3	40	0	14	7	1
12	15	0	3	2.7	0.8	40	0	13	7.6	1.4

Table B-10 Production yield from xylan at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without catalyst, range of time at 0 to 12 minute.

Time (min)	% Yield									
	Without catalyst					With catalyst				
	glucose	xylose	AHG	HMF	furfural	glucose	xylose	AHG	HMF	furfural
0	1.75	2.25	0	0	0.9	0	3.5	7.5	0.1	7.4
2	1.75	3.5	18	0	1.5	0	7.5	2.5	0.1	8
5	0	2	15	0	3	0	2	14	0.1	10.3
7	0	0.05	7.5	0	3	0	0.5	14.1	0.1	9.1
10	0	0	0	0	3.3	0	0	0	0.1	9
12	0	0	0	0.1	4	0	0	0	0.1	7.9

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**Conversion of Cassava Waste to 5-Hydroxymethy Furfural in Hot-
Compressed Water Process**

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Abstract

In this study, the production of 5-hydroxymethylfurfural (HMF) from cassava waste was investigated in a batch type hot compressed water system. First, experiments were conducted to examine the optimum condition (temperature between 473 K and 523 K and reaction time between 0 to 12 min) without added catalyst. The optimum condition was found to be at 498 K for 10 min, and the production yield was found to be 6.3 wt %. At this temperature, catalysts (TiZrO_4 , H_2SO_4 , and a new carbon based catalyst) were then used and their effects on the production yield were investigated. The results showed that the novel carbon based catalyst could promote the production of HMF giving the maximum production HMF yield of 8.46 wt% at 498 K and reduced reaction time of 5 min. This result was similar to those obtained using conventional catalysts (TiZrO_4 and H_2SO_4). However, the lower cost of carbon based catalyst makes it attractive.

1. Introduction

In the view of declining petroleum resources and rising oil prices, it is necessary to develop alternative ways to fulfill the energy needs of our industrialized society. To meet the growing demand for energy, 5-Hydroxymethylfurfural (HMF) is alternative ways because it is a particularly suitable starting material for the preparation hydrocarbons (C_9 - C_{15}) which have the same property as petroleum fuels and can be derived from biomass. One of the most promising approaches for converting biomass to HMF is by hydrothermal means, which employs hot compressed water (HCW) as a reaction medium. HCW offers the potential of high degree of conversion within short residence time, minimizes formation of toxic products during pretreatment and neither acid nor base is used. In general, biomass is converted to HMF in HCW, through homogeneous acid-catalyzed reaction [1]. The homogeneous catalyst cannot be separated easily from the system of reaction, and therefore, several attempts have been made to develop new catalytic processes, mainly based on heterogeneous catalysis, for the transformation of biomass to HMF. Recently, Gao et al. (2007) reported a use of a new type of sulfonated catalyst for acid catalyzed acetalization

reaction. The advantages of this catalyst include low cost, simple preparation, high acid density and stability. Therefore in this work, this new type of catalyst was tested for the production of HMF from Cassava waste feedstock in HCW.

2. Materials and Methods

2.1 Chemicals

Sulfuric acid and naphthalene were purchased from Fluka and Merck, Singapore.

2.2 Preparation of catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (>96%, 200 ml) at 523 K under a flow of N_2 . After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 523 K for 5 h, which resulted in a black solid. The solid was then ground to a powder and was washed repeatedly in boiling water until impurities such as sulfate ions were no longer detected in the washing water [2].

2.3 Catalyst characterization

The total surface area, pore volume and pore size of catalysts were determined using a Micromeritics model ASAP 2020. The sulfur content of sulfonated carbon based catalysts was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using 7500a ICP-MS (from Agilent, Japan).

2.4 Conversion of Cassava waste in HCW

2.4.1 Without catalyst

The reaction was carried out in a SS 316 stainless steel 8.5 ml reactor. For the preliminary conditions, 0.1 g of the dry powder of cassava waste and 1 ml of water were charged into the reactor. The reaction system was heated to the set temperature (473, 523, 573, 623, and 673 K). After a specified reaction time (0-12 min) was reached, the reaction was quenched in a water bath and the reaction product was then removed for analysis.

2.4.2 With catalyst

0.1 g of cassava waste powder, 1 ml of water, and 0.01 g of the novel carbon based catalyst were charged into the reactor. The reaction was then carried out at the optimal temperature determined without catalyst as described in the previous section. The result was compared with the reaction catalyzed by conventional catalysts (TiZrO_4 and H_2SO_4), whose the reactions were carried out using 0.1 g of TiZrO_4 and 0.14 ml of 0.1 M H_2SO_4 respectively for the same 0.1 g of cassava waste powder.

2.5 HPLC Analysis of HMF

The quantification and identification of HMF was conducted by High Performance Liquid Chromatography equipped with a Shodex RSpak KC-811 (8.0mmIDx300mm) column.

3. Results and Discussion

3.1 Catalyst characterize

The physical properties of the novel carbon based catalyst are shown in Table 3.1. The BET measurement indicates that the catalyst shows low specific surface area with insignificant pore volume, while the acid site densities calculated in the form of sulfonic acid site (estimated by

elemental analysis) was found to be 1.46 mmol/g.

Table 3.1 Physical properties of catalyst

BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Sulfur content (mmol/g)
1.1	0.07	1.46

3.2 Effect of temperature and reaction time on the formation of HMF and furfural from cassava waste

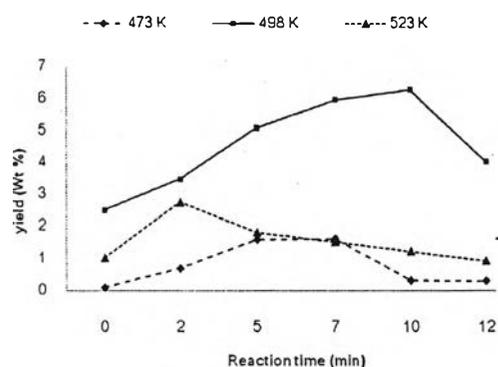


Figure 1 Effect of temperature and reaction time on the yield of HMF

Figure 1 shows that the relationship between HMF yield and reaction time is different for different reaction temperatures. The yields were increased from 473 K to 498 K at which point, the highest yields of HMF were obtained before it decreased at higher temperatures. Considering the effect of reaction time, the HMF yield first rose with increasing reaction time to a certain point where it started to decrease. This was perhaps due to the decomposition of HMF at high temperature and long reaction time. The result shows that maximum HMF yield (6.3 wt%) was obtained at 495 K and 10 min.

3.3 Effect of novel carbon based catalyst on HMF production from cassava waste

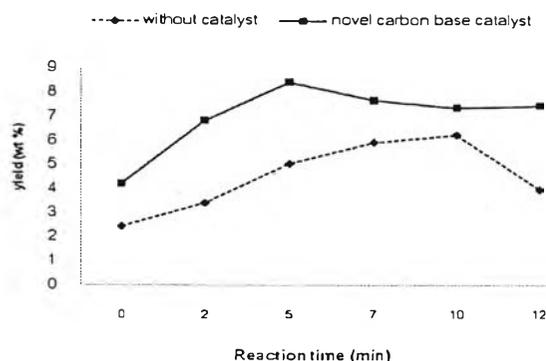


Figure 2 Effect of the novel carbon base catalyst on the yield of HMF at 495K

At 495 K, the synthesis of HMF in the presence of novel carbon base was compared with that without the catalyst. The result in Figure 2 shows that with the catalyst, the maximum production yield of HMF was found to be 8.46 wt% at 498 K for 5 min, indicating that the novel carbon based catalyst reduced the reaction time and promoted the HMF production.

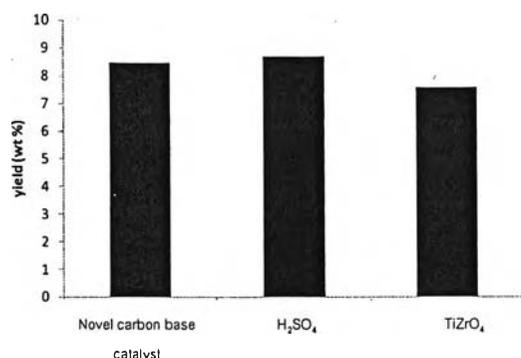


Figure 3 Effect of catalysts on HMF yield (at 495K and 5 min).

As shown in Figure 3, the HMF yield for the reaction catalyzed by the novel carbon was comparable with those catalyzed with TiZrO₄ and H₂SO₄ catalyst.

4. Conclusions

The maximum yield of HMF (6.3 wt%) from cassava waste was obtained at 523 K for 10 min in the

absence of catalyst and the novel carbon based catalyst reduced the reaction time and promoted the production HMF.

5. References

- [1] F. Salak ,H. Yoshida Acid-catalyst production of 5- Hydroxymethyl Furfural from d-fructose in Subcritical Water, *Ind.Eng.Chem.Res.*45, 2006, 2163-2173.
- [2] Gao Shan. High efficient acetalization of carbonyl compounds with diols catalyzed by novel carbon-based solid strong acid catalyst, *21*, 2007, 2892-289

VITA

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