

CHAPTER IV

RESULTS AND DISCUSSION



This chapter presents the result of 5-Hydroxymethyl furfural (HMF) and furfural production from cassava waste using carbon based catalyst. Firstly, the cassava waste were used as a substrate for the production of HMF and furfural in various compositions of medium, consisting of dimethylsulfoxide (DMSO), acetone and water without and with use of the catalysts. The most suitable composition of medium for this process was then selected for the study to determine the suitable operating conditions such as temperature and time. Then the effect of catalyst quantity and the possibility for catalyst recycling were determined and compared with commercial catalysts (sulfate zirconia catalyst and H_2SO_4 catalyst). Finally, to understand the role of catalyst in the reaction pathways of HMF and furfural production from cassava waste, the reactions of various substrates (glucose, fructose, xylose, xylan and cellulose) without and with use of the catalyst were conducted.

4.1 Determination of suitable conditions for production of HMF and furfural from cassava waste

4.1.1 Effect of medium composition

Although, acetone/DMSO mixtures is the most suitable medium for production of HMF and furfural because furanoid form of D-fructose is highly favored in this medium and it can react with fructose to form HMF readily. Moreover, HMF rehydration into many by-products is minimized in the reaction carried out in these medium. However, the substrate in this experiment was cassava wastes that want the hydrolysis process to decompose biomass to sugar. Therefore, this process should add water for hydrolysis process with acetone/DMSO mixtures.

4.1.1.1 Effect of medium composition without carbon base catalyst

The effect of weight ratios of acetone/DMSO (70:30 w/w) to water in the range from 100:0 (w/w) (i.e. pure acetone/DMSO (70:30 w/w)) to 0:100 (i.e. pure water) were studied for conversion of cassava without use of catalyst. 0.1 g of cassava waste was used as raw material to react with medium (2 wt % dry cassava waste) of various compositions at 250°C. The results in Figure 4.1 indicated that the HMF and furfural yields increased slightly when the mass ratio of water increased. The yield of

HMF and furfural were the highest when pure water was used as a reaction medium. In contrast with fructose conversion reported by previous study [Qi et al., 2008], the presence of acetone and DMSO hindered the production of HMF and furfural when the reactant for the reaction was cassava waste. To understand the reaction pathway and the effect of reaction medium and catalyst used for the production of HMF and furfural from Cassava waste, the composition of the substrate must be considered. Cassava waste is generally composed of starch 60%, cellulose 16%, hemicellulose 5% and lignin 19%. Similar to cellulose and starch, the main component of cassava waste consists of a linear chain of several linked glucose. Therefore, cellulose, were used as substrate to explain the effect result of medium composition. However, cellulose should be hydrolyzed to glucose, which then isomerizes to form fructose. Glucose and fructose then dehydrate to HMF and furfural. Therefore, in this study, glucose and fructose were also used as a substrate to explain the effects of medium composition. The reaction of each these substrates was carried out in reaction medium at various compositions: 20:80 (w/w), 10:90 (w/w) and 0:100 (w/w) of acetone/DMSO (70:30 w/w) to water. The results shown in Table 4.1 revealed that when fructose was used as a substrate, the yield of HMF and furfural decreased. On the other hand, the yield of HMF and furfural increased when glucose and cellulose were used as substrates. Previous research reported high HMF yield from D-fructose that when acetone and DMSO alone was used as the solvents, to the solvent would induce the furanoid form of D-fructose, which is only form to produce HMF [Bicker et al., 2005]. However, when glucose was used as a substrate, acetone and DMSO form the cis-diol hydrogen bonding in the β -f-tautomer of glucose as demonstrated in Figure 4.2. This furanoid form of glucose in the presence of with DMSO (and/or acetone) may not easily isomerize further to fructose, and thus lower the yield of HMF and furfural (Figure 4.3). Similarly, the yield of HMF and furfural from cellulose and cassava waste decreased with increasing DMSO and acetone in the medium since cellulose and cassava waste are composed of glucose. In addition, starch, cellulose and hemicelluloses require water for the hydrolysis reaction to form small glucose before it can then be dehydrated to form HMF and furfural.

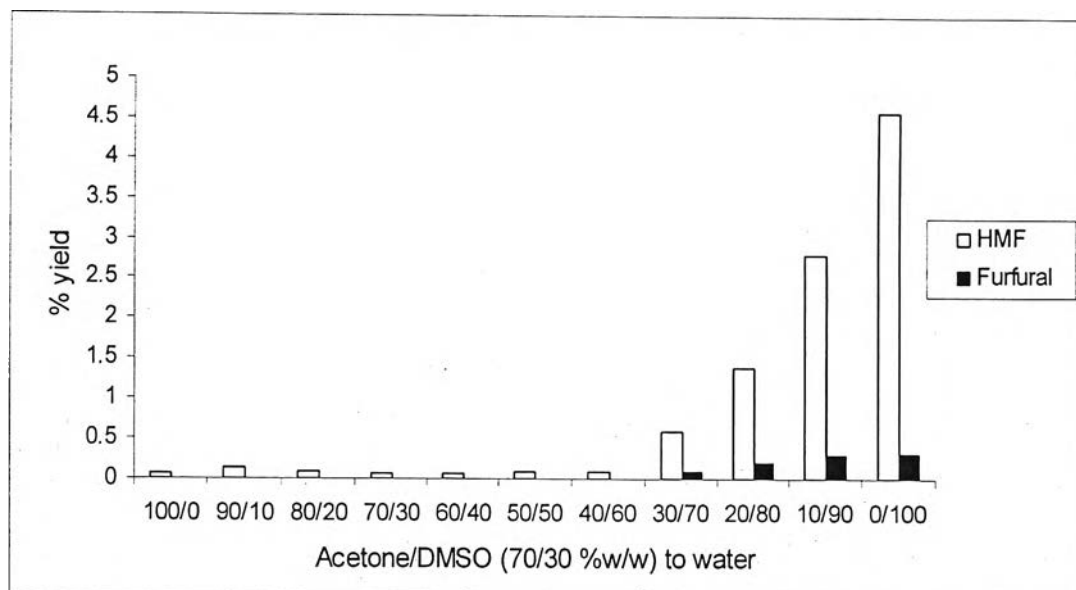


Figure 4.1 Effect of the composition of medium (Acetone/DMSO (70/30 %w/w) to water) on HMF and furfural yield at 250°C

Table 4.1 HMF and furfural yield from fructose glucose and cellulose at composition of medium (Acetone/DMSO (70/30 %w/w) to water) 20/80, 10/90 and 0/100 at 250 °C

Substrate	Composition of Medium Acetone/DMSO (70/30 w/w) / water	% Yield	
		HMF	Furfural
Fructose	20/80	22.9	2.2
	10/90	21.9	2.1
	0/100	19	1.8
Glucose	20/80	12.6	1.5
	10/90	13.3	1.5
	0/100	14.9	1.6
Cellulose	20/80	2.8	0.4
	10/90	3.2	0.5
	0/100	5.3	0.7

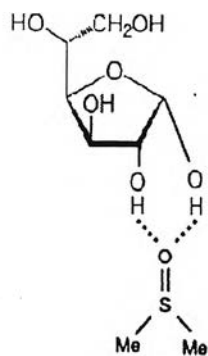


Figure 4.2 d-glucose/DMSO associate

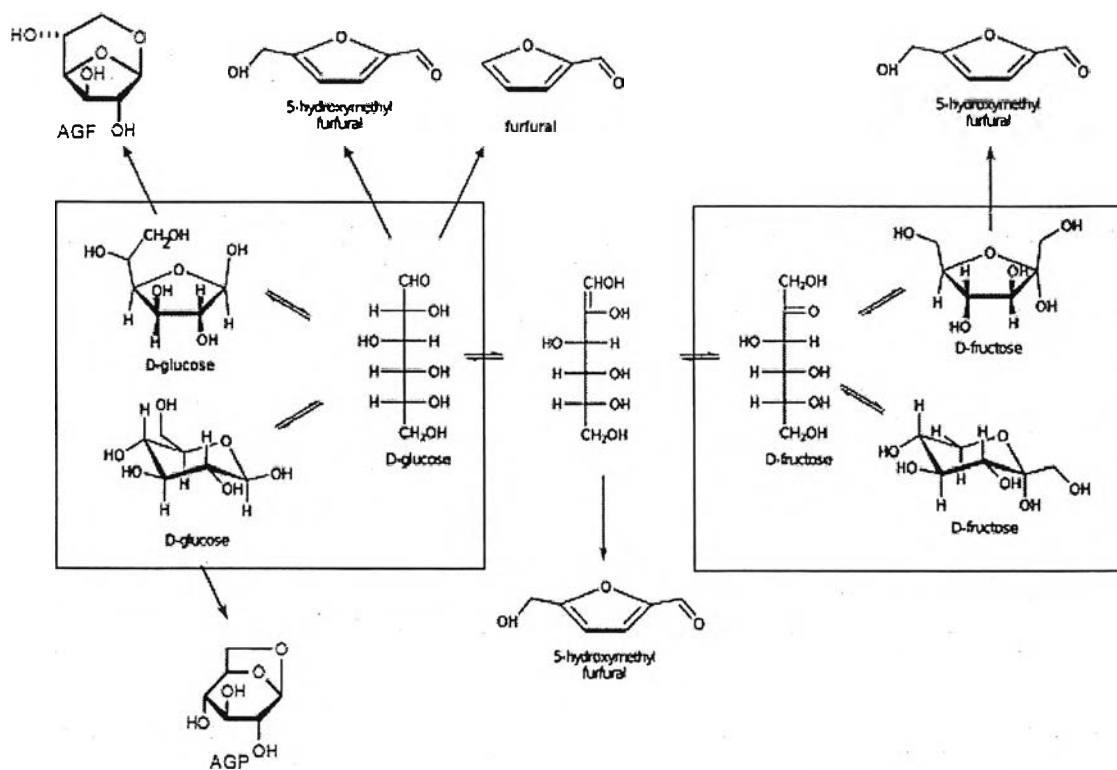


Figure 4.3 Isomerization and dehydration of glucose

4.1.1.2 Effect of medium composition on HMF and furfural production from cassava waste with carbon base catalyst

In previous work, acetone and dimethylsulfoxide (DMSO) mixture medium was an effective medium for the dehydration of fructose to 5-HMF in the presence of sulfated zirconia catalyst (Qi et al., 2009). Similar to sulfated zirconia, the carbon based catalyst employed in this study contain sulfonic group, which therefore show high catalytic activity for conversion of cassava waste to HMF and furfural in DMSO and acetone medium. The results in Figure 4.4 and 4.5 showing the HMF and furfural yields with and without use of carbon based catalyst demonstrated that the production yield of HMF and furfural from cassava waste conversion with carbon based catalyst were higher than the yield that without the catalyst for all compositions of medium. In this study, further experiment was carried out to determine the effect of carbon based catalyst in medium of various weight ratios of acetone/DMSO (70:30 w/w) to water ranging from 100:0 to 0:100 (i.e. pure water). Here the reaction was carried out at 250°C and the amount of catalyst used was 0.1 g for 0.1 g of cassava waste. The effect of medium composition with carbon base catalyst is shown in Figure 4.6, which indicates that the production yield of HMF and furfural in the process with catalyst was increased slightly when the mass of water increased from 40:60 (w/w) to 10:90 (w/w) of acetone/DMSO (70:30 w/w) to water. The yield then decreased when pure water was employed as medium. Thus, the suitable medium composition with carbon base catalyst is 10:90 (w/w) of acetone/DMSO (70:30 w/w) to water. With this medium, 10.8 % and 2.1 % yields of HMF and furfural were obtained respectively.

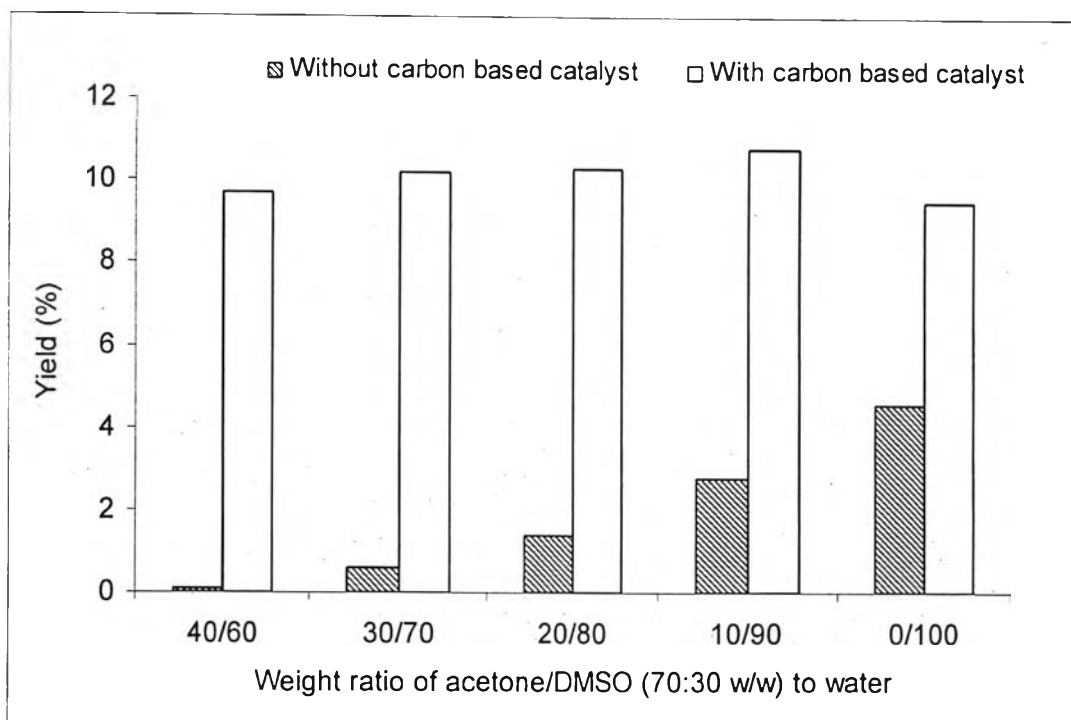


Figure 4.4 The comparison yield of HMF between with and without catalyst process at various composition of medium (Acetone/DMSO (70/30 %w/w) to water)

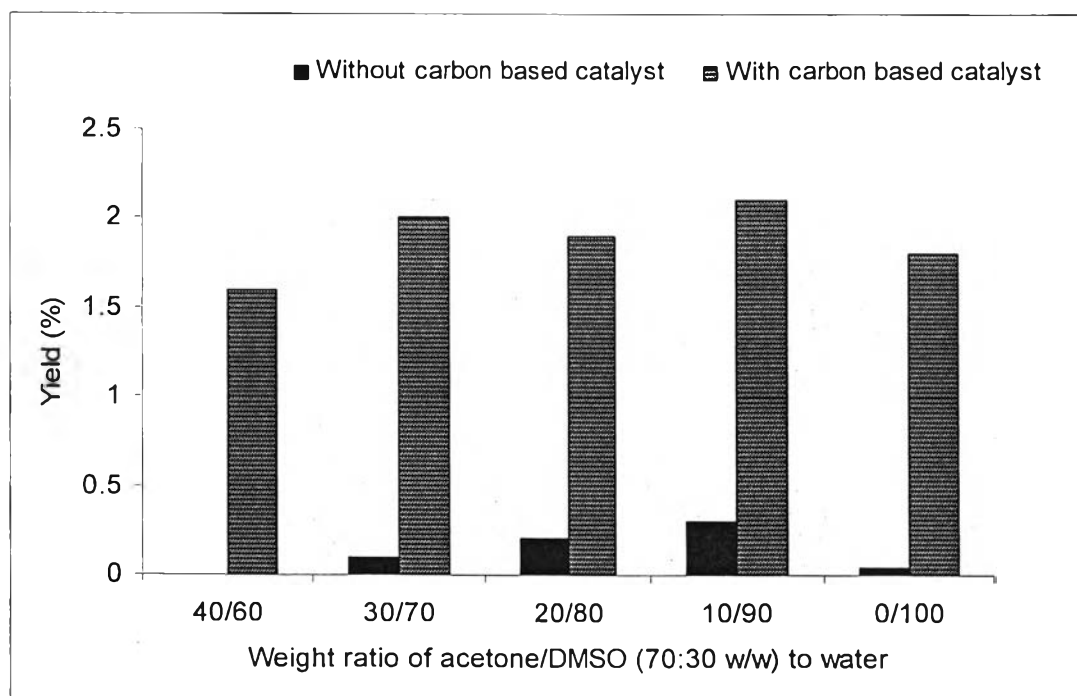


Figure 4.5 Comparison yield of furfural between with and without catalyst process at various composition of medium (Acetone/DMSO (70/30 %w/w) to water)

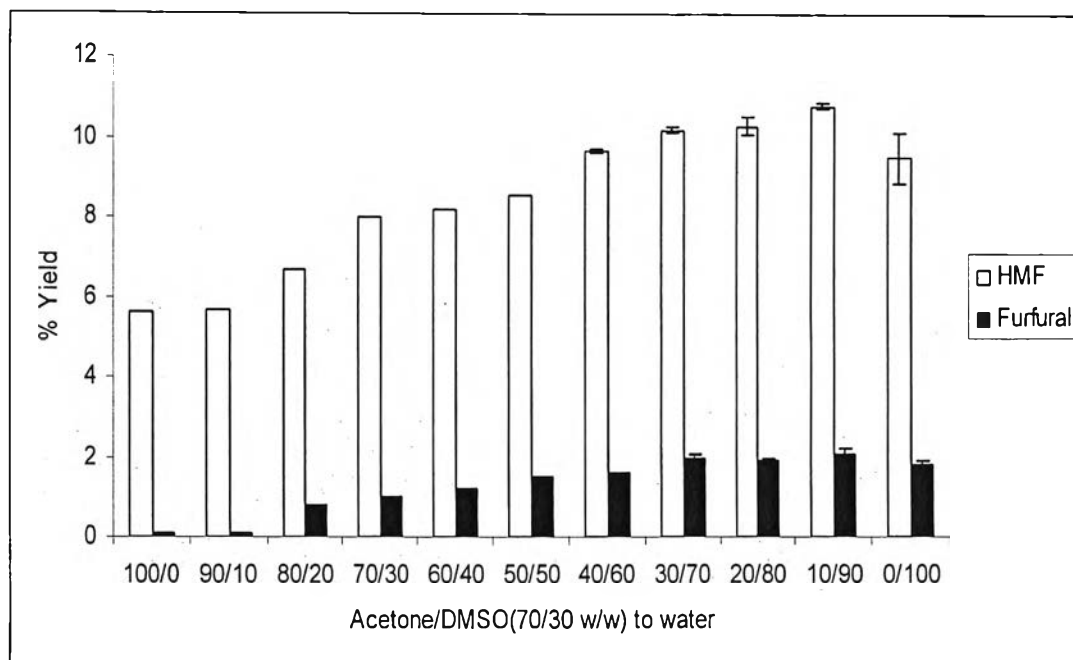


Figure 4.6 Effect of the composition of medium (Acetone/DMSO (70/30 %w/w) to water) on HMF and furfural yield at 250°C with carbon based catalyst

It should be noted that for the process with catalyst, the reaction medium in which the highest production yields of HMF and furfural were obtained contains water as the main component. Therefore, the carbon based catalyst may have the high effect on hydrolysis. To determine the effects of catalysts on the cassava waste conversion to HMF and furfural, cellulose, glucose and fructose were used as substrate. Each of these substrates was reacted in 20:80 (w/w), 10:90 (w/w) and 0:100 (w/w) of acetone/DMSO (70:30 w/w) to water mixture in presence of carbon based catalyst. The results on HMF and furfural yields are summarized in Table 4.2. The production yields from fructose with catalyst were lower than that obtained without catalyst. Although the yields were expected to be higher with use of catalyst, the decrease in yield in this experiment was due to the decomposition of HMF and furfural at high temperature at 250°C. On the other hand, the yield of HMF and furfural from glucose with catalyst was lower than that without catalyst. This was also true for at other temperatures (data shown in the following section) which indicated that the carbon based catalyst did not promote the dehydration from glucose to HMF at this condition. This result was supported by the work of Watanabe et al (2005), which reported that the isomerization of glucose and fructose was promoted by based catalyst while acid catalyst promoted the dehydration process. However, the HMF and

furfural yields from cellulose with carbon based catalyst were higher than those obtained in absence of the catalyst, and therefore it can be inferred from this study that the catalyst enhanced the hydrolysis process. From the above results, cassava waste conversion to HMF and furfural requires hydrolysis and dehydration. The hydrolysis of cellulose to fructose could be promoted by the carbon based catalyst. The dehydration reaction was also promoted by the carbon based sulfonated catalyst in which, fructose was converted to HMF and furfural in the presence of DMSO and acetone (Qi et al., 2009). However, acetone and DMSO limit to isomerization of glucose to fructose. Thus, the suitable composition of medium in the process with catalyst was 10:90 (w/w) of acetone/DMSO (70:30 w/w) to water.

Table 4.2 HMF and furfural yield from fructose glucose and cellulose at composition of medium (Acetone/DMSO (70/30 %w/w) to water) 20/80, 10/90 and 0/100 at 250 °C

Substrate	Composition of Medium Acetone/DMSO (70/30 w/w) : water	% Yield			
		Without catalyst		With catalyst	
		HMF	Furfural	HMF	Furfural
Fructose	20 : 80	22.9	2.2	14.6	1.8
	10 : 90	21.9	2.1	13.5	1.4
	0 : 100	19	1.8	10.1	1.1
Glucose	20 : 80	12.6	1.5	8.8	1.6
	10 : 90	13.3	1.5	9.9	1.6
	0 : 100	14.9	1.6	10.6	1.5
Cellulose	20 : 80	2.8	0.4	9	1.5
	10 : 90	3.2	0.5	9.3	2
	0 : 100	5.3	0.7	8.7	1.8

4.1.2 Effect of temperature

To determine the suitable temperature, 0.1 g of dry cassava waste, 0.1 g of carbon based catalyst and 10/90 %w/w acetone/DMSO (70/30 %w/w) to water were charged into the reactor. The reaction temperatures were varied in the range of 230-270 °C and the HMF and furfural yields are shown in Figure 4.7. This result indicated that the HMF and furfural yields increased with reaction temperature from 220 to 240 °C. When the temperature was 250°C, the HMF and furfural yields were the highest at 10.8% and 2.1 % respectively. This was due to the decomposition of biomass was completed at temperature about 250 to 320°C that depend on the structure of biomass [Ando et al., 2005]. However at temperature higher than 250°C, HMF and furfural yields were decrease because of decomposition of HMF and furfural at high temperature, in which HMF can be dehydration to 1,2,4 benzenetriol. Furthermore, the main medium of this process was water that can react with HMF to levulinic acid and formic acid, while furfural can convert to phenol and acids/aldehydes by dehydration and bond-breaking reaction, respectively.

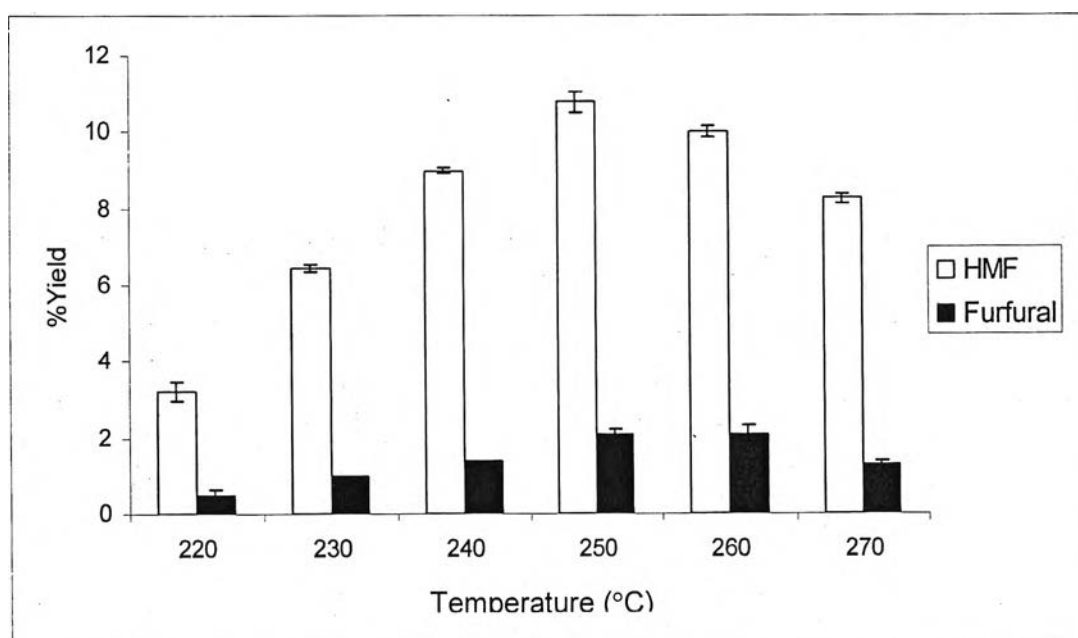


Figure 4.7 Effect of temperature on HMF and furfural yield at 10/90 (Acetone/DMSO (70/30 %w/w) to water) with carbon based catalyst.

4.1.3 Effect of reaction time

In this work, the effect of reaction time between 0-12 minutes was determined at 250°C following the method described in section 4.1.3. The effect of reaction time is shown in Figure 4.8. From this result, the HMF and furfural yields increased from 0 to 1 minute and then both yields slightly decreased with increase the reaction time due to the decomposition of HMF and furfural to other products such as 1,2,4 benzenetriol, levulinic acid, formic acid, as well as various gaseous products.

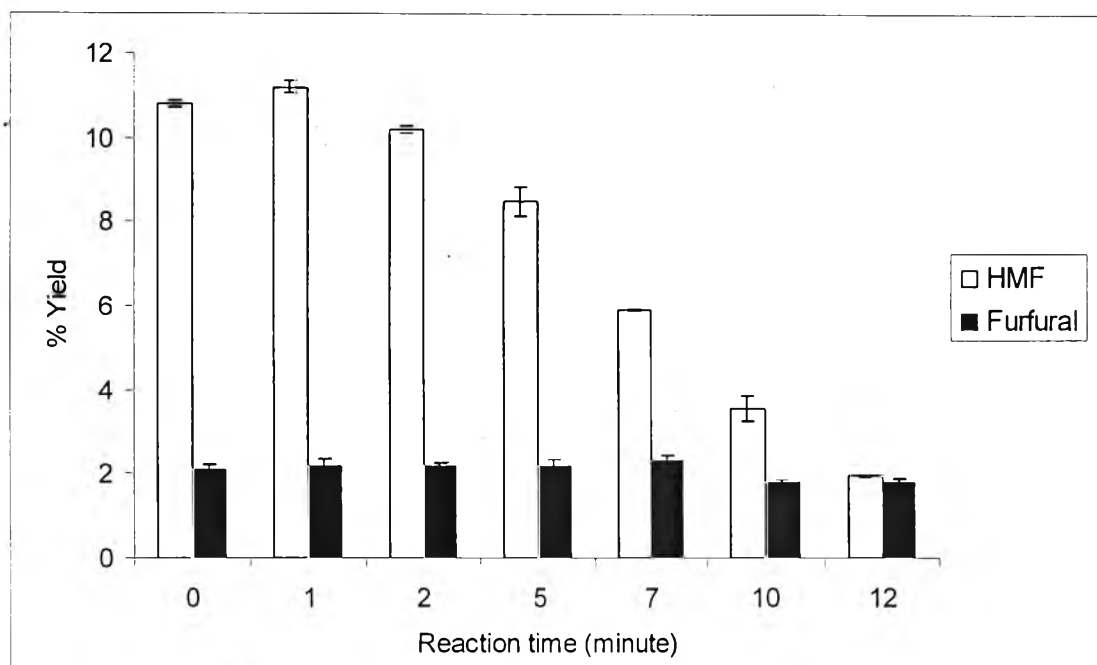


Figure 4.8 Effect of time on HMF and furfural yield at 10/90 (Acetone/DMSO (70/30 %w/w) to water), reaction temperature 250°C with carbon based catalyst

4.1.4 The effect of dose of carbon based catalyst

The quantities of the catalysts have been shown to have an influence on the yield of HMF and furfural. Therefore, this experiment was carried out to determine the suitable quantity of carbon based catalyst required for HMF and furfural production. Here, the reaction of 0.1 g of cassava waste and 10/90 of acetone/DMSO (70:30 w/w) to water (2 %,w dry cassava waste) were carried out at 250°C for 1 minute with various amounts: 0.05 g, 0.1g and 0.15 g of carbon based catalyst. The effect of the dose of catalysts is shown in Figure 4.9, in which the highest production yield of HMF and furfural (29.8 % and 1.7 % respectively) were obtained when the

dose of catalyst was 0.05 g. The yields of the products then decreased with increasing the mass of carbon based catalyst.

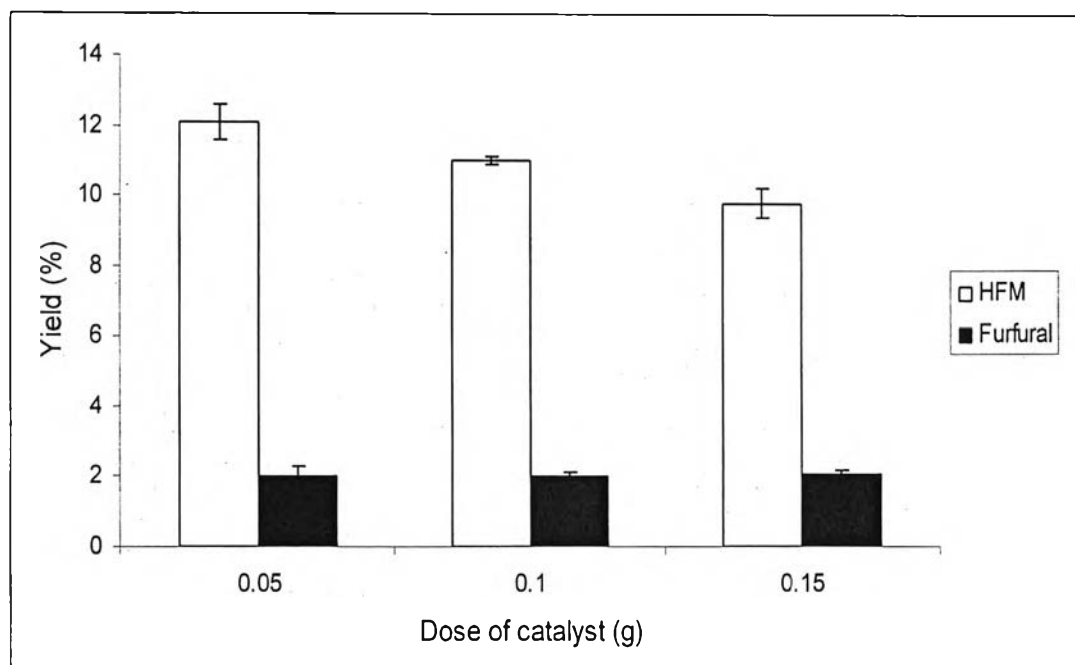


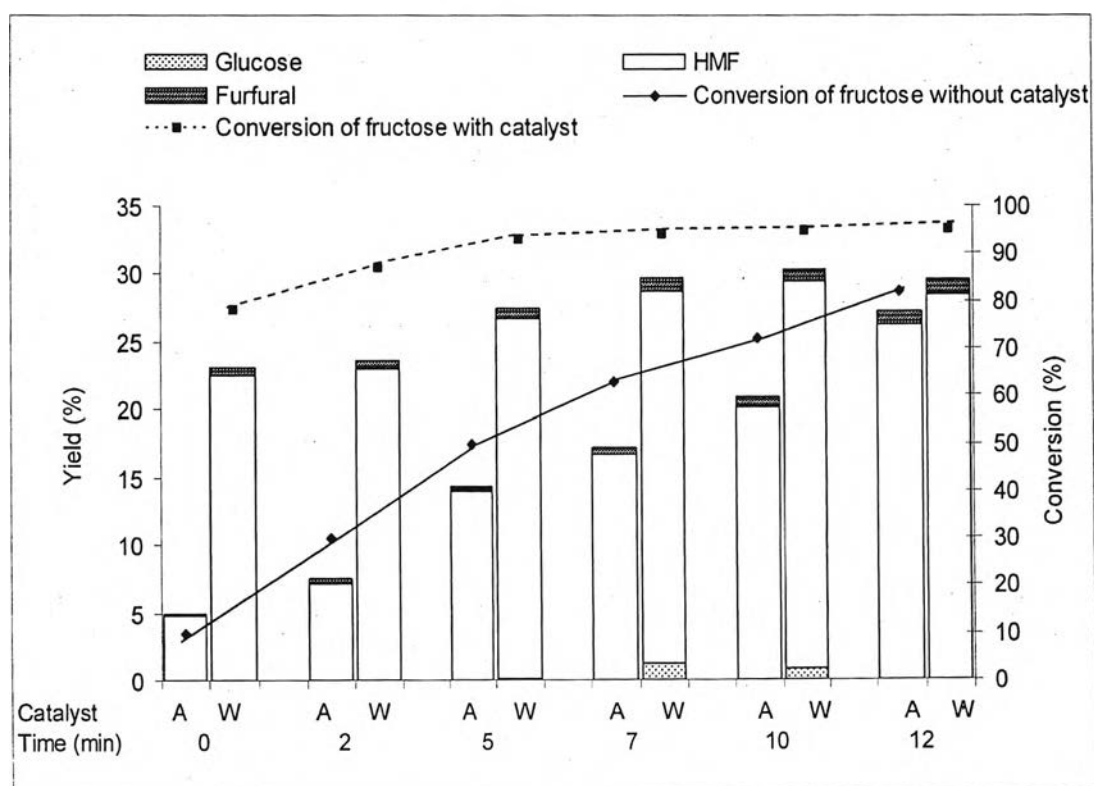
Figure 4.9 Effect of dose of catalyst on HMF and furfural yield at 250°C, 1 min and 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium.

4.2 The effect of carbon based catalyst on the reaction pathway of HMF and furfural production from biomass

Generally, the synthesis HMF and furfural from biomass consist of hydrolysis and dehydration process. As the first step, biomass decomposes to cellulose, hemicelluloses and lignin by hydrolysis process. Subsequently, cellulose hydrolyzes to glucose while hemicellulose hydrolyzes to glucose and xylose. Finally, glucose dehydrates to HMF and furfural while xylose dehydrates to only furfural. Thus, to determine the effect of carbon based catalyst on the reaction pathway of HMF and furfural production from biomass, the reactions of fructose, glucose, xylose, hemicelluloses and cellulose were examined at the suitable component of medium determined from previous section. Because the temperatures of decompositions of each substrate are different, fructose, glucose and xylose were therefore reacted at lower temperature (200°C) while hemicellulose and cellulose are reacted at higher temperature (230°C). The reactions were carried out without and with 0.1 g of carbon based catalyst for various reaction times: 0, 2, 5, 7, 10 and 12 min.

4.2.1 Effect of carbon based catalyst on fructose conversion

Fructose is the main substrate for production of HMF and furfural and it can isomerize from glucose. Therefore, the dehydration of HMF and furfural from fructose was studied and the result was reported in Figure 4.10. The yields of HMF and furfural increased with increasing reaction time both with and without catalyst. However, the yields of HMF and furfural from the reactions with catalyst were higher than those from the reactions without catalyst especially at the initial time. Thus, from these results, it can be concluded that the carbon based catalyst enhanced the dehydration fructose to HMF and furfural.



A : Absence/Without carbon based catalyst

W : With catalyst

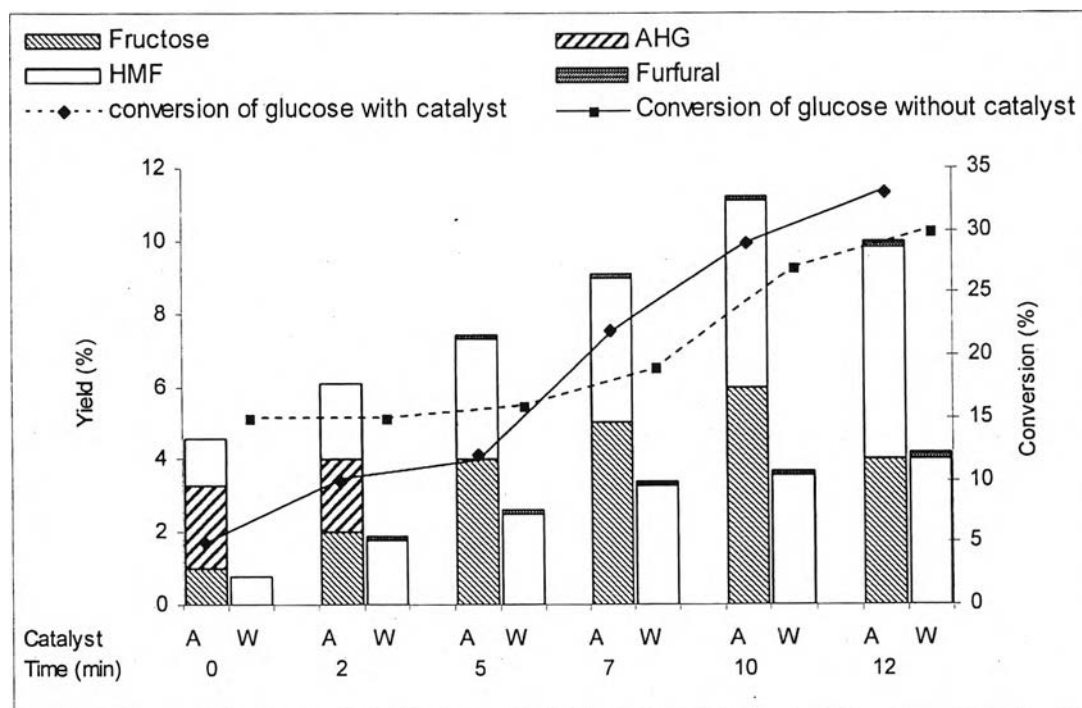
Figure 4.10 Production yield from fructose at 230°C, 10/90 (Acetone/DMSO (70/30 %w/w) to water as medium, with and without catalyst, range of time at 0 to 12 minute

4.2.2 Effect of carbon based catalyst on glucose conversion

Generally, the products from glucose conversion consist of fructose, AHG, HMF and furfural. Glucose isomerizes to fructose then glucose dehydrates to AHG, HMF and furfural while fructose dehydrates to HMF and furfural. The glucose conversion and production yield from glucose are shown in Figure 4.11, with and

without catalyst. In the process without catalyst, fructose and HMF increased with long reaction time while AHG appeared at 0 to 2 minute, and was no longer observed at long reaction time possibly due to the decomposition of AHG to other organics acids (as demonstrated in Figure 2.6). In the process with carbon based catalyst, fructose could not be observed possibly because it dehydrated to HMF and furfural rapidly. However, the yields of HMF and furfural from the reactions with catalyst were lower than those from the reactions without catalyst. Thus, this carbon based catalyst which was acid catalyst can not promote the isomerization from glucose to fructose. This result was supported by the work of Watanabe et al (2005), which reported that the isomerization of glucose and fructose was promoted by based catalyst while acid catalyst was promoted the dehydration process.

It should be noted that not only the carbon based catalyst did not affect isomerization, the yields of HMF and furfural from the reaction with the catalyst were lower than those from the reaction without catalyst. Therefore, the carbon based catalyst may not enhance the process to HMF and furfural.



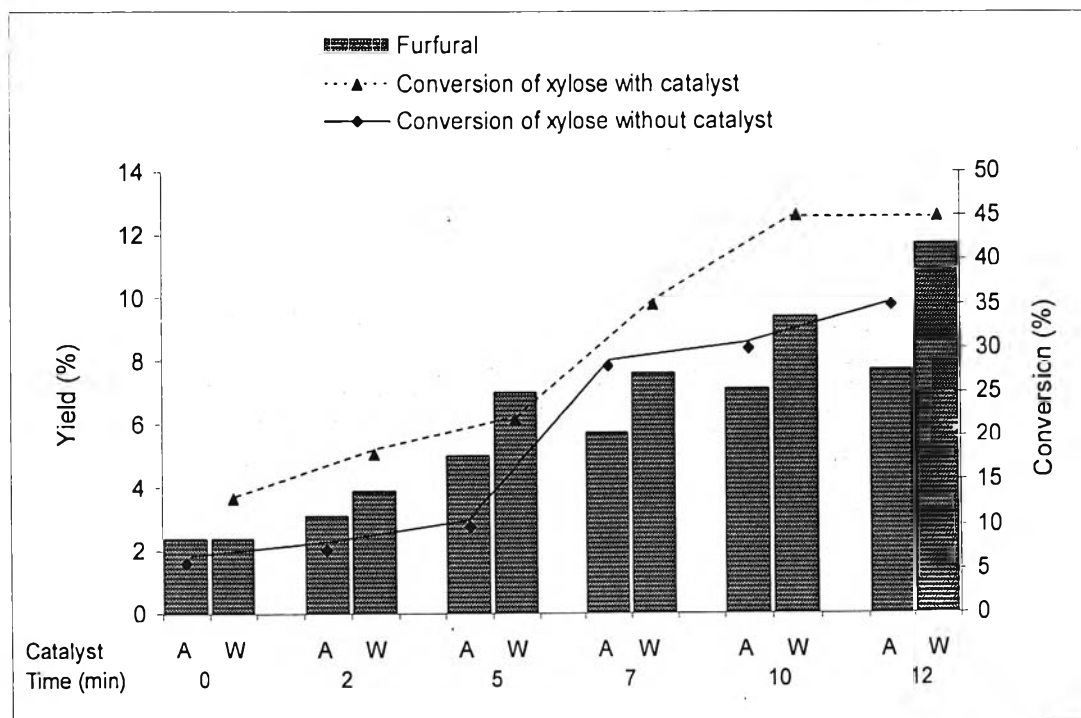
A : Absence/Without carbon based catalyst

W : With carbon based catalyst

Figure 4.11 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.

4.2.3 Effect of carbon based catalyst on xylose conversion

Xylose is the main composition of hemicellulose. Thus, it was used as a substrate to investigate the dehydration to furfural. The conversion of xylose, with and without carbon based catalyst was demonstrated in Figure 4.12. The yield of furfural increased with increasing reaction time both with and without catalyst. However, the yield of furfural from the system with catalyst was higher than that without catalyst. Thus, the carbon based catalyst promotes the dehydration xylose to furfural.



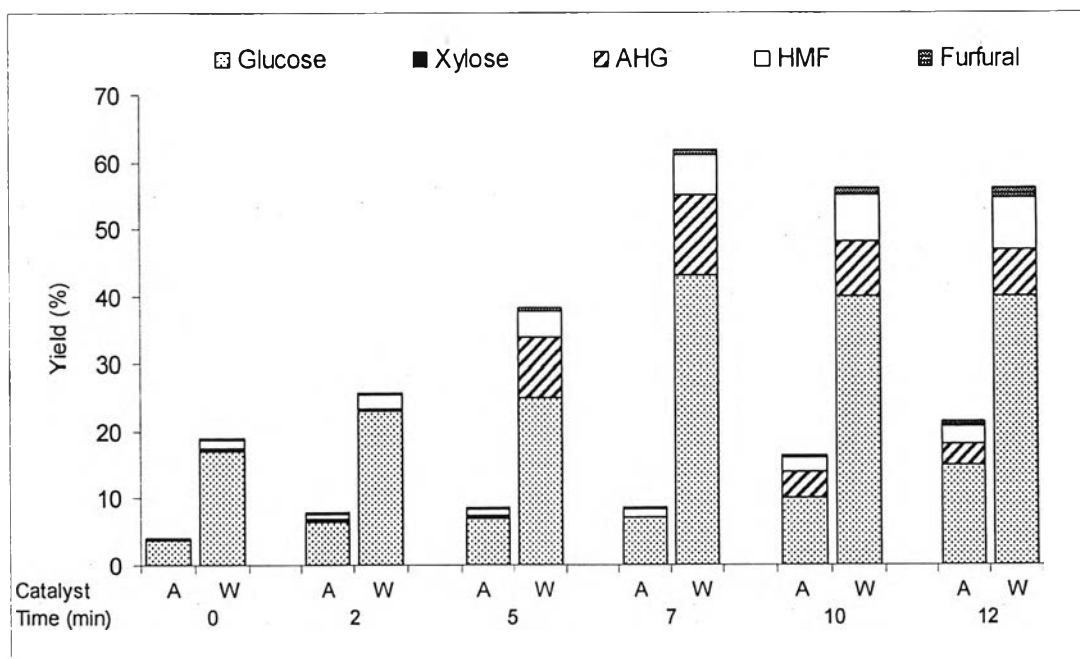
A : Absence/Without carbon based catalyst

W : With catalyst

Figure 4.12 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.

4.2.4 Effect of carbon based catalyst on cellulose conversion

The reaction of cellulose for various times is presented in Figure 4.13, without and with carbon based catalyst. This figure shows the product yield from cellulose conversion were glucose, xylose, AHG, HMF and furfural. The yield of glucose, HMF and furfural increased with time for both the reaction with and without catalyst, while the yield of AHG began to occur at 5 minutes, and then increased with time. This reason for the decrease in glucose was because at long reaction time, glucose can dehydrate to AHG, HMF and furfural. Moreover, the product yields from cellulose which was glucose HMF and AHG with catalyst were higher than those without the catalyst. Especially, the yield of glucose with catalyst was approximately 30 % higher than that for the reaction without catalyst. Thus, from this study, it can be concluded that the catalyst promoted the hydrolysis process from cellulose to glucose. However from the result in section 4.2.2, the production yield of HMF, furfural and AHG from glucose were not promoted by the carbon based catalyst. Therefore, increasing of HMF, furfural and AHG in the reaction with catalyst was observed because of the increase in glucose, which was promoted by carbon based catalyst.



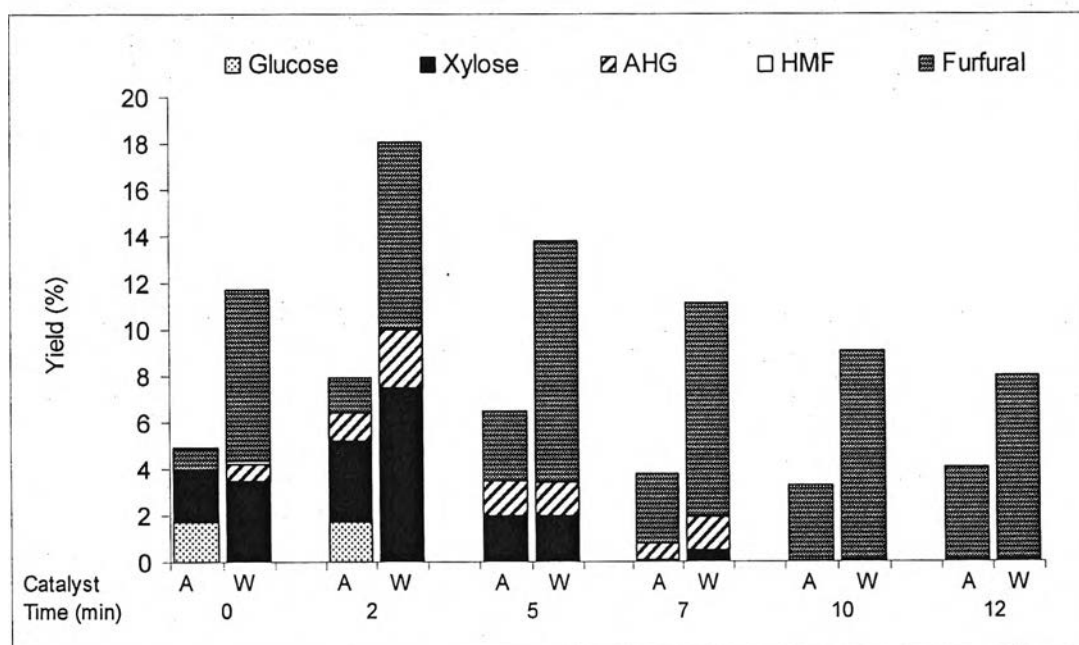
A : Absence/Without carbon based catalyst

W : With carbon based catalyst

Figure 4.13 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

4.2.5 Effect of carbon based catalyst on xylan (hemicellulose) conversion

The product yields for the conversion of xylan at various reaction times are present in Figure 4.14, without and with carbon based catalyst. For the process without catalyst, xylan decomposes to glucose and xylose at 0 and 2 minute, then glucose and xylose decreased with reaction time as these products dehydrate further to AHG and furfural. However, from with catalytic processes, the production yield of AHG was higher than that obtained with the process without catalyst. Since AHG was dehydrated from glucose only, thus from this result, it can be inferred that the carbon based catalyst enhanced the hydrolysis from xylan to glucose. Moreover, the yield of xylose and furfural in the process with catalyst was much higher than the process without catalyst. From these results, it can be inferred that the carbon based catalyst promotes the hydrolysis of xylan to xylose and promote the dehydration from xylose to furfural.



A : Absence/Without carbon based catalyst

W : With carbon based catalyst

Figure 4.14 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.

Therefore, from this study, it can be concluded that the carbon based catalyst promoted the hydrolysis from cellulose to glucose and from hemicellulose to xylose and glucose. Furthermore, this catalyst promoted the dehydration from xylose to furfural and fructose to HMF and furfural as indicated by pathway presented in Figure 4.15

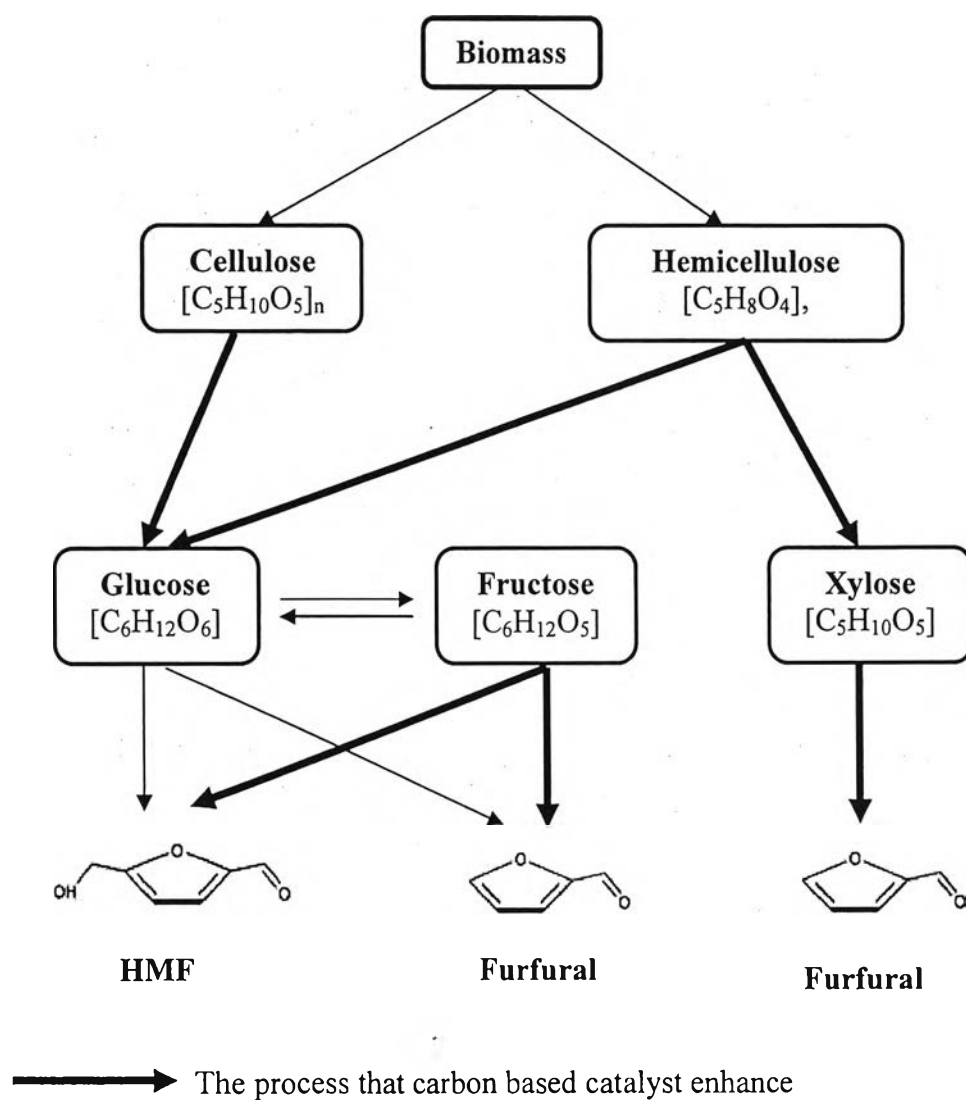


Figure 4.15 The effect of carbon based catalyst on pathway of HMF and furfural production from biomass

4.3 Comparison of catalyst activity

The activity of carbon based catalyst was compared with those of commercial catalysts: sulfuric acid catalyst (H_2SO_4) and sulfate zirconia catalyst. The reaction was carried out at 250°C for 1 minutes, following the method described in section 4.1.4, whose the reactions were carried out using 0.05 g of carbon based catalysr, 0.05 g of sulfate zirconia and 0.57 ml of 0.1 M H_2SO_4 for the same 0.1 g of cassava waste powder. The result shown in Figure 4.16, the carbon based catalyst has effectiveness as homogenous catalyst due to when use carbon based and sulfuric acid as catalyst, the production yield of HMF and furfural are nearly equal. However, sulfate zirconia catalyst was obtained low yields of HMF and furfural due to this process has most of water as medium. When sulfated zirconia was exposed to water, the absorption of water molecules on sulfated zirconia leads to the less acidic Bronsted centers associated with are formed [Qi et al., 2009], thus this probably reduced the catalytic activity of biomass hydrolysis and dehydration to HMF and furfural.

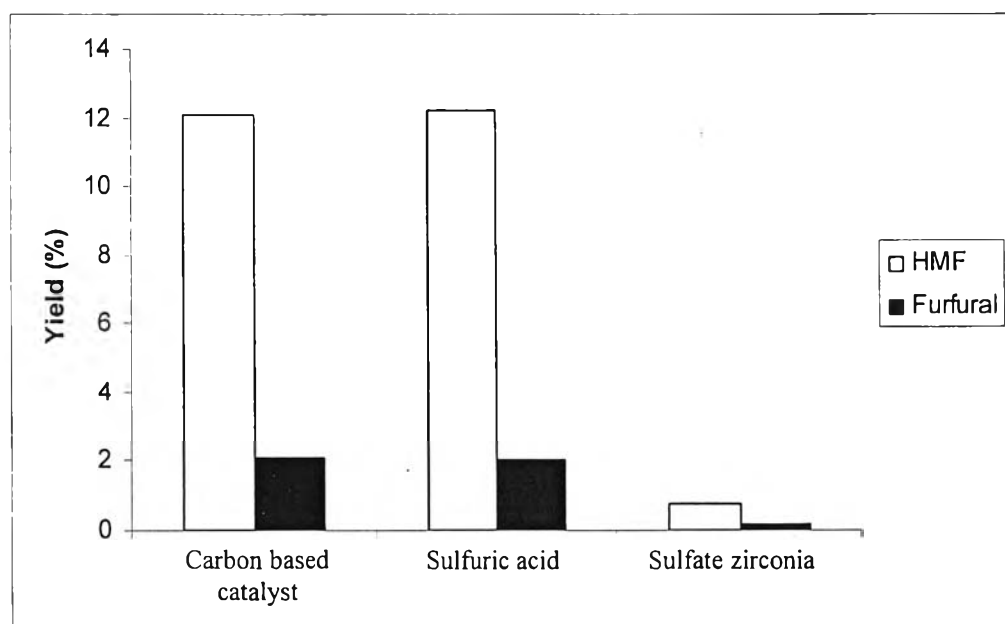


Figure 4.16 The activity of carbon based catalyst was compared with the commercial Catalyst

4.4 Catalyst recyclability

The recyclability of catalyst is one of the advantages for heterogeneous catalyst and it is the important factor for choosing a catalyst in a particular process. The stability and reusability study of carbon based catalyst was carried out by 4 times repeated reactions, each carried out at 230 °C with 0.1 g of fructose and 10/90 of acetone/DMSO (70:30 w/w) to water (2 %,w fructose). For each reaction, 0.05 g of carbon based catalyst was used. The results are shown Figure 4.17. From the experiment data, the yield of HMF and furfural only slightly decreased from initial use. The fact that only 3% decrease in yield after 4 times of indicated high catalyst stability and that the carbon based catalysts can be effectively be reused.

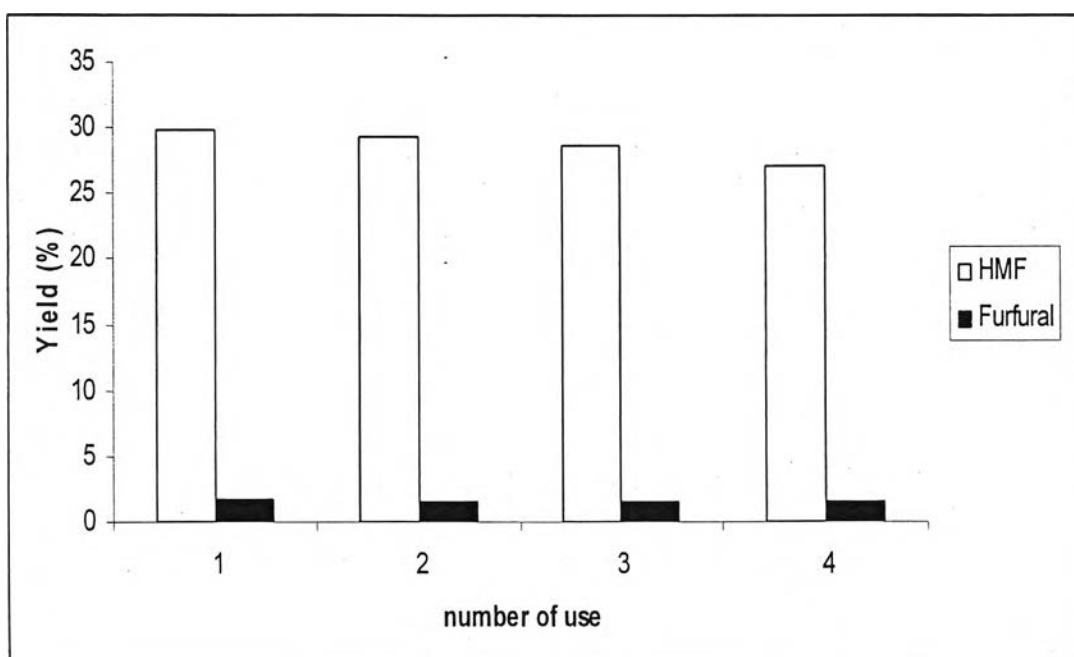


Figure 4.17 Effect of carbon based catalyst recycling