



## **INVESTIGATION OF CONVERSION OF FRUCTOSE TO 5-HYDROXYMETHYLFURFURAL OVER CARBON SKELETON-BASED ACID CATALYSTS**

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### **ABSTRACT**

Two carbon skeleton-based acid catalysts were the amberlyst-15 and the sulfonated activated carbon (AC-SO<sub>3</sub>H). The sulfonated activated carbon was sulfonated by concentrated acid H<sub>2</sub>SO<sub>4</sub>. The formation of SO<sub>3</sub>H groups was detected by infrared spectroscopy and elemental analysis by EDX method. A commercial acidic ion-exchange resin, amberlyst-15, was also studied as a reference. Catalytic activity of both catalysts were estimated by conversion of fructose to 5-hydroxymethylfurfural (HMF). The influence of temperature and time reaction on the yield of HMF has been studied. With reaction time of 90 mins and reaction temperature of 120°C, the maximum of HMF yield attained 60% for catalyst AC-SO<sub>3</sub>H. In case of amberlyst-15, this one was 81% at 160°C and 60 min. Basing on sulphur content and morphologies of catalysts. It seems that the HMF yield was proportional to the number of accessible sulfonic groups -SO<sub>3</sub>H on catalyst surface.

**Key words:** 5-Hydroxymethylfurfural, Activated carbon, Fructose.

### **INTRODUCTION**

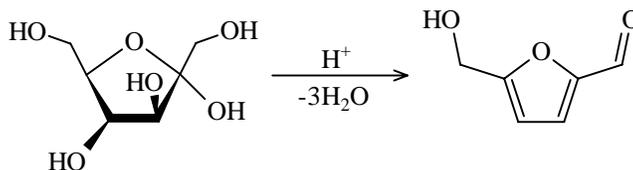
The rapid development of human society requires much more energy and chemicals. However, at present, the fossil fuel, which is main source of fuels and chemicals is decreasing<sup>1</sup>. A new renewable energy source to fill up this deficiency becomes indispensable and biomass seems to be a good candidate to solve this problem. Apart from fossil fuel, biomass is known as the most abundant renewable carbon source. A lot of researches show that it is possible to effectively convert biomass into liquid fuel and other value-added chemicals. Among them, 5-hydroxymethylfurfural (HMF) represents a good platform chemical. HMF is very useful not only as intermediate compound for the production of

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biofuel but also as raw material for productions of important compounds such as levulinic acid, 2,5-furandicarboxylic acid (FDA), and 2,5-diformylfuran (DFF). These compounds have been well known in polymer and pharmaceutical fields<sup>2</sup>.

HMF can be easily prepared by triple dehydration of fructose in the presence of acid catalyst as following reaction:



Catalysts used are homogenous such as acid  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ <sup>3,4</sup> or heterogeneous acids such as  $\text{ZrO}_2\text{-SO}_4$ <sup>2</sup>,  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ <sup>5,6</sup>. Solvent also plays an important role in HMF conversion from fructose. In water, the dehydration is not thermodynamically favourable. Hence, for the aqueous homogenous catalytic reaction, the dehydration reaction of fructose was carried out in biphasic solvent system where an added organic solvent phase played a role of HMF extraction phase. However, such homogenous catalytic system was quite cumbersome and there was always an environmental problem caused by mineral acid waste. In comparison with homogenous catalyst, a heterogeneous catalytic system seems to have more advantages. Normally, such system is smaller, facile to operate and avoid the separation step of product and catalyst.

In this study, an activated carbon was sulfonated and used as an acid catalyst. This catalyst is inexpensive and easy to prepare and environmentally friendly. Different parameters such as reaction temperature, reaction time, and solvent were examined. The commercial resin, amberlyst-15, was tested to compare.

## EXPERIMENTAL

### Catalyst preparation

All used chemicals compounds have analytical purity: Activated carbon (AC) (Sigma-Aldrich, 99%), amberlyst-15 (Sigma-Aldrich),  $\text{H}_2\text{SO}_4$  (China, 98%), Fructose (Merk, 99%), dimethyl sulfoxide (DMSO) (Sigma-Aldrich, 99%), and ethylene glycol (EG) (Sigma-Aldrich, 99%).

The sulfonation of AC was performed as following: 1 g of activated carbon (AC) was added in 20 mL of  $\text{H}_2\text{SO}_4$  98% and heated at 100°C under nitrogen flow for 12 hr; the

obtained mixture was cooled down to room temperature and diluted by distilled water, then filtered and washed by warm distilled water (80°C); the solid obtained was dried at 100°C for 6 hr.

### Catalyst characterization

IR spectrum of catalysts was measured on FTIR 8101M SHIMADZU. SEM-EDS analysis were performed by Nova nanoSem 450 (FEI).

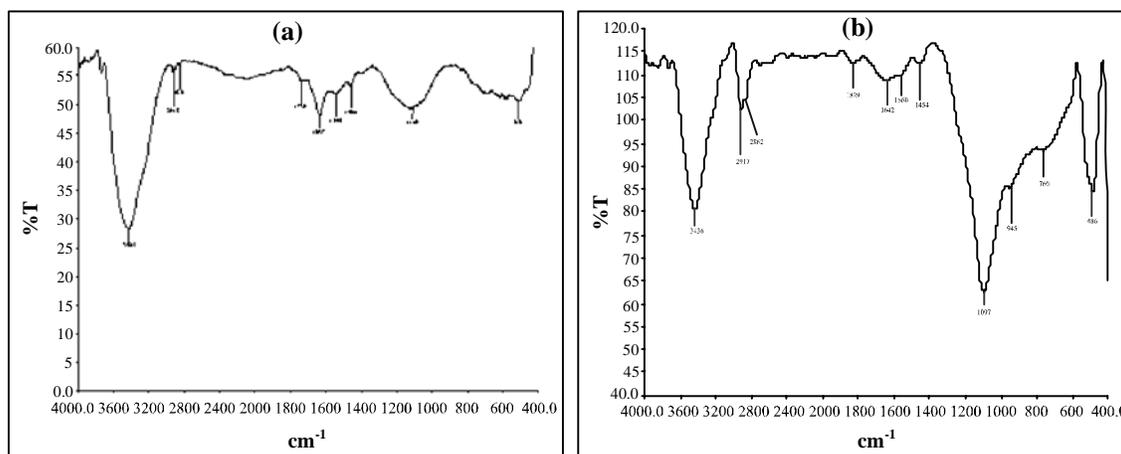
### Catalytic activity test

For each catalytic test, 0.5 g of fructose and 0.5 g of catalyst were added, mixed and stirred in 10 mL of DMSO. The reaction was carried out under nitrogen atmosphere in an autoclave. HMF was quantified by Shimadzu HPLC, using a detector PDA and Cadenzal C18 column (250 mm x 4.6 mm, 3  $\mu$ m) at 30°C. A mixture of acetonitrilne and water was used as the mobile phase with a flow rate of 1ml/min.

## RESULTS AND DISCUSSION

### Characterization of catalysts

The Fig. 1 presents the IR spectra of AC before (1a) and after (1b) sulfonation.

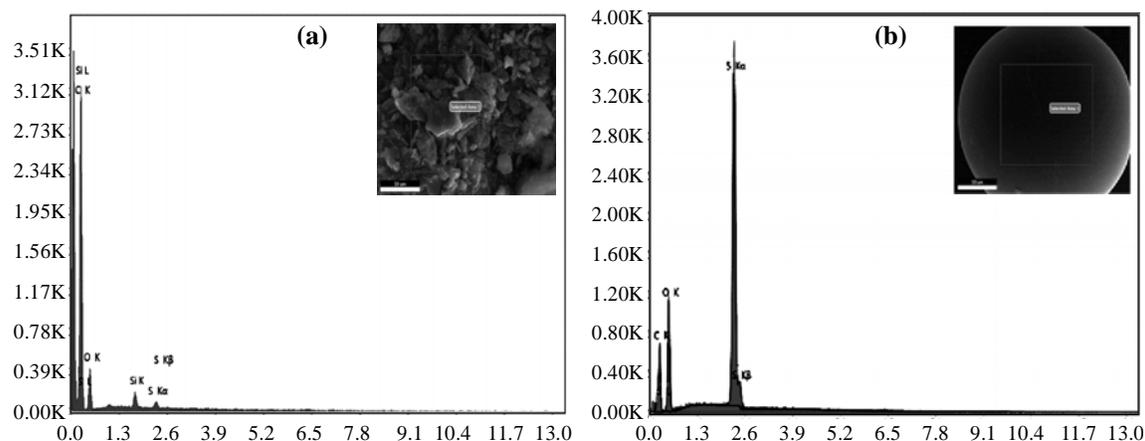


**Fig. 1: IR spectra of AC before (a) and after (b) sulfonation**

From obtained IR spectra, it was obvious that the appearance of the peak at 1097  $\text{cm}^{-1}$  is attributed for symmetric stretching vibration of S=O bond<sup>7,8</sup>. Another vibrations at

3436  $\text{cm}^{-1}$  and 1642  $\text{cm}^{-1}$  correspond to  $-\text{OH}$  and  $\text{C}=\text{O}$  stretching vibrations<sup>7,8</sup>. Hence, IR spectra show the formation of  $-\text{SO}_3\text{H}$  groups at AC surface.

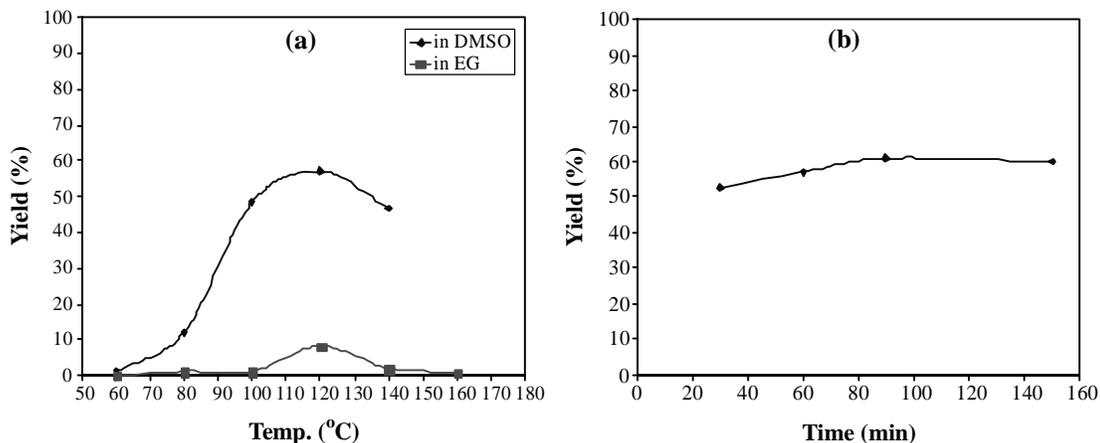
The presence of sulfur in all samples was made in evidence by SEM-EDS spectrum (Fig. 2). It was clear that the quantity of sulfur in ambelyst-15 sample 19.7% is much higher than one in AC- $\text{SO}_3\text{H}$ , 0.25%.



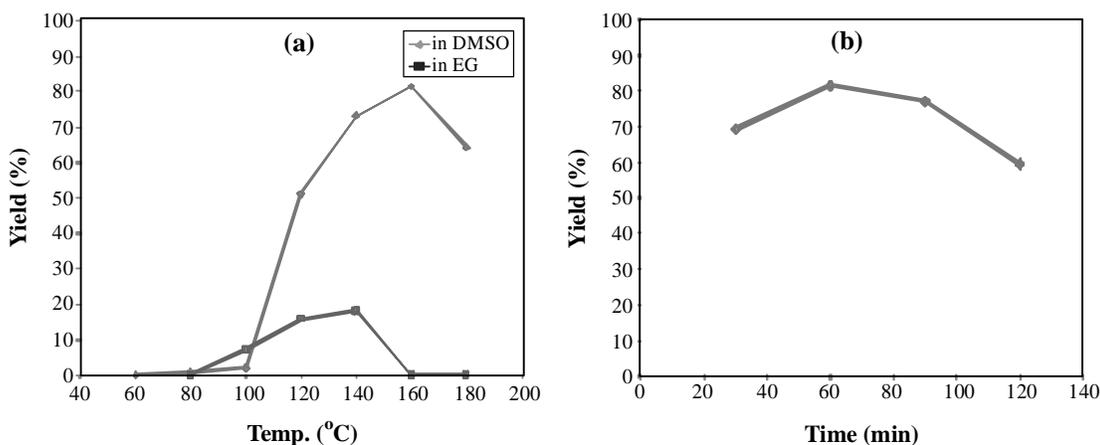
**Fig. 2: SEM-EDS spectra of AC- $\text{SO}_3\text{H}$  (a) and amberlyst-15 (b)**

### Catalytic activity

Catalytic activity was estimated for the two catalysts AC- $\text{SO}_3\text{H}$  and amberlyst-15. The reaction temperature, the reaction time and the solvent were three parameters envisaged. The Fig. 3a presents the HMF yield in function of temperature in case of catalyst AC- $\text{SO}_3\text{H}$ . In DMSO solvent, the HMF yield increased rapidly with the augmentation of temperature, from 60 to 100°C, and attained maximum value of 57% at 120°C. At higher temperature, the HMF yield diminished. It was possible that at higher temperature, the second reactions took place, such as levulinic acid or/and humic formations<sup>9</sup>. In EG solvent, the HMF yield was very weak and the maximum value is only 8% at 120°C. It is possible that, in EG solvent, there are interactions of  $-\text{OH}$  groups of EG molecule with  $-\text{SO}_3\text{H}$  groups of catalyst conducting to diminution of the number of active centre on catalyst surface. That leads to the blocking of acid site, which is the catalytic site for dehydration of fructose into HMF<sup>10</sup>. In addition, the result of Tsilomelekis and al.<sup>11</sup> indicated that HMF molecules were stabilized in DMSO solvent. This one avoided further reaction with HMF formed. The same behaviours were also observed in case of catalyst amberlyst-15 (Fig. 4). However, HMF yield was still higher than the one for AC- $\text{SO}_3\text{H}$  catalyst. The maximum values were 81%, 19% for solvent DMSO, EG and at 160°C, 140°C, respectively.



**Fig. 3: HMF yield in function of temperature (a) and time reaction (b) on AC-SO<sub>3</sub>H catalyst**



**Fig. 4: HMF yield in function of temperature (a) and time reaction (b) on amberlyst-15**

At optimal condition of temperature and in solvent DMSO, the reaction time was also estimated. The Figs. 3b and 4b represent the obtained results. It was observed that for catalyst amberlyst-15, reaction time had more influences on yield of HMF than in case of AC-SO<sub>3</sub>H. The best HMF yields attained were 60%, 81% for reaction time of 90 min, 60 min for AC-SO<sub>3</sub>H, amberlyst-15, respectively.

In general, the number of catalytic centre -SO<sub>3</sub>H is proportional with S content of catalyst. That explains why catalytic activity of amberlyst-15 was better than one of

AC-SO<sub>3</sub>H. However, it was noted that S content of amberlyst-15 is nearly 80 times higher than one of AC-SO<sub>3</sub>H, 19% and 0,25%, while the activity difference between tow catalysts was only 21%. It was possible that the catalyst morphologies also concerns to catalytic activity. In case of amberlyst-15, although this catalyst owned much higher number groups -SO<sub>3</sub>H, the number accessible groups -SO<sub>3</sub>H for reaction was limited. Observing the SEM-EDS spectra, it was clear that amberlyt-15 particle was much larger and denser than AC-SO<sub>3</sub>H catalyst particle. This observation was in accordance with the explanation above. Indeed, catalytic activity of these catalysts was promotional with the number accessible of groups -SO<sub>3</sub>H.

## CONCLUSION

The fructose conversion into HMF was investigated with the presence of acid solid catalysts: sulfonated active carbone and amberlyst-15. The sulfonation on activated carbone surface was confirmed by IR spectra and EDX analysis. Their catalytic activity results showed the much higher yield of HMF in DMSO solvent than in EG due to the interaction between groups -OH of EG with ones -SO<sub>3</sub>H, which caused the blocking of this catalytic acidic site. In case of catalyst amberlyst-15, the highest HMF yield was 81% in optimal condition of 160°C, 60 mins. In case of catalyst AC-SO<sub>3</sub>H, the maximum value of HMF yield was 60%, at 120°C and 90 mins. This result indicated that HMF yield seems to be proportional with the number of accessible groups -SO<sub>3</sub>H reflected by SEM-EDS analysis. Therefore, a better sulfonation process is needed to find out to improve catalytic activity of catalyst AC-SO<sub>3</sub>H, which is a cheaper and more environmental friendly than amberlyst-15 made from fossil material source.

## ACKNOWLEDGEMENT

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