Article

Journal of
Nanoscience and Nanotechnology
Vol. 16, 4631–4637, 2016
www.aspbs.com/jnn

Catalytic Fast Pyrolysis of Cellulose Using Nano Zeolite and Zeolite/Matrix Catalysts in a GC/Micro-Pyrolyzer

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Cellulose, as a model compound of biomass, was catalyzed over zeolite (HY, HZSM-5) and zeolite/matrix (HY/Clay, HM/Clay) in a GC/micro-pyrolyzer at 500 °C, to produce the valuable products. The catalysts used were pure zeolite and zeolite/matrix including 20 wt% matrix content, which were prepared into different particle sizes (average size; 0.1 mm, 1.6 mm) to study the effect of the particle size of the catalyst for the distribution of product yields. Catalytic pyrolysis had much more volatile products as light components and less content of sugars than pyrolysis only. This phenomenon was strongly influenced by the particle size of the catalyst in catalytic fast pyrolysis. Also, in zeolite and zeolite/matrix catalysts the zeolite type gave the dominant impact on the distribution of product yields.

Keywords: Cellulose, Catalytic Fast Pyrolysis, Zeolite (or Zeolite/Matrix), Particle Size of Catalyst, Valuable Products.

1. INTRODUCTION

Biomass is a renewable resource with high potential for energy production, and includes wood, wood wastes, agricultural residues, municipal solid wastes and energy crops, etc.,[1] which is the fourth largest energy source in the world with about 15% of the world's primary energy consumption.[2,3] Furthermore, lignocellulosic biomass as a sustainable carbon source is an abundant and inexpensive energy resources.

Because of the production of renewable energy as an alternative energy source for conventional energy like petroleum and coal, the conversion of biomass into bio-oil has an attractive option in the past few ten years.[4–6] Among the several conversion technologies, fast pyrolysis for producing mainly bio-oil has received a significant attention; it is accomplished by a simple thermal decomposition process that occurs at atmospheric pressure, moderate temperature, and oxygen-absent environments with a high heating rate.[7] However, the bio-oil produced from fast pyrolysis has low quality being more acidic, viscous, reactive and thermally unstable,[8,9] which are characteristics considerably different from those of petroleum oils.

Thus, in order to produce high quality bio-oil, the use of a catalyst in fast pyrolysis is necessary. Among the potential catalysts, a catalyst including zeolite has received much attention, due to its great effect in the cracking and deoxygenation of oxygenated biomass.[10–15] The physicochemical properties of the catalyst has an important impact on the production of high quality bio-oil from catalytic pyrolysis of biomass.[1,16–20]

The cellulose was used as a model compound in this reaction. In the catalyst, two patterns of zeolite and zeolite/matrix catalysts with clearly different particle sizes were screened in a micro-pyrolyzer system to produce the valuable products from *in situ* catalytic fast pyrolysis of cellulose. Thus, this study aimed at exploring the effect of the particle size of catalyst and also the zeolite type in zeolite and zeolite/matrix catalysts, to determine their relative abilities to crack into light hydrocarbon products for the cellulose and moreover produce aromatic hydrocarbons by means of the cyclization of light hydrocarbons.

2. EXPERIMENTAL DETAILS

2.1. Materials

Cellulose with a micro-particle size (50 μm) bought from Sigma-Aldrich, as a reactant, was used in this experiment. The content of moisture, volatile compounds, fixed carbon and ash of cellulose was measured by a TGA.

1533-4880/2016/16/4631/007

doi:10.1166/jnn.2016.11015

Approximately 20 mg of cellulose was used for each analysis. This was heated in 100 mL/min of N_2 from 25 °C to 105 °C with 10 °C/min and held at 105 °C for 40 minutes to measure the content of moisture in the cellulose, and then it was raised up to 900 °C with 10 °C/min and held for 20 minutes to quantify the volatiles. Finally, 100 mL/min of air was introduced at 900 °C for 30 minutes to measure the fixed carbon. The content of ash was determined by the final weight of the sample in the TGA analysis. This result revealed that the volatile compounds had 91.8 wt% content, the fixed carbon was about 4.1 wt% and the ash had a very low content at about 0.05 wt%, as shown in Table I.

As a solid acidic catalyst, commercial zeolites (HY, HZSM-5) were obtained from Zeolyst Co. (U.S.A.), and also commercial zeolite/matrix catalysts including 20 wt% clay content (HY/Clay, HM/Clay) were obtained from Tosoh Co. (Japan). The zeolites have different pore size and pore structure. Among the zeolite catalysts, HY and HZSM-5 are well known as further efficient acidic catalysts used widely in commercial processes like petroleum refinery process. Clay, alumina and silica-alumina were also used as a matrix in commercial catalysts. Commercial HZSM-5 and HY catalysts have three-dimension pore structure with different pore size, whereas HM catalyst shows one-dimension pore structure with medium pore size, as shown in Table II.

In order to ascertain the effect of the particle size of the catalyst in catalytic fast pyrolysis, the catalyst was ground into a particle size of about 0.1 mm and was also used with a commercial particle size of 1/16 inch (as 1.6 mm), without grinding it. Their particle size is clearly differed with 15 times or over. These catalysts were appeared as the name of Zeolite/Clay (0.1) or Zeolite/Clay (1.6).

Before the reaction, the catalysts were preheated at 500 °C for 3 hours in air. The surface area and total pore volume of the catalyst were obtained from nitrogen adsorption isotherms measured at liquid-nitrogen temperature (Micromeritics, ASAP-2000). Surface areas were determined using the BET equation within a relative pressure of 0.2, and total pore volume was obtained at a relative pressure of about 0.99.

Table III shows physical properties of zeolite and zeolite/matrix catalysts. In zeolite catalysts HY catalyst had higher surface area and total pore volume than HZSM-5 catalyst. On the other hand, in a comparison of zeolite and zeolite/clay catalysts HY/Clay catalyst had lower surface area and pore volume than pure HY, and Further HM/Clay catalyst including HM with one-dimensional pore structure had lower surface area and pore volume than HY/Clay catalyst.

Table I. TGA analysis of cellulose (wt%).

Items	Values
Moisture	4.032
Volatile	91.852
Fixed carbon	4.063
Ash	0.053

Table II. Pore structure of zeolites.

Zeolite type	Frame work	Pore dimension	Pore size (Å)
HZSM-5	MFI	3	5.1 × 5.5 5.3 × 5.6
HY	FAU	3	7.4 × 7.4
HM	MOR	1	6.5 × 7.0 2.6 × 5.7

2.2. Micro-Pyrolyzer-GC/FID Experiments

The pyrolysis and catalytic pyrolysis experiments were conducted using a single-shot micro-pyrolyzer equipped with an autosampler (Frontier Laboratories, Japan). The micro-pyrolyzer was directly connected to a GC analyzer with a FID, which was automatically conducted by the operation control in a combination system between the micro-reactor and gas analyzer.

For the experimental conditions, the furnace was mainatined at a temperature of 500 °C. The reactant of about 500 μg was first placed into a stainless steel sample cup and then the catalyst of about 5 g was loaded at upper of reactant. Finally, the quartz wool was put at top of the sample cup and thus both the catalyst and reactant were fixed within sample cup, which was dropped into the furnace of pyrolyzer with very short drop time (with unit of milliseconds) under the flow of 20 cm/s helium gas.

In product analysis, the products were separated using an alloy capillary column (Ultra Alloy-1701, Frontier Laboratories, Japan) with a carrier gas flow of 1 ml/min. For GC conditions, the injector temperature and split ratio were 300 °C and 1:100, respectively, and the oven temperature program began at 35 °C, held 3 min at 35 °C and then heated to 300 °C at 5 °C/min, held for 4 min at that temperature.

2.3. Qualitative and Quantitative Analysis of Product Compounds

Qualitative analysis of each product in all the compounds was conducted by a comparison with both the mass spectra of the peaks and the standard spectra using the NIST library in the GC-MS. In addition, literatures of other researchers were used to identify the peaks in a

Table III. Physical properties of catalysts.

Catalyst type	Catalyst name	Ave. particle size (mm)	BET surface area (m^2/g)	Total pore volume (cc/g)
Pure zeolite	HY(0.08/0.1/1.6)	0.08/0.1/1.6	690	0.51
	HZSM-5(0.1/1.6)	0.1/1.6	351	0.37
Zeolite/ matrix	HY/Clay(0.1/1.6)*	0.1/1.6	476	0.32
	HM/Clay(0.1/1.6)*	0.1/1.6	390	0.20

Note: *Zeolite content in zeolite/matrix catalysts : 80 wt%.

gas chromatograph.[21] Literature comparison over identified compounds was performed for all products obtained in a pyrolyzer-GC/FID system using a similar column and reactant. In addition, pure compounds bought from commercial companies like Sigma-Aldrich were used to identifiy the peaks in the gas chromatograph of products as a function of the retention time.

Quantative analysis of the confirmed compounds in the gas chromatograph was also conducted by calibration of pure compounds in the GC/FID system. The calibration curves were calculated from a straight line of three points or over, in which solution concentrations made by methanol with HPLC grade were determined by a consideration of the concentration range of each compound in the product.

3. RESULTS AND DISCUSSION

3.1. Zeolite

For the fast pyrolysis in the micro-pyrolyzer, the catalyst that was prepared into both large or small particle sizes was horizontally placed above the reactant within a very small steel cup reactor. When the catalytic fast pyrolysis was conducted, the cellulose decomposed in a very short time to produce a complex mixture of the product. The product composition depended on the experimental condition (temperature, pressure, catalyst amount, etc.,) and catalyst type.[12, 22] In this study, the products were measured using only the GC-FID system. Thus, this system cannot dictate the gas products like carbon monoxide, carbon dioxide and hydrogen products.

In gas chromatograph of Figure 1, volatile products that appeared at a shortest retention time consist of a few compounds in the product like CO, CO_2 and CH_4, but are presented as one biggest peak, because of the difficulty of separation of volatile products in the GC column at 35 °C oven temperature. The peak area of volatile products obtained in both non-catalytic and catalytic pyrolysis depends on the degree of cracking reaction of the cellulose with high molecular weight. If the cellulose is much more cracked into light products by using the catalyst, the peak area of the volatile products among all the products is strongly increased. On the contrary, low molecular products like acetic acid, acetaldehyde, etc., were clearly presented as the sharp peak of each component in the gas chromatograph. Thus, these products can be quantatively calculated as product yields, based on the amount of reactant.

Figure 2 shows the relative peak area (RPA) values of volatile products based on the same reactant amount, according to type of catalyst. There is a clear difference between non-catalytic and catalytic pyrolysis. Catalytic pyrolysis has a much higher RPA value than non-catalytic pyrolysis, because of good cracking activity of acidic catalyst. In catalytic pyrolysis, the HZSM-5 catalyst has a higher RPA value than the HY catalyst, which is influenced by the zeolite type. Also zeolite catalysts with small particle size has a much higher RPA value than zeolite catalysts with large particle size. Zeolite with a small particle size has much large external surface area per gram of catalyst. This can be explained that zeolite with a large external surface area has a merit in the cracking reaction against cellulose with a large molecular weight, because the cellulose is unable to enter the micropores of zeolite catalysts. This reaction mechanism suggests that the cellulose is first cracked at active sites on external surface of particle in zeolite and then the cracked intermediates is further cracked and transformed into small light products in

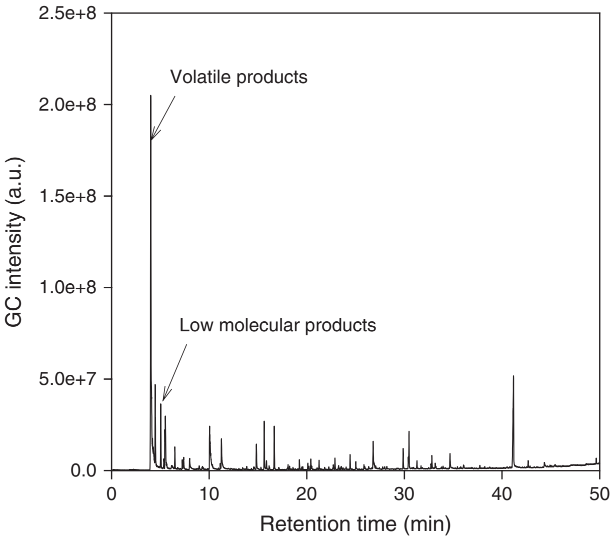

Figure 1. Sample of GC chromatograph of products obtained from catalystic fast pyrolysis of cellulose at 500 °C.

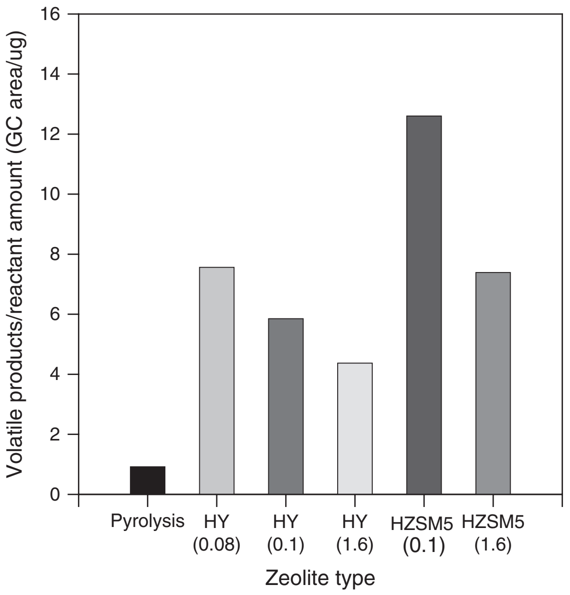

Figure 2. Effect of particle size of zeolite catalysts on volatile products (as a main product) from catalystic fast pyrolysis of cellulose at 500 °C.

active sites within micropores of zeolite. Thus, this result shows that the HZSM-5 catalyst with a small particle size is much prevalent in cracking activity to produce a light product, compared to the HZSM-5 of large particle size.

Table IV shows the distribution of product yields obtained from fast non-catalytic and catalytic pyrolysis over pure zeolites (HY, HZSM5) with different particle sizes. A large components from non-catalytic and catalytic fast pyrolysis of cellulose were produced. We describe the main products with 28 components present in at least 0.01 wt% yield among many products, which are classified as groups of low molecular products, furans, methylcyclopentenone, mono-rings, phenol, polyaromatic hydrcarbons (PAHs) and sugars. Volatile products described previously as the lightest components in all products are excepted from these groups, although volatile products are largest amount amoung all the products obtained in catalytic pyrolysis, like the high peak for volatile products in GC peaks shown in Figure 1. From this reason, the total yield of other main products obtained in catalytic pyrolysis is a very low value, compared to non-catalytic pyrolysis.

The distribution of product yields was relatively compared over both pyrolysis only and catalytic pyrolysis, and also in catalytic pyrolysis the effect of the zeolite type (HY, HZSM-5) was studied. In the non-catalytic pyrolysis, the sugars with high molecular weight had high yield with about 62 wt% in the product and further main product among sugars was levoglucosan component, which is produced by the structural properties of the stereochemistry of cellulose. This result shows that non-catalytic pyrolysis of cellulose at 500 °C temperature does not crack well into light products with low molecular weight. On the other hand, in the catalytic pyrolysis the sugar products had very low yields, because of more cracking of cellulose using acidic zeolite catalyst. For other products, non-catalytic pyrolysis has a higher yield of light products

Table IV. Distribution of product yields from catalytic pyrolysis of cellulose over pure zeolites with different particle size at 500 °C.

	Yield (wt%)					
Name	Pyro.	HY(0.08)	HY(0.1)	HY(1.6)	HZSM5(0.1)	HZSM5(1.6)
Low molecular products						
Acetic acid	0.17	0.04	0.34	0.03	0.50	0.37
Acetaldehyde	0.58	3.62	3.44	3.66	1.81	2.09
Glycolaldehyde	7.16	0.47	0.11	1.64	–	1.97
Methyl glyoxal	1.02	–	–	0.17	0.13	0.20
Acetone	0.04	0.32	0.41	0.26	0.25	0.17
Acetol	0.36	0.01	0.02	0.13	0.01	0.14
Sum	**9.33**	**4.47**	**4.32**	**5.89**	**2.70**	**4.94**
Furan groups						
Furan	0.07	0.24	0.30	0.51	0.12	0.31
2-Methylfuran	0.04	0.04	0.07	0.21	0.05	0.17
Furfural	0.33	0.13	0.07	0.66	0.04	0.65
2-Furanmethanol	0.07	0.02	0.03	0.06	0.01	0.10
3-Furanmethanol	0.04	0.01	0.02	0.04	0.01	0.04
5-Methyl furfural	0.05	0.01	0.01	0.05	0.01	0.05
2(5H) Furanone	0.10	0.01	0.01	0.05	0.41	0.07
5-Hydroxymethylfurfural	0.98	0.01	0.01	0.13	0.05	0.34
Sum	**1.67**	**0.45**	**0.50**	**1.70**	**0.68**	**1.74**
Methylcyclopentenone	0.08	0.01	0.01	0.04	0.01	0.05
Mono-rings						
Benzene	–	0.08	0.08	0.08	0.87	0.41
Toluene	–	0.17	0.18	0.13	1.74	0.77
p-Xylene	–	0.07	0.10	0.07	0.99	0.42
O-Xylene	0.01	0.02	0.04	0.03	0.24	0.10
Sum	**0.01**	**0.34**	**0.40**	**0.35**	**3.84**	**1.70**
Phenol	0.88	0.05	0.04	0.10	0.21	0.20
PAHs						
Naphthalene	–	0.09	0.07	0.08	0.79	0.43
2-Methylnaphthalene	–	0.04	0.05	0.05	0.76	0.38
Dimethylnaphthalene	–	0.01	0.02	0.01	0.14	0.07
Anthracene	–	–	0.01	0.01	0.17	0.09
Sum		**0.14**	**0.15**	**0.15**	**1.85**	**0.98**
Sugars						
Levoglucosene	0.11	0.03	0.02	0.04	0.17	0.15
Anhydroxylopyanose	2.58	0.02	0.01	0.36	–	0.97
Levoglucosan-pyranose	55.50	0.10	0.01	5.32	0.10	12.40
Levoglucosan-furanose	3.84	0.02	0.01	0.24	0.01	1.24
Sum	**62.03**	**0.17**	**0.03**	**5.93**	**0.11**	**14.61**

like glycoaldehyde, acetol, etc., than those of catalytic pyrolysis using HY and HZSM-5 catalysts, whereas catalytic pyrolysis (HY, HSZM-5) produced much prevalent in aromatic products, such as mon-rings and polyaromatic hydrocarbons (PAHs), by means of the cyclization of the intermediates cracked within pores of zeolite catalysts. Moreover, in aromatic product distribution the HZSM-5 catalyst shows much higher yields of polyaromatic hydrocarbons like naphthalene and methylnaphthalene etc., as well as a mono-rings structure than those of the HY catalyst. This means that HZSM-5, which has a 3D network of interconnected pores arranged in straight 5–6 Å pore diameter channels, has an advantage over the production of aromatic components with one- or two-ring structures. In this study, the efficiency of the zeolite catalysts was monitored by comparing quantitative analysis to all compounds associated with the zeolite type. From these results, the product distribution from catalytic fast pyrolysis of cellulose strongly depends on zeolite type.

On the other hand, the effect of particle size of the catalyst on the distribution of product yield from catalytic fast pyrolysis of cellulose using pure zeolite was investigated. The catalyst with a large particle size had a diameter size of about 16 times larger, compared to that of the small particle size, which clearly differed by particle size of the catalyst for both catalysts. In the distribution of product yields for pure HY and HZSM-5 catalysts, catalytic pyrolysis using zeolite with large particle size produced much more acids and aldehydes products with light molecular weight, and also more furan groups and sugar produsts than that using zeolite with small particle size. According to the increase in particle size of zeolite catalysts, this tendency over the distribution of product yields gradually approached that of pyrolysis only, whereas the case using zeolite catalysts with a small particle size, with the reverse effect, is much improved for mono-rings and polyaromatic hydrocarbon products produced from cyclization of straight light hydrocarbons. This means that the reduction of particle size of the catalyst improves the catalyst ability in the catalytic pyrolysis of polyorganic hydrocarbons. This explanation is that because the catalyst with a small particle size has large external surface area, the organic polymer reactant with a large molecular weight is easily cracked into light hydrocarbons on active sites of large external surface area and then cracked intermediaries are aromatized into mono-ring and polyaromatic compounds within the pores of the zeolite. This result is very apparent in the HZSM-5 catalyst prepared into a small particle size. This is attributed to the impact of the particle size of zeolite as well as the zeolite type on distribution of product yields.

3.2. Zeolite/Matrix

The characteristics of catalytic pyrolysis products over the mixing catalysts consisting of both zeolite and clay (HY/Clay, HM/Clay) is investigated. The RPA values of volatile products, as lightest products among all products, over the mixing catalysts with a different zeolite type and also particle size is shown in Figure 3. The degree of RPA value means the cracking ability of catalyst to produce light products like described previously. As a zeolite type in the mixing catalysts, two cases including H-mordenite(HM) or HY are relatively compared. HM has one-dimensional pore structure and also consists of small pores as well as medium pores, whereas HY is a three-dimensional pore structure with medium pores, as shown in Table II. In addition, the HY/Clay catalyst has larger surface area and larger pore volume than HM/Clay, as shown in Table III. This means that the diffusion ability of the reactant and product within pores of catalyst are much more prevalent over HY than that of HM. These physical properties suggest that the catalysts including HY have higher cracking activity of cellulose than the HM/Clay catalysts. Thus, the HY/Clay catalysts have a much higher RPA value as the production degree of light products than the HM/Clay catalysts, as shown in Figure 3.

The effect of particle size of catalysts in volatile products over both HY/Clay and HM/Clay catalysts is also investigated. These results are appeared in Figure 3. The case having a small particle size has a higher RPA value in volatile products than that of the catalyst with a large particle size, like the case of pure zeolite described previously, because of efficient cracking of large molecules at active sites existed on a large external surface area of catalyst. However, the case including mordenite that has poor physical properties show only a slight difference on the degree of volatile products between HM/Clay with a small particle size and that of large particle size. There is no effect of particle size in HM/Clay catalysts. This implies

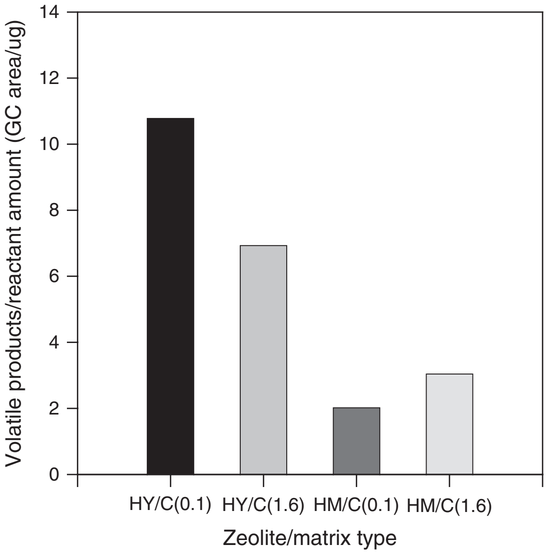

Figure 3. Effect of particle size of zeolite/matrix catalysts on volatile products(as a main product) from catalytic fast pyrolysis of cellulose at 500 °C.

that mordenite as a main activity, rather than clay, does not has a sufficient role in catalytic cracking of cellulose. Thus, in the catalysts including mordenite with poor physical properties the particle size of catalyst does not a key role in the cracking ability of large molecules, whether the particle size of the catalyst is large or small.

The distribution of product yields obtained from catalytic fast pyrolysis of cellulose over HY/Clay and HM/Clay catalysts with different particle sizes is shown in Table V. In a comparison of both pyrolysis only and catalytic pyrolysis using a zeolite/clay catalyst, the catalytic pyrolysis had lower sugar content and more ring compounds than those of pyrolysis only, which is similar to the case of pure zeolite described previously. The particle size of the catalyst in zeolite/clay catalysts has a strong influence on the distribution of product yields from catalytic pyrolysis of cellulouse. That is, according as the particle size of the catalyst is decreased, its external surface area is much increased. Thus, the content of sugars with large molecule weight in product distribution is much lowered, because of more cracking of large molecule materials at external active sites of mixing catalysts with large external surface area. This means that the large molecule compounds are easily cracked into light molecules at external active sites existing on large external surface area of the catalyst having small particle size. Also, owing to the pore influence of zeolite in zeolite/clay catalysts, the small intermediates cracked are again diffused into micropores of zeolite and then cracked into smaller light products like volatile products, and cycled into the ring compounds like mono-rings and polyaromatic hydrocarbon products at internal active sites within pore of zeolite. However, in zeolite/clay catalysts the mixing catalysts including HM that has poor physical properties has higher content of sugars, furan groups and much less mono-ring products than those of HY/Clay. This tendency over the HM/Clay

Table V. Distribution of product yields from catalytic pyrolysis of cellulose over zeolite/matrix with different particle size at 500 °C.

	Yield (wt%)				
Name	Pyro.	HY/Clay(0.1)	HY/Clay(1.6)	HM/Clay(0.1)	HM/Clay(1.6)
Low molecular products					
Acetic acid	0.17	0.27	0.10	0.23	0.30
Acetaldehyde	0.58	3.61	4.34	1.04	1.19
Glycolaldehyde	7.16	0.22	1.39	2.26	2.38
Methyl glyoxal	1.02	0.13	0.20	0.43	0.15
Acetone	0.04	0.33	0.33	0.08	0.06
Acetol	0.36	0.03	0.10	0.25	0.32
Sum	**9.33**	**4.59**	**5.46**	**4.29**	**4.40**
Furan groups					
Furan	0.07	0.15	0.34	0.24	0.15
2-Methylfuran	0.04	0.05	0.10	0.11	0.08
Furfural	0.33	0.01	0.38	0.97	0.69
2-Furanmethanol	0.07	0.01	0.05	0.10	0.11
3-Furanmethanol	0.04	0.04	0.02	0.04	0.04
5-Methyl furfural	0.05	–	0.03	0.13	0.09
2(5H) Furanone	0.10	–	0.04	0.04	0.12
5-Hydroxymethylfurfural	0.98	0.01	0.27	0.59	0.76
Sum	**1.67**	**0.27**	**1.25**	**2.21**	**2.04**
Methylcyclopentenone	0.08	0.01	0.04	0.05	0.09
Mono-rings					
Benzene	–	0.14	0.09	0.01	–
Toluene	–	0.27	0.15	0.04	0.05
p-Xylene	–	0.11	0.07	0.04	0.03
O-Xylene	0.01	0.04	0.04	0.02	0.04
Sum	**0.01**	**0.59**	**0.38**	**0.12**	**0.16**
Phenol	0.88	0.02	0.08	0.09	0.08
PAHs					
Naphthalene	–	0.09	0.09	0.05	0.07
2-Methylnaphthalene	–	0.04	0.04	0.02	0.04
Dimethylnaphthalene	–	0.01	0.01	0.02	0.02
Anthracene	–	–	0.01	0.01	0.01
Sum		**0.15**	**0.16**	**0.10**	**0.13**
Sugars					
Levoglucosene	0.11	0.03	0.03	0.47	0.05
Anhydroxylopyanose	2.58	0.01	0.45	2.21	1.57
Levoglucosan-pyranose	55.50	0.02	10.35	11.01	32.58
Levoglucosan-furanose	3.84	0.02	0.77	1.64	2.64
Sum	**62.03**	**0.08**	**11.60**	**15.33**	**36.84**

catalyst is approached to that of pyrolysis only. This means that if the ability of a catalyst like the HM/Clay catalyst is not sufficient, the result obtained is roughly similar to that of pyrolysis only, as high sugar and low ring compounds content in product distribution.

On the other hand, in a comparison of both the zeolite/clay catalyst (Table V) and pure zeolite catalyst (Table IV), the distribution of product yields over HY/Clay (0.1, 1.6) and pure HY (0.1, 1.6) has a slight difference in low molecular products, furan groups, ring compounds and sugars. HY/Clay catalysts, compared to pure HY catalyst, consists of 80 wt% zeolite content and 20 wt% clay content. Although the content of zeolite in the zeolite/clay catalyst is lowered and also the HY/Clay catalyst has much less surface area than pure HY catalyst (Table III), the performance of the catalyst in both pure zeolite and zeolite/clay catalysts does not clearly differ. In the case of pure HY (0.1) and HY/Clay (0.1) catalysts with a small particle size, HY/Clay (0.1) catalyst with low zeolite content and also low BET surface area produces rather a higher fraction of volatile products, little more mono-ring products and less furan groups than those of pure HY (0.1) catalyst, although mono-ring products mainly occur from the zeolite effect. This means that the clay with mesopore in zeolite/clay catalyst is a little role at fast pyrolysis of cellulose with large molecular weight. Thus, the support like clay must be also well controlled in the prearation of mixing catalyst to have the adequate cracking of reactant with large molecular weight and also to lower the price of catalyst. Although the particle size and zeolite type in both zeolite and zeolite/clay catalysts are key factors in catalytic fast pyrolysis of large molecular.

4. CONCLUSIONS

Catalytic fast pyrolysis of cellulose using zeolite and zeolite/matrix catalysts in a GC/pyrolyzer was investigated. The catalysts were prepared into different particle size with 0.1 and 1.6 mm diameter, respectively. Catalytic pyrolysis had high fraction of volatile products and little content of sugars with high molecular weight, compared to those of pyrolysis only. In catalytic pyrolysis, more volatile products was produced, according to decrease the particle size of the catalyst, and also the zeolite type gave much more influence on the distribution of product yields than the matrix. Among the catalysts used, HZSM-5 catalyst with a small particle size produced much more mono-rings and also naphthalene groups, as valuable products without oxygen. This can be concluded that the particle size of catalyst, as well as the zeolite type in the catalytic fast pyrolysis of cellulose were keys to controlling the distribution of product yields.

Acknowledgments: This work was partially conducted under the framework of Research and Development Program of the Korea Institute of Energy Research(KIER) (B4-2434-02).

References and Notes

1. J. Yanik, C. Kornmayer, M. Saglam, and M. Yuksel, *Fuel Process. Technol.* 88, 942 (**2007**).
2. I. Demiral, A. Eryazici, and S. Sensoz, *Biomass Bioenergy* 36, 43 (**2012**).
3. S. Czernik and A. V. Bridgwater, *Energy Fuels* 18, 590 (**2004**).
4. M. Krzesinska, M. B. Pilawa, S. Pusz, and J. Ng, *Biomass Bioenergy* 30, 166 (**2006**).
5. H. B. Goyal, D. Seal, and R. C. Saxena, *Renew. Sust. Energy Rev.* 12, 504 (**2008**).
6. Y.-K. Park, S. J. Choi, J.-K. Jeon, S. H. Park, R. Ryoo, J. Kim, and K.-E. Jeong, *J. Nanosci. Nanotechnol.* 12, 5367 (**2012**).
7. P. Pan, C. Hu, W. Yang, Y. Li, L. Dong, L. Zhu, D. Tong, R. Qing, and Y. Fan, *Bioresour. Technol.* 101, 4593 (**2010**).
8. D. Mohan, C. U. Pittman, and P. H. Steele, *Energy Fuels* 20, 848 (**2006**).
9. Q. Zhang, J. Chang, T. J. Wang, and Y. Xu, *Energy Convers. Manage.* 48, 87 (**2007**).
10. P. T. Williams and P. A. Horne, *J. Anal. Appl. Pyrol.* 31, 39 (**1995**).
11. J. D. Adjaye and N. N. Bakhshi, *Fuel Process. Technol.* 45, 161 (**1995**).
12. S. Vichaphund, D. Aht-ong, V. Sricharoenchaikul, and D. Atong, *Renew. Energy* 65, 70 (**2014**).
13. M. Olazar, R. Aguado, J. Bilbao, and A. Barona, *AICHE J.* 46, 1025 (**2000**).
14. Z. G. Ma and J. A. van Bokhoven, *Chem. Cat. Chem.* 4, 2036 (**2012**).
15. K.-H. Lee, *J. Anal. Appl. Pyrolysis* 94, 209 (**2012**).
16. H. Zhang, R. Xiao, B. Jin, G. Xiao, and R. Chen, *Bioresour. Technol.* 140, 256 (**2013**).
17. S. Thangalazhy-Gopakumar, S. Adhikari, S. A. Chattanathan, and R. B. Gupta, *Bioresour. Technol.* 118, 150 (**2012**).
18. K.-H. Lee and S. H. Oh, *J. Anal. Appl. Pyrolysis* 93, 19 (**2012**).
19. J. W. Kim, S. H. Joo, B. Seo, S.-S. Kim, D.-H. Shin, S. H. Park, J.-K. Jeon, and Y.-K. Park, *J. Nanosci. Nanotechnol.* 13, 2566 (**2013**).
20. H. W. Lee, T. H. Kim, S. H. Park, J.-K. Jeon, D. J. Suh, and Y.-K. Park, *J. Nanosci. Nanotechnol.* 13, 2640 (**2013**).
21. D. Fabbri, C. Torri, and V. Baravelli, *J. Anal. Appl. Pyrolysis* 80, 24 (**2007**).
22. G. Lu, Y. Zhang, Z. Tang, W.-Z. Li, and X.-F. Zhu, *Fuel* 89, 2096 (**2012**).

Received: 9 October 2014. Accepted: 20 November 2014.