

## 커피 잔류물을 함유한 폐종이컵의 촉매 열분해

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### Catalytic Pyrolysis of Waste Paper Cup Containing Coffee Residuals

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#### 초 록

고정층 반응기와 파이롤라이저-가스크로마토그래피/질량분석기를 이용하여 커피 잔류물이 함유된 폐종이컵의 열분해 및 촉매 열분해를 진행하였다. 커피 잔류물이 함유된 종이컵의 무촉매 열분해에서는 많은 양의 오일이 가스 및 촉매와 함께 형성되었다. HZSM-5와 HY 촉매의 사용에 따른 추가적인 분해 반응에 의해 오일의 양은 줄고 가스의 양은 증가하였다. HZSM-5와 HY의 산촉매 특성 때문에 커피 잔류물이 함유된 종이컵의 촉매 파이롤라이저-가스크로마토그래피/질량분석기 분석은 생성오일 중 방향족 화합물의 선택도를 증가시켰다. HY보다 강한 산세기와 중간 기공을 가진 HZSM-5의 특성으로 인해, HZSM-5상에서 커피 잔류물이 함유된 종이컵을 촉매 열분해한 경우 HY를 사용한 경우보다 훨씬 더 많은 양의 방향족 화합물이 생성되었다.

#### Abstract

Catalytic pyrolysis of the waste paper cup containing coffee residual (WPCCCR) was performed using a fixed bed reactor and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). Non-catalytic pyrolysis of WPCCCR produced a large amount of oil together with gas and char. The use of both HZSM-5 and HY decreased the yields of oil and increased the yield of gas due to the additional catalytic cracking. Owing to the acidic catalytic properties of HZSM-5 and HY, catalytic Py-GC/MS analysis of WPCCCR increased the selectivity to aromatic hydrocarbons in product oil. Owing to properties of HZSM-5 having a stronger acidity and medium pore size, the catalytic pyrolysis of WPCCCR over HZSM-5 produced much larger amounts of aromatic hydrocarbons than that of using HY.

**Keywords:** waste paper cup, coffee residual, Py-GC/MS, HZSM-5, HY

### 1. Introduction

Owing to the increasing global environmental pollution, climate warming, and energy depletion, many researchers are focusing on research to produce energy from wastes[1,2]. In addition, the amount of daily disposable products used in the modern society is being increased exponentially together with the rise in national income and living standard. Although annual consumption of paper cups, a typical disposable product, is continuously increasing, most of them are recycled as low quality paper boxes even if only a part of them are recycled and recyclable. Recycling ratio of paper cups is low because most of

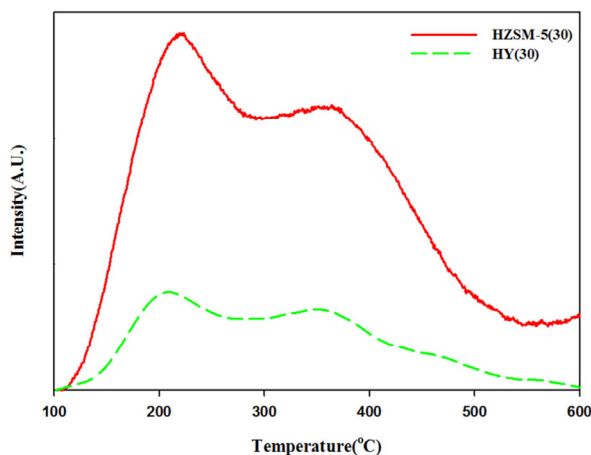
paper cups are coated with plastics such as polyethylene and considerable quantity of waste paper cup (WPC) contain beverages and coffee residues. Citizens' movement is actively centered on environmental groups that want to reduce the use of low-recycling disposable items such as paper cups, but the use of disposable paper cups is still increasing. Most of WPC are treated by landfill or incineration. Degradation efficiency of WPC in a landfill site is low because the polyethylene plastic coating material used in the paper cup blocks the movement of air and moisture required for microbial propagation. Large amount of environmental pollutants can be emitted when plastic coated WPCs are treated by incineration. Therefore, the more efficient method is demanded for the treatment of WPCs.

Research on heat conversion technology of combustible waste such as pyrolysis and gasification is actively being performed not only to overcome the limitation of the conventional treatment method but also to increase waste to energy conversion efficiency. Pyrolysis is a proc-

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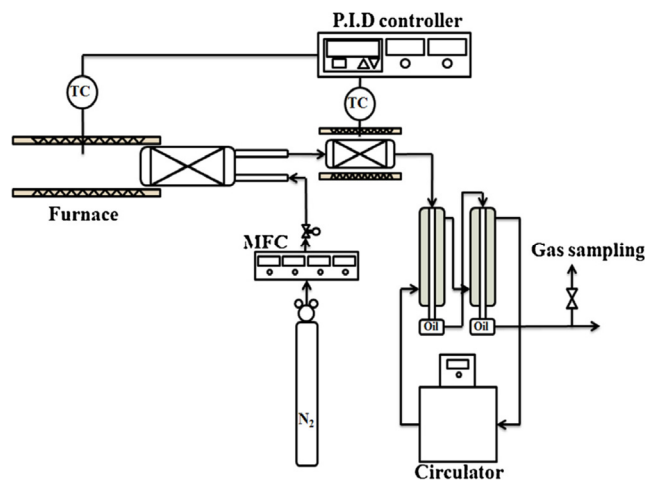
**Table 1. Physicochemical Properties of Zeolite Catalysts**

Catalyst	HZSM-5(CBV 3024E)	HY(CBV720)
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	30	30
Surface area (m <sup>2</sup> /g)	405	780
Pore size (Å)	5.1 × 5.5, 5.3 × 5.6	7.4 × 7.4
Internal pore space (Å)	6.36	11.24
IZA code	MFI	FAU

**Figure 1. NH<sub>3</sub>-TPD curves of catalysts.**

ess that can produce gas, oil and solid by-products by decomposing organic wastes at medium-high temperatures (400~600 °C) under non-oxygen atmosphere[3]. In the case of paper cups, it is possible to recover gas and oil byproducts by applying pyrolysis technology because it is made of paper, consisted with cellulose as its main component, and polyethylene coating film having high calorific value. Also, pyrolysis can be applied even other food residues, such as coffee residues, are remained in the waste paper cup because coffee residues are also consisted with lignocellulosic biomass components which also can produce gas, oil, and solid products by its pyrolysis. Although WPC containing coffee residual (WPCCCR) can be expected to be pyrolyzed, the pyrolysis product will contain large amounts of oxygen containing pyrolyzates because coffee residues also contain oxygen in its network structure. High oxygen contents in pyrolysis oil can lower the stability of product oil and difficult to be used as a fuel, directly. Although polyethylene, used as a paper cup coating material, can be pyrolyzed easily, the large contents of large molecular hydrocarbons such as wax is also considered as a main limitation on its actual commercialization [4]. In order to overcome the limitation of simple pyrolysis, many researchers have been actively investigating catalytic pyrolysis using zeolite-based catalysts[5,6].

In this study, catalytic pyrolysis of WPC and WPCCCR was performed using a fixed bed reactor. In order to know the value of the products obtained from the catalytic pyrolysis of WPCCCR over each catalyst, the yields of gas, oil, and solid obtained over each catalyst were compared together with the selectivity of aromatic hydrocarbons in product oil.

**Figure 2. Schematic diagram of two stage fixed bed reactor[7].**

## 2. Materials and Methods

### 2.1. WPC and WPCCCR

Paper cup, coated with polyethylene film, was used as WPC sample. WPC which was used to drink a coffee, KANU De-Caffeine Americano of Dongsuh Foods Corporations, was used as WPCCCR sample. Both WPC and WPCCCR were dried at 80 °C for 4 hours. To ensure homogeneity of the sample, all samples were pulverized using scissors, and only the particles having the smaller diameter than 5 mm selected the sample for the thermal and catalytic pyrolysis. Proximate analysis result indicated that the moisture, volatiles, fixed carbon, and ash content of WPCCCR were 3.8, 84.7, 11.0, and 0.5%, respectively.

### 2.2. Catalysts

Two kinds of commercial microporous catalysts, HZSM-5 and HY, having different pore sizes and acid strength were purchased from Zeolyst. Table 1 and Figure 1 show the textural properties, supplied from the manufacturer, and acidity, measured by the temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), of the catalysts, respectively.

### 2.3. Ex-situ catalytic pyrolysis

2 g of WPCCCR and 2 g of catalyst were loaded inside the 1<sup>st</sup> and 2<sup>nd</sup> reactor of a fixed bed reactor shown in Figure 2, respectively. After purging the reactor using nitrogen for 30 minutes, the temperatures of 1<sup>st</sup> and 2<sup>nd</sup> heaters was heated to 500 °C. After the stabilization of

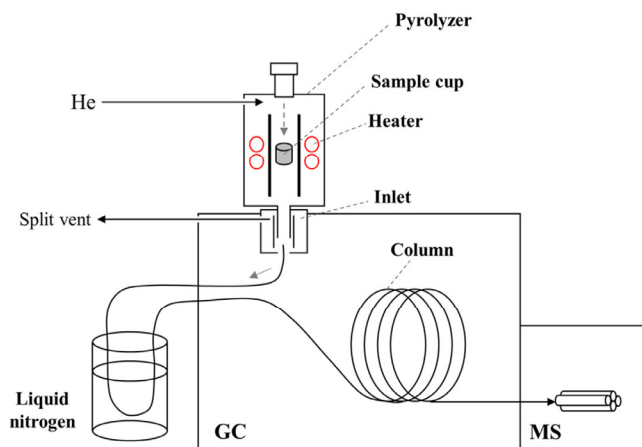


Figure 3. Schematic diagram of Py-GC/MS[8].

heater temperature, the pyrolysis of WPCCCR was initiated by sliding the 1<sup>st</sup> furnace to the reactor. The pyrolysis vapor emitted from 1<sup>st</sup> reactor was transferred to 2<sup>nd</sup> furnace and upgraded over the catalyst loaded in 2<sup>nd</sup> reactor. Final products was condensed in oil condensers (-20 °C) and uncondensed gas was collected using a Teflon gas sampling bag attached to the outlet of 2<sup>nd</sup> oil condenser.

#### 2.4. Py-GC/MS analysis

The mixture of WPCCCP (2 mg) and catalyst (2 mg) in a deactivated metal cup was free fallen into the center position of pre-heated pyrolyzer reactor at 500 °C as shown in Figure 3. The pyrolysis product vapor was transferred to the on-line coupled GC/MS. In the GC/MS, the pyrolysis products was separated by a GC oven program in a capillary column and finally detected by MS. Each peak on MS chromatogram obtained from the catalytic pyrolysis of WPCCCP was identified by MS library searching and integrated to compare the amount of each chemical indirectly.

### 3. Results and Discussion

#### 3.1. The yields of gas, oil, char, and coke

Table 2 revealed the yields of gas, oil, char, and coke obtained from the ex-situ catalytic pyrolysis of WPCCCR at 500 °C. The yields of gas, oil, and char obtained from the non-catalytic pyrolysis of WPCCCR were 21, 63, and 16% respectively. This indicates that large amount of oil product can be obtained from the pyrolysis of WPCCCR. The amount of oil product was decreased together with the increased of gas yield by applying catalytic pyrolysis using HZSM-5 or HY. This suggests that the pyrolysis vapor emitted from the 1<sup>st</sup> reactor was additionally cracked in the 2<sup>nd</sup> reactor due to additional catalytic cracking over the catalysts. Owing to the catalytic reaction over both catalysts, the yields of coke deposited on the HZSM-5 and HY were 2 and 3%, respectively. Compared to the catalytic pyrolysis over HY, that over HZSM-5 produced larger amount of gas. This can be explained by the stronger acidity of HZSM-5 compared to HY (Figure 1). Meanwhile, deposited coke amount on HY was larger than that on

Table 2. Yields of Gas, Oil, Char, and Coke Obtained from the Thermal and Catalyst Pyrolysis of Coffee Contained Paper Cup over HZSM-5 and HY (Pyrolysis Temperature : 500 °C)

	No Catalyst	HZSM-5	HY
Gas	21	46	34
Oil	63	39	49
Char	16	13	14
Coke	-	2	3

Table 3. Peak Area %s of Aromatic Hydrocarbons on the Chromatograms Obtained from the Thermal and Catalytic Pyrolysis-Gas Chromatography/Mass Spectrometry Analysis of Coffee Contained Paper Cup (Pyrolysis Temperature : 500 °C)

	No Catalyst	HZSM-5	HY
Mono-Aromatics	< 0.1%	12.5	7.8
Poly-Aromatics	< 0.1%	5.3	1.8
Total Aromatics	< 0.1%	17.8	9.8

HZSM-5 due to its larger pore size as shown in Table 1. Coke formation generated by the oligomerization of reaction intermediates over HZSM-5 can be less progressed than HY due to the smaller pore size of HZSM-5 compared to HY. Catalytic deactivation of the catalyst can be accelerated when larger amount of catalyst is deposited on the catalyst. This indicates that HZSM-5 is more proper for the catalytic pyrolysis of WPCCCR because it can provide not only the higher cracking efficiency but also the longer life time[9].

Table 3 shows the selectivities of the aromatics obtained for the thermal and catalytic pyrolysis of WPCCCR using a pyrolyzer-gas chromatography / mass spectrometry. In the case of non-catalytic pyrolysis, the peak area % of the aromatic compound was very small, less than 0.1% of the total peak area. However, when the catalyst was used, the ratio of aromatic compounds (Mono-aromatics) including BTEXs (benzene, toluene, ethylbenzene xylenes) were 7.8% over HY and 12.5% over HZSM-5, respectively. The total amount of aromatic chemicals including poly-aromatics also increased significantly when the catalyst was used. Between two catalysts, HZSM-5 showed the better performance on the production of aromatic hydrocarbons than HY due to its stronger acidity and medium pore property[10].

Large amount of aromatic compounds formed from WPCCCR over zeolite catalysts can be explained by the catalytic pyrolysis reaction mechanism of biomass, polyethylene and coffee residue, which are raw materials consisting WPCCCR. Cellulose, main biomass component of paper, can produce levoglucosan by its pyrolysis and converted to ketones and furans by the additional dehydration, decarbonylation, and decarboxylation over the acid catalysts. The ketones and furans can be finally converted to aromatic hydrocarbons and light olefins due to their additional deoxygenation, oligomerization, and aromatization reaction inside the pore of acid catalysts[11]. In case of the catalytic pyrolysis of polyethylene, olefins are formed by the first decompositions and aromatic hydrocarbons can be produced by the further decom-

position, oligomerization, and aromatization of these olefins over the acid catalysts[12]. Coffee residue also can produce the aromatic hydrocarbons via its catalytic pyrolysis because it also has the lignocellulose as the basic structure[13]. In addition, some recent studies have reported that the larger amount of aromatic hydrocarbons can be produced by co-feeding polyethylene to the catalytic pyrolysis of biomass [14]. This indicates that additional formation of aromatic hydrocarbons can be achieved on the catalytic pyrolysis of WPCCCR because more effective interaction between the catalytic pyrolysis intermediates of biomass (paper and coffee residue) and polyethylene. Effective role of polyethylene as a hydrogen donor to biomass and efficient Diels-Alder reaction between the oxygenated intermediates of biomass and light olefins produced from the catalytic pyrolysis of polyethylene were reported as the main mechanism for the additional formation of aromatic hydrocarbons during the catalytic co-pyrolysis of biomass and polyethylene[15]. Above results suggests that the catalytic pyrolysis of WPCCCR can produce a relatively large amount of aromatic hydrocarbons without any pretreatment method such as water washing and will be able to be used as a candidate method for the treatment method of waste paper cups.

#### 4. Conclusion

In this study, it was confirmed that the catalytic pyrolysis of WPCCCR can be an efficient treatment method of waste paper cups which can produce gas, oil, and solid byproducts without any pretreatment. Non-catalytic pyrolysis of WPCCCR produced large amount of oil. The amount of oil was decreased together with the increase of gas yield by applying catalytic pyrolysis due to the additional cracking of oil over the catalysts. The larger amounts of value added aromatic hydrocarbons were also obtained by the catalytic pyrolysis of WPCCCR. Between two catalysts, HZSM-5 produced larger amounts of aromatic hydrocarbons due to its stronger acidity and more proper pore structure than HY.

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