Catalytic Pyrolysis of Biomass by Tandem Micro-Reactor

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Abstract: Many kinds of catalytic pyrolysis reaction, such as *ex*-situ catalytic pyrolysis of *citrus* peel and *in*-situ catalytic co-pyrolysis of Cork Oak with waste plastic film, were tested using a tandem micro-reactor-gas chromatography/mass spectrometry (GC/MS). The experimental results indicated that tandem micro-reactor-GC/MS can provide easy, rapid, and simple catalytic reaction test together with its product analysis in a system.

Keywords: Tandem micro-reactor-GC/MS, acid catalyst, biomass, catalytic co-pyrolysis,

1. Introduction

Tandem micro-reactor-GC/MS system is constructed with two reactors online coupled with a conventional GC/MS as shown in Fig. 1. Gas, liquid, or solid samples can be introduced into 1st reactor using a micro-syringe, micro-feeder, or inert sample cup for gas preheating, liquid vaporization, or solid pyrolysis. The product vapor emitted from 1st reactor as a results of heating or pyrolysis is transferred to 2nd reactor having catalyst bed and converted to other chemicals by the ex-catalytic reaction. If the sample and catalyst was mixed and introduced to 1st reactor, with no catalyst loading on 2nd reactor, *in*-situ catalytic reaction also can be performed. Final products are moved to GC and detected in MS after the separation in a capillary column in GC oven. In this study, two kinds of experiment using tandem micro-reactor-GC/MS system were performed to check its feasibility as an effective catalytic reaction test tool related with biomass conversion research.

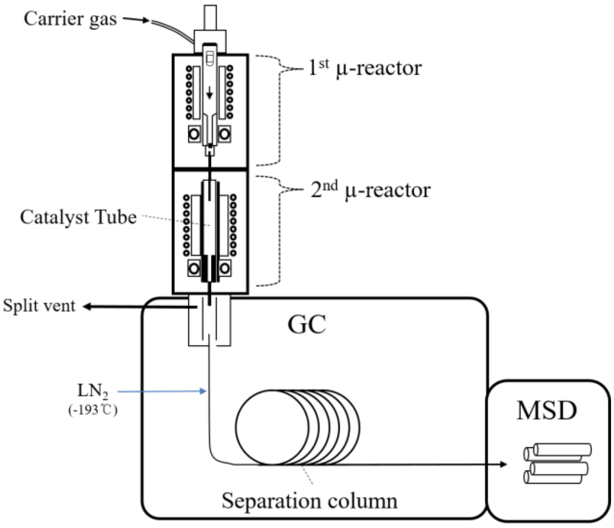

Fig. 1. Schematic diagram of tandem micro-reactor-GC/MS

2. Experimental

1) Tandem micro-reactor-GC/MS

Tandem micro reactor, named “Tandem μ-reactor”, (Rx-3050TR, Frontier Laboratory, Japan) interfaced to a commercial GC/MS was used for the catalytic pyrolysis reaction test.

2) *Ex*-situ catalytic pyrolysis of citrus peel.

2 mg of *citrus* peel in an inert sample cup was fallen into 1st reactor (500°C) and the pyrolysis vapor was upgraded in 2nd reactor (600°C) containing catalytic bed loaded with 2 mg of catalysts, HZSM-5(SiO_2/Al_2O_3: 23), HBeta(25), HY(30). Final products emitted from 2nd reactor were analyzed by GC/MS and BTEXs (benzene, toluene, ethylbenzene, and xylenes) carbon yields (C%) were quantified by external standard (ESTD) calibration methods.

3) *In*-situ catalytic copyrolysis of Cork Oak (COak) and waste plastic film (WPF).

1 mg of COak and WPF mixture (CO/WPF: 1/1) physically mixed with 5 mg of catalysts, HZSM-5(23), HBeta(25), or HY(30) in an inert sample cup was free fallen into 1st reactor (600°C) and the product vapor was analyzed by GC/MS and the yields (wt. %) of aromatic hydrocarbons were quantified by ESTD calibration method.

3. Results and discussion

As shown in Table 1, HZSM-5(23) produced largest amounts of BTEXs followed by HBeta(25) and HY(30) on the *ex*-situ catalytic pyrolysis of *citrus* peel due to its stronger acidity and shape selectivity for aromatics formation [1].

Table 1. Carbon yield (C%) obtained from the ex-situ catalytic pyrolysis of *citrus* peel over different catalysts.

Catalyst(SiO_2/Al_2O_3)	HY(30)	HBeta(25)	HZSM-5(23)
Carbon Yield(C%)	1.40	4.05	4.18

Theoretical and experimental yields (wt. %) of aromatic hydrocarbons obtained from the catalytic copyrolysis of COak and WPF were shown in Table 2. Compared to HBeta(25) and HY(30), HZSM-5(23) produced larger amounts of aromatic hydrocarbons from the catalytic pyrolysis of COak, WPF, and COak/WPF. Additionally, theoretical yields for aromatic hydrocarbons obtained from catalytic pyrolysis of COak/WPF over all catalysts tested in this study were higher than their theoretical yields. This indicates that synergistic formation of aromatic hydrocarbons can be achieved by adding WPF as a co-feeding material on the catalytic pyrolysis of biomass. Effective hydrocarbon pool formation and Diels-Alder reaction between the pyrolyzates of biomass and WPF can make this synergistic formation of aromatic hydrocarbons [2].

Table 2. Yields (wt%) of aromatics obtained from the catalytic pyrolysis of COak, WPF, COak/WPF.

Catalyst(SiO_2/Al_2O_3)	COak	WPF	COak/WPF	
			Theoretical[a]	Experimental
HZSM-5(23)	8.14	20.76	14.45	16.28
HBeta(25)	2.95	11.74	7.35	7.84
HY(30)	0.77	6.51	3.64	4.33

[a] Calculated with the individual yields obtained from the catalytic pyrolysis of COak and WPF over each catalyst.

4. Conclusions

Compared to HBeta(25) and HY(30), HZSM-5(23) produced large amount of aromatic hydrocarbons from both *ex*-situ catalytic pyrolysis of *citrus* peel and *in*-situ catalytic pyrolysis of COak and WPF due to the strong acidity of shape selectivity of HZSM-5(23). Synergistic aromatics formation was achieved by applying catalytic copyrolysis of COak/WPF due to the formation of efficient hydrocarbon pool.

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