



Thermal and catalytic degradation of pyrolytic oil from pyrolysis of municipal plastic wastes

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ABSTRACT

Thermal and catalytic degradation of pyrolytic oil obtained from the commercial rotary kiln pyrolysis plant for municipal plastic waste was studied by using fluid catalytic cracking (FCC) catalyst in a bench scale reactor. The characteristics of raw pyrolytic oil and also thermal and catalytic degradation of pyrolytic oil using FCC catalyst (fresh and spent FCC catalyst) under rising temperature programming was examined. The experiments were conducted by temperature programming with 10 °C/min of heating rate up to 420 °C and then holding time of 5 h. During this programming, the sampling of product oil was conducted at a different degradation temperature and also different holding time. The raw pyrolytic oil showed a wide retention time distribution in GC analysis, from 5 of carbon number to about 25, and also different product characteristics with a comparison of those of commercial oils (gasoline, kerosene and diesel). In thermal degradation, the characteristics of product oils obtained were influenced by reaction temperature under temperature programming and holding time in the reactor at 420 °C. The addition of FCC catalyst in degradation process showed the improvement of liquid and gas yield, and also high fraction of heavy hydrocarbons in oil product due to more cracking of residue. Moreover, the characteristic of oil product in catalytic degradation using both spent and fresh FCC catalysts were similar, but a relatively good effect of spent FCC catalyst was observed.

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1. Introduction

Recently, the generation amount of plastic wastes in Korea is about 4 million tones per year [1]. Among these disposal methods, the incineration and landfilling show high portion, but the portion of recycling method is low. Although incineration can provide a large volume reduction and energy recovery, it generates emissions into the air [2]. Also, disposal by landfilling requires a lot of space and has a potential environmental hazard [2]. Thus, the recycling in an economically and environmentally acceptable manner, such as material recycling and chemical recycling, is one of the important issues in Korea. For the recycling of plastic wastes, the pyrolysis technology is becoming a promising alternative, in order to recover fuel oil and hydrocarbon feedstock [2–4]. The advantage of this method is simple pyrolysis into the oil for all thermoplastic mixtures without using the separation treatment for plastic type in the mixture and lessening of the environment resistance for air pollutant and soil contamination, in contrast to the incineration and landfill methods. However, the quality of oils that was produced by pyrolysis of plastic wastes including other

materials, such as inorganic material and thermosetting material, etc., was not good to use as alternative fuel oils [5,6]. Moreover, the pyrolysis of polyethylene in plastic type produced much more wax material as low-grade product [7] and also the coke in the pyrolysis of plastic waste was sharply increased with increasing degradation temperature. Here, the coke and inorganic material included in the product oil can be easily removed by physical treatment [8]. However, the low-grade oil requires the change of chemical structure and needs thermal and catalytic degradation technology [9–12]. In the case of catalytic degradation, the most commonly used catalysts are solid acid catalysts such as zeolite, silica-alumina, fresh FCC catalyst and MCM-41, etc. [10–17] that are expensive. In addition to fresh FCC catalyst as a cracking catalyst for heavy hydrocarbons into gasoline, spent FCC catalyst has been used in this study. The utility of spent FCC catalyst can lessen the cost of catalyst in the catalytic degradation process [12,18]. These researchers have mainly studied over catalytic degradation of plastic waste, as a solid material, using fresh and spent FCC catalyst.

The objective of present study was to investigate the degradation of the low-grade pyrolytic oil supplied from a commercial pyrolysis plant (Dongmyong RPF Co., Korea) on a stirred tank bench scale reactor using fluid catalytic cracking (FCC) catalysts. As far as the qualities of the degraded oil were concerned, the oils obtained

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by thermal and catalytic degradation of pyrolytic oil with low grade were studied in more detail. Thus, the characteristics of pyrolytic oil as raw material and effect of both thermal and catalytic degradation of pyrolytic oil using fresh and spent FCC catalysts on the characteristic of products was examined.

2. Experimental

2.1. Raw material and catalyst

Raw pyrolytic oil was supplied by Dongmyong RPF Co., Korea. This was produced by pyrolysis of municipal plastic waste (MPW) in the commercial rotary kiln pyrolysis plant located in Kyonggi-do. Municipal plastic waste was supplied from a self-governing body located in Kyonggi-do.

FCC catalyst was used as a cracking catalyst for pyrolytic oil with low grade, which is used in the FCC process to produce the gasoline from the cracking reaction of heavy hydrocarbon. Spent FCC catalyst was slightly discharged from FCC process, after fresh FCC catalyst was used. FCC catalyst, which is mainly composed of zeolite and matrix such as alumina and silica-alumina, is prepared by spray drier to make a strong fine powder type. The characteristics of fresh and spent FCC catalysts are shown in Table 1. The surface area and pore volume of this catalyst were obtained from nitrogen adsorption isotherms measured at liquid nitrogen temperature (Micromeritics, ASAP-2000). Total surface areas were determined using the BET equation within a relative pressure of 0.2, and a distinction between micropores and mesopores was made using the T-plot method. These catalysts consist of both micropores and mesopores. This pore structure is beneficial for cracking of heavy hydrocarbon with a big kinetic diameter, which is cracked

Table 1
Physical properties of FCC catalyst.

Items	Surface area (m ² /g)			Total pore volume (cm ³ /g)
	Total	Micro-	Meso-	
Fresh cat.	216	96	120	0.2481
Spent cat.	151	76	75	0.2533

by step-by-step diffusion of heavy hydrocarbon within mesopore firstly and then in micropore.

2.2. Equipment and experimental procedure

The degradation experiment of pyrolytic oil was carried out in a stirred bench scale reactor (volume; about 6 L) under atmospheric pressure, and the schematic diagram is shown in Fig. 1. 3 kg of pyrolytic oil was charged in the reactor. After charging, it was sufficiently purged with a nitrogen flow and then stopped before pyrolysis. The temperature in the reactor increased up to 420 °C at rate of 10 °C/min and maintained at 420 °C for 5 h. The speed of impeller rotation was 100 RPM. During programming of degradation temperature, the loading time of catalyst in the reactor was conducted at 420 °C. Gas products were analyzed by GC after cooling by condenser to 7 °C. Liquid products, as a function of reaction time, were measured by weight. Each liquid product was quantified and qualified by gas chromatography, using FID and MS detectors. Residue was determined by the material remained in the reactor after the reaction was finished. This value was defined as the weight percentage of the residue amount remained in the reactor to the initial reactant amount. Also, gas yield was calculated from the difference between 100 and percentage yield of liquid product plus residue.

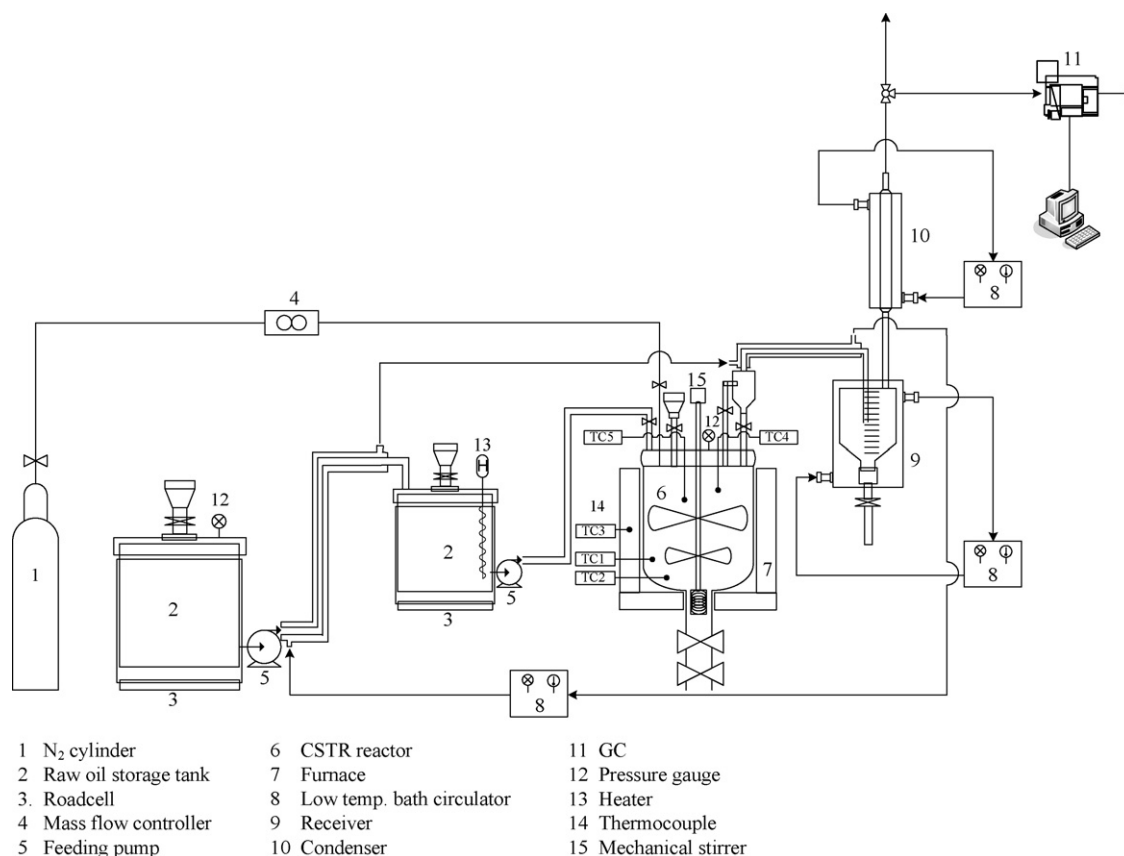


Fig. 1. Schematic diagram of experimental pyrolysis system.

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