

Spouted Bed Reactor를 이용한 다양한 탄소수 원료유 촉매 열분해

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Catalytic Pyrolysis of Various Carbon Number Feed Oil Using a Spouted Bed Reactor

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본 연구에서는 원료의 직접 주입법과 다양한 탄소수를 갖는 화합물을 이용하여 휘발유와 등유 등의 고급 유분을 생성할 수 있는 상업용 촉매 공정의 반응특성을 평가하고자 하였다. 이를 통하여 순간주입 반응기(spouted bed reactor) 상에서 상용촉매를 사용하여 반응 특성을 평가하였다. 또한 decane과 pentadecane을 이용하여 고정층 반응기와 순간주입 반응기의 특성을 비교하였다. 본 연구 결과, 반응온도 550 °C에서 가장 높은 휘발유 및 등유 수율을 기록하였다. 또한 순간주입 반응기의 경우 주입량을 분할하여 주입하는 것보다 1회에 주입하는 것이 보다 효과적이었으며, 탄소수가 큰 물질을 사용할수록 반응활성이 증가하였다.

We focus on a catalytic process based on direct injection method that can produce high-quality oils of gasoline and kerosene with various carbon-number feed oils. The reaction characteristics of a commercial catalyst were analyzed using a spouted bed reactor. Decane and pentadecane were used to compare the characteristics of the fixed bed and the spouted bed reactor. The yield of gasoline plus kerosene was highest at the reaction temperature of 550 °C. For the spouted bed reactor, the at-a-pulse injection was more effective for catalytic cracking of feed oils than multiple consecutive injections. The reaction activity became higher as the carbon number of feed oil is larger.

Keywords: pyrolysis, high quality oil, spouted bed reactor, catalyst, various carbon number feed

1. Introduction

Polymers such as plastics are used increasingly due to their low price, small density, and easiness of processing. Lots of waste plastics are being discarded rather than being recycled partly because of their low price, causing an environmental pollution. Waste plastics are difficult not only to move and store due to their large volume (small density) but also to decompose by landfilling.

Recycling of waste plastics is divided into physical, chemical and thermal recyclings. Among them, chemical recycling refers to production of valuable fuels from pyrolysis of waste plastics. Technology for pyrolysis of waste plastics has been continuously improved for the last two decades. It has drawn large attention in that it can not only recycle wastes but also produce low-carbon fuels. Large energy supply required for pyrolysis reaction and low economic value of produced oil, however, are problems yet to be solved for large-scale application.

Therefore, it is needed to convert the product oil into more valuable fuel, e.g., gasoline or kerosene.

The process to produce alternative fuels from waste plastics generally consists of pre-treatment of waste plastics, melting, pyrolysis, condensation and distillation while catalytic cracking can be added after pyrolysis to improve the yield and properties of produced oil fraction[1-10]. Because the properties of the oil fraction produced from catalytic cracking depend on the catalyst used, reaction temperature, and contact time, selection of appropriate catalyst and process optimization play important roles in improving the productivity of the process. Hydrocarbons, which are main components of waste plastics, are decomposed into low-molecular-mass species upon contact with catalysts. During this catalytic cracking, some mass is carbonized and deposited onto the catalyst surface deactivating the catalyst. If a moving phase reactor is used, catalyst particles pass through the reactor successively and the catalyst particles deactivated by carbon-deposition are sent to the regeneration column, in which deposited carbon is burned off. Regenerated catalyst particles are sent back to the reactor

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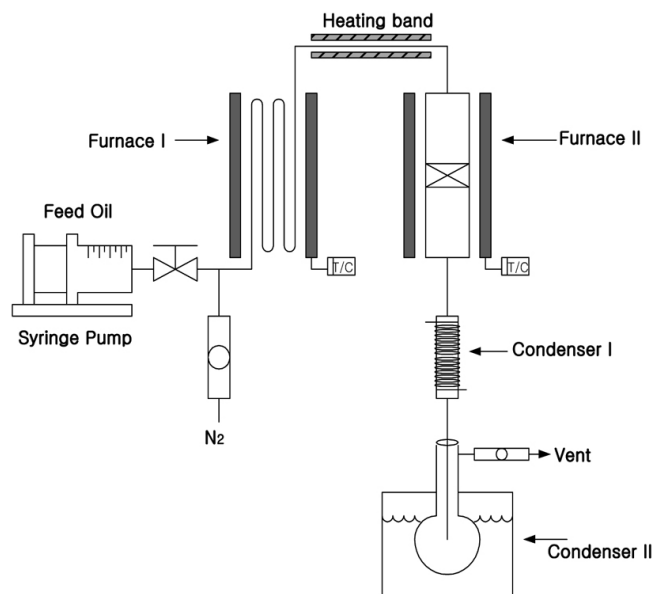


Figure 1. Schematic diagram of the fixed bed reactor system.

where they are reused.

The catalytic cracking process used for production of alternative oil from waste plastics is similar to that used in oil refineries. Large-scale imported catalytic cracking facilities have been installed and are operated in the oil refineries in Korea. Due to the difference in raw material property and operation scale, however, these facilities cannot be used for treatment of waste plastics. Therefore, it is required to optimize the waste plastics treatment process considering the raw material property and pre- and after-processes to improve the cost competitiveness.

In this study, the cracking performances of commercial catalyst was evaluated for various carbon-number direct-injected plastics. The results of this study are expected to contribute to building the database required for developing processes for high-quality alternative liquid fuel production from waste plastics. In particular, aiming at providing basic data needed for moving phase reactor design, a spouted bed reactor was used, while a fixed bed reactor was also used for comparison.

2. Experimental

2.1. Method

Figure 1 shows the schematic of the fixed bed reactor system used for catalytic cracking of pyrolysis product oil of waste plastics. The system consists of sample inlet, vaporizer (furnace I), catalytic cracking reactor (furnace II), and condenser. Two different methods were used for feeding in the pyrolysis product oil samples. In the first method, which was used for fixed bed reactor, each sample was fed in continuously with a constant feed rate of 0.5 mL/min by a syringe pump, while in the second method, which was used for the spouted bed reactor, a fixed amount of sample was fed in instantly. Nitrogen gas was used as the carrier gas to deliver the sample to the reactor with a flow rate of 100~300 mL/min. The temperature in the evaporator was maintained at 300 °C using a 1-kW heater and a PID controller to

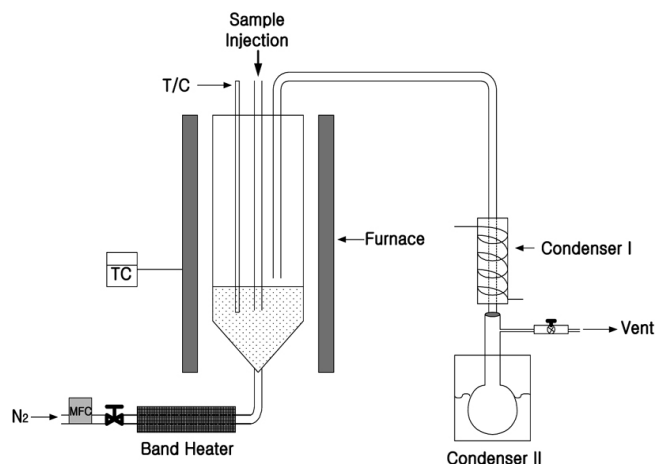


Figure 2. Schematic diagram of the spouted bed reactor system.

evaporate the pyrolysis product oil sample completely before entering the catalytic reactor. The catalytic reactor, with a dimension of 20 mm inner diameter, 24 mm outer diameter, and 500 mm length, was made of quartz to be used under high-temperature conditions. Quartz fritz was installed in the middle of the reactor to equip the reactor with catalysts. The temperature in the reactor was measured and controlled at a set temperature using a K-type thermocouple and a programmable PID controller. A 4-kW removable electric heater was installed on the outer wall of the reactor to change the reaction temperature within the range of 350~550 °C. Product oil and gas were collected using a condenser and a gas-liquid separator installed at the reactor outlet. They were dissolved in CS₂ and then were analyzed using a GC (Agilent 6890, HP-1, HP-5 capillary column). The degree of coking of the catalysts recovered after reaction was analyzed by a TGA (Thermo-gravimetric Analyzer). Figure 2 shows the schematic of the experimental system developed to evaluate oil conversion through instant feeding of samples. The carrier gas flow condition was the same as that for the case of continuous sample feeding. The samples were fed in instantly using a syringe pump.

2.2. Materials and Product Analyses

A commercial catalyst made by R manufacturer was used in this study. In order to deduce the optimal operation condition for oil converting system, high-boiling-temperature species contained in diesel fuel, which have similar characteristics with pyrolysis product oil of waste plastics, were separated from diesel fuel to be used as the feed oil in this study. This feed oil had a specific gravity of 0.89 and a color of dark brown. The GC analysis using an HP-5 capillary column showed that it consisted of high-boiling-temperature species with the carbon number of 15-30, the majority of which were C₁₉ and larger.

3. Results and Discussion

Table 1 summarizes the experimental results obtained from catalytic cracking of the feed oil performed using the 4 mm size commercial

Table 1. Results of Catalytic Cracking of the Diesel Distillation Residue in a Spouted Bed Reactor

	350 °C				450 °C				550 °C			
	1st injection	2nd injection	3rd injection	Accumulated	1st injection	2nd injection	3rd injection	Accumulated	1st injection	2nd injection	3rd injection	Accumulated
Oil injected (g)	4.30	4.30	4.30	12.9	4.30	4.30	4.30	12.9	4.30	4.30	4.30	12.9
Oil yield (g)	1.64	2.58	3.5	7.72	1.92	2.92	3.00	7.84	1.56	2.35	2.40	6.31
Gasoline + kerosene (g)	0.46	0.54	0.6	1.60	0.87	0.85	0.75	2.47	1.06	1.06	0.99	3.11
Unreacted oil (g)	1.18	2.04	2.9	6.12	1.05	2.1	2.25	5.40	0.62	1.29	1.41	3.32
Gas + coking (g)	2.66	1.72	0.8	5.18	2.38	1.38	1.30	5.06	2.74	1.95	1.90	6.59

Table 2. The Effect of the Amount of Decane Injection on Catalytic Cracking Reaction

	1 pulse injection				5 mL/inj		
	2.5 mL	5 mL	10 mL	15 mL	5 mL	5 mL (10 mL)	5 mL (15 mL)
Oil injection (g)	1.825	3.65	7.3	10.95	3.65	7.3	10.95
Oil yield (g)	1.229	2.45	5.22	7.52	2.45	5.02	7.65
Oil cracked (g)	0.286	0.71	1.68	2.81	0.71	1.34	1.94
Unreacted oil (g)	0.943	1.74	3.54	4.7	1.74	3.68	5.71
Gas + coking (g)	0.596	1.2	2.08	3.43	1.2	1.28	2.30

granule catalyst of R-manufacturer and a spouted-bed type instant-feeding reactor. The reactor was equipped with 50 g of catalyst that had been thermally treated at 600 °C for 12 h. The residue that remained after distillation of commercial diesel fuel at 300 °C, was used as the feed oil. For each injection, 4.3 g of feed oil was injected into the reactor.

It is important to note in Table 1 that the yield of gasoline plus kerosene was quite high being about 20% although excessive amount of oil was fed into the reactor. As shown in the results for the experiment at 550 °C, high temperature was favorable for high yield of gasoline plus kerosene with short contact time. For more quantitative analysis, however, energy and mass transport phenomena in the reactor have to be interpreted in more detail.

Table 2 shows the results obtained with different amounts of instant oil injection. For 10 mL and 15 mL cases, two methods were used to inject the sample. In the first method, total amount was injected at a pulse, while in the second method, two or three consecutive pulses of 5 mL injection were used. Decane was used as the model feed oil in this test.

As shown in Table 2, the at-a-pulse injection was more effective than multiple consecutive injections for spouted bed reactor probably because it was favorable for contact between catalysts and oil in the reactor. If the amount of the oil injected is too large, however, it may lead to increased pressure drop and temperature reduction. When 50 g of catalyst was used as in this study, 15 mL appeared to be the maximum instant oil injection amount.

In order to evaluate the catalytic performance of the R-manufacturer catalyst for different feed oil species, experiments were carried with two different chemicals, decane and pentadecane, using both spouted bed reactor and fixed bed reactor. The results are summarized in Tables 3 and 4. For low-carbon-number hydrocarbon, a higher conversion yield was obtained with fixed-bed reactor than with spouted

Table 3. Catalytic Cracking Results of Decane and Pentadecane Using Fixed Bed Reactor

n-C10	350 °C	450 °C	550 °C
Oil injected (g)	11	11	11
Oil yield (g)	8	6.6	4.2
Cracked oil (g)	1.2	2.1	2.3
Unreacted oil (g)	6.8	4.5	1.9
Gas + coking (g)	3	4.4	6.8
n-C15	350 °C	450 °C	550 °C
Oil injected (g)	11.5	11.5	11.5
Oil yield (g)	7.7	6.4	5.9
Cracked oil (g)	1.5	2.7	3.8
Unreacted oil (g)	6.2	3.7	2.1
Gas + coking (g)	2.8	5.1	5.6

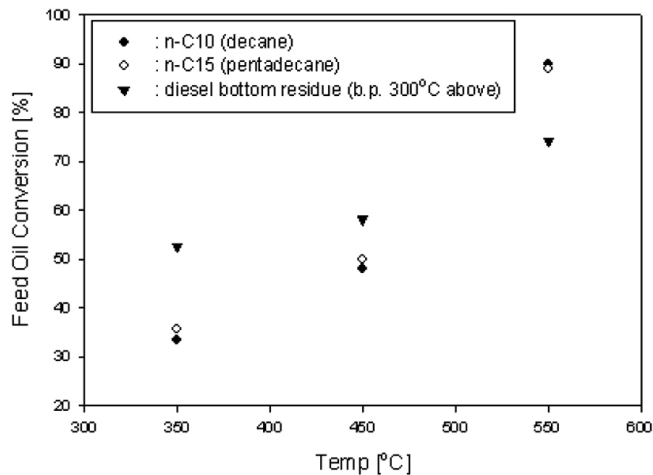
bed reactor at low temperature (at 350 °C and 450 °C), which is contrary to the results obtained for diesel distillation residue. This result is attributed to high volatility of low-boiling-point oil that suppresses the increase of contact efficiency in the spouted bed reactor. This effect is more profound under higher temperature because temperature reduction due to instant injection tends to retard the reaction. Although it was difficult to measure the temperature reduction in the reactor accurately, temperature reduction of about 30 °C occurred when 5 mL of oil was instantly injected with the catalyst amount of 50 g.

Figure 3 shows the conversion by catalytic cracking for three different feed oils as a function of temperature using a spout bed reactor. It is shown that the conversion was higher for a higher carbon number oil at low temperature (at 350 °C and 450 °C). This is because it is easier for carbonium ion to form on the catalyst surface when the carbon-number of the feed oil is higher[11]. This result implies that plas-

Table 4. Catalytic Cracking Results of Decane and Pentadecane Using Spouted Bed Reactor

n-C10	350 °C			450 °C			550 °C		
	1st injection	2nd injection	3rd injection	1st injection	2nd injection	3rd injection	1st injection	2nd injection	3rd injection
Oil injected (g)	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65
Oil yield (g)	2.9	2.6	2.97	2.45	2.57	2.63	0.94	1.12	1.20
Cracked oil (g)	0.4	0.4	0.37	0.71	0.63	0.60	0.76	0.71	0.65
Unreacted oil (g)	2.5	2.2	2.6	1.74	1.93	2.03	0.18	0.41	0.55
Gas + coking (g)	1.75	1.05	0.68	1.2	1.08	1.0	2.71	2.53	2.45

n-C15	350 °C			450 °C			550 °C		
	1st injection	2nd injection	3rd injection	1st injection	2nd injection	3rd injection	1st injection	2nd injection	3rd injection
Oil injected (g)	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85	3.85
Oil yield (g)	2.81	2.96	3	2.52	2.64	2.66	1.02	1.14	1.35
cracked oil (g)	0.51	0.44	0.4	0.76	0.70	0.62	0.82	0.74	0.67
Unreacted oil (g)	2.3	2.52	2.6	1.76	1.94	2.04	0.2	0.4	0.68
Gas + coking (g)	1.04	0.89	0.85	1.33	1.21	1.19	2.83	2.71	2.5

**Figure 3. Effect of reaction temperature on the conversion of feed oils with different carbon numbers using a spout bed reactor.**

tics with very high carbon number can be easily decomposed by catalytic cracking at low temperature.

4. Conclusions

The following conclusions were deduced from this study:

1) When diesel distillation residue was treated in the spouted bed reactor with the commercial catalyst within the reaction temperature range of 350~550 °C, the highest gasoline plus kerosene yield was obtained at 550 °C.

2) For the case of spouted bed reactor, the at-a-pulse injection is more effective than multiple consecutive injections because it is favor-

able for contact between catalysts and oil in the reactor.

3) The reaction activity was higher for feed oil with a larger carbon number.

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