

Effect of heating rate on pyrolysis of low-grade pyrolytic oil

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Abstract—The low-grade pyrolytic oil produced from pyrolysis of municipal plastic waste in a commercial rotary kiln reaction system cannot be an acceptable fuel oil due to its low quality. Thus, the degradation of pyrolytic oil was conducted in a bench scale batch reactor, which was done by two experiment conditions of high heating rate (about 7 °C/min) and low heating rate (1.5-3.6 °C/min) up to 420 °C of reaction temperature. The characteristics of raw pyrolytic oil were examined and also the characteristics of products obtained by different heating rates were compared. Raw pyrolytic oil had higher H/C ratio and higher heating value than commercial oils, and also its peak range in GC analysis showed wide distribution including all the range of gasoline, kerosene and diesel. In the upgrading of pyrolytic oil, cumulative amount profile of product oil, as a function of reaction time, was similar in shape to the degradation temperature profile. All product oils obtained by different degradation temperature had higher H/C ratio and slightly higher heating value than those of raw pyrolytic oil. Also, the characteristics of product oils were influenced by heating rate and reaction temperature.

Key words: Municipal Plastic Waste, Pyrolysis, Low-grade Pyrolytic Oil, Upgrading, Heating Rate, Characteristic of Products

INTRODUCTION

With industrial development the amount of municipal plastic wastes has been increasing, resulting in the growth of environmental pollution. In the same manner, the plastic industry of Korea has been developing with the petroleum chemical industry, and then the amount of plastic wastes produced from both industries and life environment has also been growing. It is generally known that simple incineration and landfilling are the main techniques for plastic wastes disposal and the recycling method is minor. Subsequently, it is necessary that the plastic wastes should be reused more effectively in terms of environmental preservation and raw material recycling.

As one of the promising methods, the production of alternative fuels obtained from pyrolysis has been suggested in Korea because the amount of plastic wastes has become approximately hundreds of thousands of tons and the raw materials are not sufficient [1-4]. However, mixed oil produced from pyrolysis of plastic wastes has contained a different type of oil and characteristics owing to mixed types of plastic wastes with different structures [5-8]. For instance, the pyrolysis of plastics with olefin style gives rise to the production of oil with a wide range of molecular weights, resulting in the degradation of oil products [5]. Here, the pyrolytic oil produced includes wax with low quality. Therefore, one might need to investigate the characteristics of oil produced from pyrolysis of municipal plastic materials and also the upgrading of pyrolytic oil with low quality like wax [9]. In the upgrading methods, thermal degradation is easily applied to commercial pyrolysis plants as a simple process unit and an adequate method to produce the fuel oil to be used in industrial companies. On the other hand, catalytic degradation is a

costly method due to expensive catalyst and complex process. Also, the cracking catalyst can easily be deactivated by low-grade pyrolytic oil. There are several oil producing processes used in Korea. These are semi-continuous processes that repeatedly increase and decrease the reaction temperatures on a regular basis. Since these types of processes are used in the production of pyrolytic oil at similar reaction conditions, the reaction temperature and heating rates can influence the properties of final products.

Based on this background, it is our main purpose to investigate the characteristics of pyrolytic oil and also the upgrading of low-quality pyrolytic oil by using mixtures of municipal plastic wastes and a semi-continuous rotary kiln pyrolysis reactor. At the same time, this study is examining the characteristics of oil obtained by using different reaction temperatures at several heating rates. These results could be utilized for a semi-continuous rotary kiln reactor as a fundamental data base, and also for the sale of final products with obvious characteristics of different oils.

EXPERIMENTAL

1. Raw Materials

The raw materials used in this study are low-grade pyrolytic oils produced from the mixtures of municipal plastic wastes using a rotary kiln pyrolysis reactor (Dongmyong RPF, Inc.).

2. Experimental Apparatus and Procedure

The experimental apparatus for pyrolysis of low-grade oil is composed of a batch style tank reactor, a high temperature furnace and a product condenser (Fig. 1). The batch reactor is made of stainless steel with 6 L of reactor volume and contains a stirrer on the top of reactor in order to effectively facilitate the heat transfer of samples in the reactor. The impeller rotation was controlled by a speed controller. After reaction, the amount of residue was also controlled by

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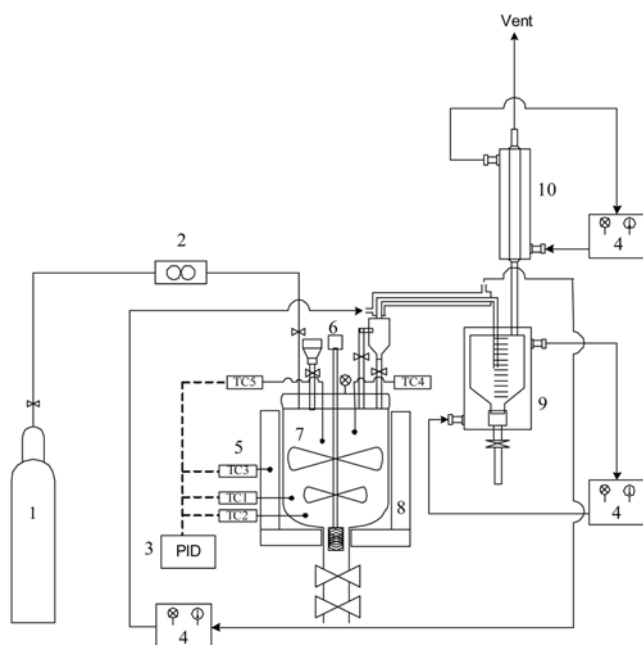


Fig. 1. Schematic diagram of experimental pyrolysis system.

1. N₂ cylinder
2. Mass flow controller
3. PID temp. controller
4. Low temp. bath circulator
5. Thermocouple
6. Mechanical stirrer
7. CSTR reactor
8. Furnace
9. Sample receiver
10. Condenser

a valve located at the bottom of the reactor. Four K type thermocouples in the reactor and one in furnace were used to check the temperature change. The high temperature furnace contains a PID temperature controller to increase the temperature at constant heat rates and to maintain it at setting points. A thermostatic container was used to maintain a constant temperature around the condenser while the products were collected from the reactor.

The pyrolysis experiments were performed using low-grade pyrolytic oil from mixed plastic wastes as follows. First, around 3 kg of low-grade pyrolytic oil was loaded inside the batch reactor and sealed.

Then the sealing was checked for 5 min using nitrogen gas. A PID controller was used to set the temperature at 420 °C and maintain it for 5 hours. The temperature was increased from the room temperature at two different heating rates of 5 and 10 °C/min. During the heating, the impeller speed was retained at 33 rpm. While the experiments were conducted, the temperature was measured at 10 min interval using five thermocouples attached in the reactor and furnace. For the efficient discharge of produced oil, the connecting line between the reactor and condenser was kept at 70 °C, and the surrounding temperature of the condenser was ~5 °C using a thermostatic container. Liquid products produced at constant temperature were collected and amounted at 10 min interval using 1,000 ml container. Collected liquid products were stored after sealing for one day at room temperature so as to check the precipitates and wax components. Total amount of liquid products collected during the reaction was defined as residue of liquid products, and the yield of liquid products was calculated from weight percent of liquid product residue divided by the amount of initial reactant.

3. Analysis

Analysis experiments for elements and heating values were performed for both low-grade pyrolytic oil from mixed plastic wastes and liquid products from the reaction. Elemental analysis was conducted using a Truspec CHN Elemental Analyzer (LECO Co., USA). Amongst several elements, C, H, and N analysis was made after complete combustion of dried samples at 1,050 °C. Nitrogen gas was used for transport, and oxygen and helium were used for combustion. The calorific values of product oil were estimated by using a Parr 6320EF calorimeter. GC/MS analysis was made for the mixed plastic low-grade pyrolytic oil and liquid products a day after collecting from pyrolytic reaction at 10 min interval. The used GC and Mass equipment were 6890N model and 5890 model of Agilent Co., respectively. The analysis conditions for GC and Mass are described in Table 1.

RESULTS AND DISCUSSION

1. Characteristics of Raw Materials

Table 2 shows elemental analyses and heating values for raw pyro-

Table 1. Analysis conditions for GC and mass

Items	GC analysis	GC-MS analysis
Apparatus	Agilent 6890N	Agilent 6890 GC/MSD
Detector	FID (Flame ionization detector)	MSD (Mass selective detector)
Column	HP-5 (30 m×0.32 mm×0.25 μm)	UA-5 (30 m×0.25 mm×0.25 μmID)
Carrier gas	Helium, 30 ml/min	Helium, 30 ml/min
Injection amount	2 μl	2 μl
Injection temp.	250 °C	250 °C
Detector temp.	310 °C	320 °C
Oven temp. program	30 °C (10 min in hold) to 310 °C (10 min in hold) with 10 °C/min	30 °C (10 min in hold) to 310 °C (10 min in hold) with 10 °C/min
Ion source temp.		230-250 °C
Interface temp.		250 °C
Mass data acquisition		Scan
Scan rate (s/scan)		2
Mass scan range		20-300

Table 2. Elemental analyses and heating values of raw pyrolytic oil and commercial oils

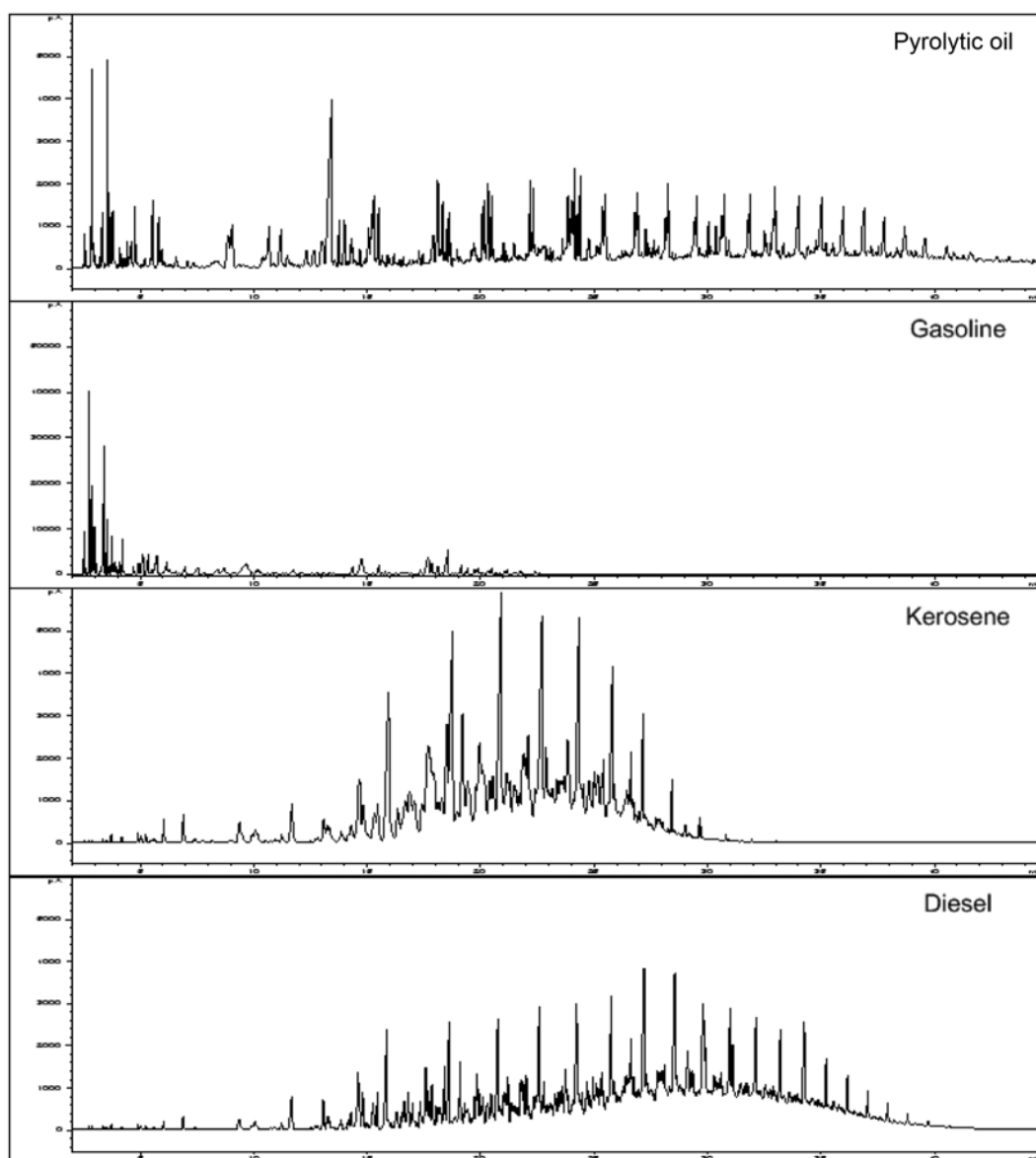
	Elements (wt%)				Heating value (kcal/kg)
	Carbon	Hydrogen	Nitrogen	H/C ratio	
Raw pyrolytic oil	82.89	16.25	0.14	0.196	10,710
Gasoline	83.87	14.03	-	0.167	8,300*
Kerosene	85.20	13.97	-	0.164	8,700*
Diesel	86.35	13.18	-	0.153	9,200*

*Data obtained from Korea Institute of Petroleum Management

lytic oil and commercial gasoline, kerosene, and diesel. As can be seen, the carbon amount of raw pyrolytic oil is smaller than that of commercial gasoline, kerosene, and diesel. However, the amount of hydrogen for raw pyrolytic oil is larger than that of other oils. These results are obviously shown in H/C ratios. Namely, the H/C ratio of raw pyrolytic oil is approximately 0.2 while that of com-

mercial gasoline, kerosene, and diesel ranges from 0.15 to 0.17. These differences can be shown in heating values as well. The heating value of raw pyrolytic oil with 10,710 Kcal/kg is higher than that of commercial gasoline, kerosene, and diesel ranging from 8,300 to 9,200 Kcal/kg.

As shown in Fig. 2, GC analyses were performed to investigate

**Fig. 2. Comparison of GC peaks of the raw pyrolytic oil and commercial oils (gasoline, kerosene and diesel).**

the characteristics of pyrolytic oil components. At the same time, the GC peak patterns for three kinds of commercial oils that can be purchased in gas stations were also obtained at the same experimental conditions and compared to others. Fig. 2 shows that the GC analyses were completed at the shorter holding time for gasoline (30–200 °C and C₄–C₁₂) than that for kerosene (170–250 °C and C₉–C₁₈) and diesel (240–350 °C and C₁₂–C₂₈). By comparing to pyrolytic oil, it can be seen that the low boiling point products of gasoline range as well as the high boiling point products of kerosene and diesel are also obtained. The pyrolytic oil produced from municipal plastic wastes using a rotary kiln reactor shows a broad distribution ranging from gasoline to diesel. However, it should be also noted that the pyrolytic oil including the wax gives difficulty in sales as final products.

2. Thermal Degradation of Raw Pyrolytic Oil

It is necessary that raw pyrolytic oil obtained from plastic wastes using a rotary kiln reactor should be high-grade. Subsequently, one might need to investigate the characteristics of oil products that were obtained from raw pyrolytic oil during a long holding time at 420 °C after increasing from room temperature at two different low and high heating rates. Fig. 3 exhibits the cumulative amounts of liquid products as a function of reaction time for different heating rates. Here, in the case of low heating rates the actual average heating

rates were observed to be 1.5 °C/min and 3.6 °C/min due to insufficient heat capacities of furnace at the initial experiments. But for the case of high heating rate the actual average heating rate was observed to be 7.3 °C/min and was 2 or 4 times higher than that of low heating rates.

At the high heating rates, the behavior of cumulative amount of liquid product as a function of time was similar to that of reaction temperature program. The average oil yield was observed at about 80% using the thermal degradation process used in this study. By the same token, in the case of low heating rates it was shown that the cumulative amounts of liquid products were influenced by the reaction temperature program. As a result, GC analyses indicated that for raw pyrolytic oil exhibiting a broad range of holding time, the liquid products obtained by increasing the reaction temperature have been severely affected by the reaction temperature program.

3. Characteristics of Liquid Products

Table 3 shows the elemental analyses and heating values of raw pyrolytic oil and product oils obtained using high heating rate that was used for upgrading process. Here, the product oils for characterization were sampled at three different temperature ranges as described in S1, S2, and S3. The results shown in Table 3 are somewhat different from those in Table 2. As seen in Table 2, the H/C ratio and heating value for raw pyrolytic oil which is a target material in this study are higher than those of gasoline, kerosene, and diesel. However, Table 3 shows that the heating values for raw pyrolytic oil and product oils obtained at different temperatures are ranging between 10,000 and 11,000 kcal/kg. More precisely, the heating values for product oils are slightly higher than or similar to that for raw pyrolytic oil. While Table 2 shows that ~0.2 of the H/C ratio for raw pyrolytic oil is a little higher than those of commercial oils, Table 3 shows that the H/C ratio for raw pyrolytic oil is lower than that of product oils showing the ratios between 0.23 and 0.25.

Fig. 4 shows the comparison of GC peaks of product oils at several different temperatures and at two different heating rates (expressed A as low heating rate and B as high heating rate). Regardless of heating rates, the GC analyses showed similar peaks at similar reaction temperatures. But, at each heating rate the GC results revealed a big difference in peaks as a function of reaction temperature. Up to the reaction temperature of 350 °C increased from initial temperature, the GC results showed that higher boiling point products were obtained at higher holding times, but lower boiling point materials were almost not produced from thermal degradation of high boiling point products. These results indicate that the product oils were obtained from distillation rather than from thermal degradation of pyrolytic oil. However, for even higher reaction temperature of 390 °C a little higher boiling point materials were produced, and many low boiling point products between gasoline ranges were observed at

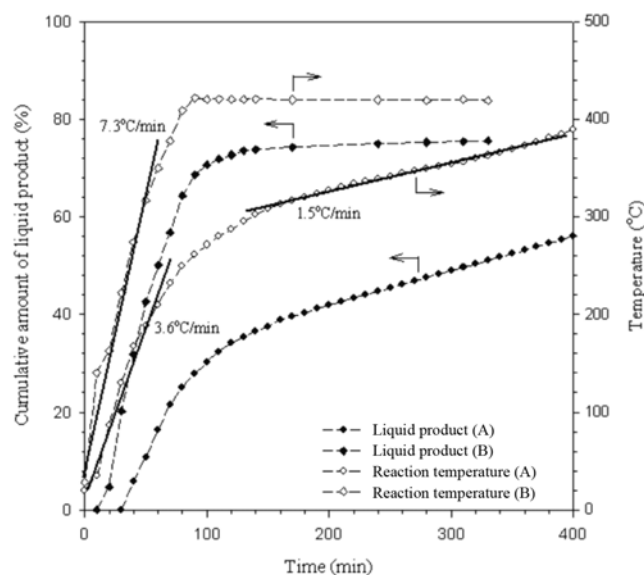


Fig. 3. Thermal degradation of raw pyrolytic oil under temperature programming (A: Low heating rate, B: High heating rate). Cumulative amount of liquid product indicates yield of liquid product (%).

Table 3. Elementary analysis and heating values of raw pyrolytic oil and product oil

	Elements (wt%)				Heating value (kcal/kg)
	Carbon	Hydrogen	Nitrogen	H/C ratio	
Raw pyrolytic oil	82.89	16.25	0.14	0.196	10,710
S1 (155–167 °C)	80.65	18.85	0.29	0.234	10,090
S2 (249–271 °C)	80.80	18.70	0.47	0.231	11,010
S3 (385–420 °C)	79.71	19.95	0.32	0.250	11,080

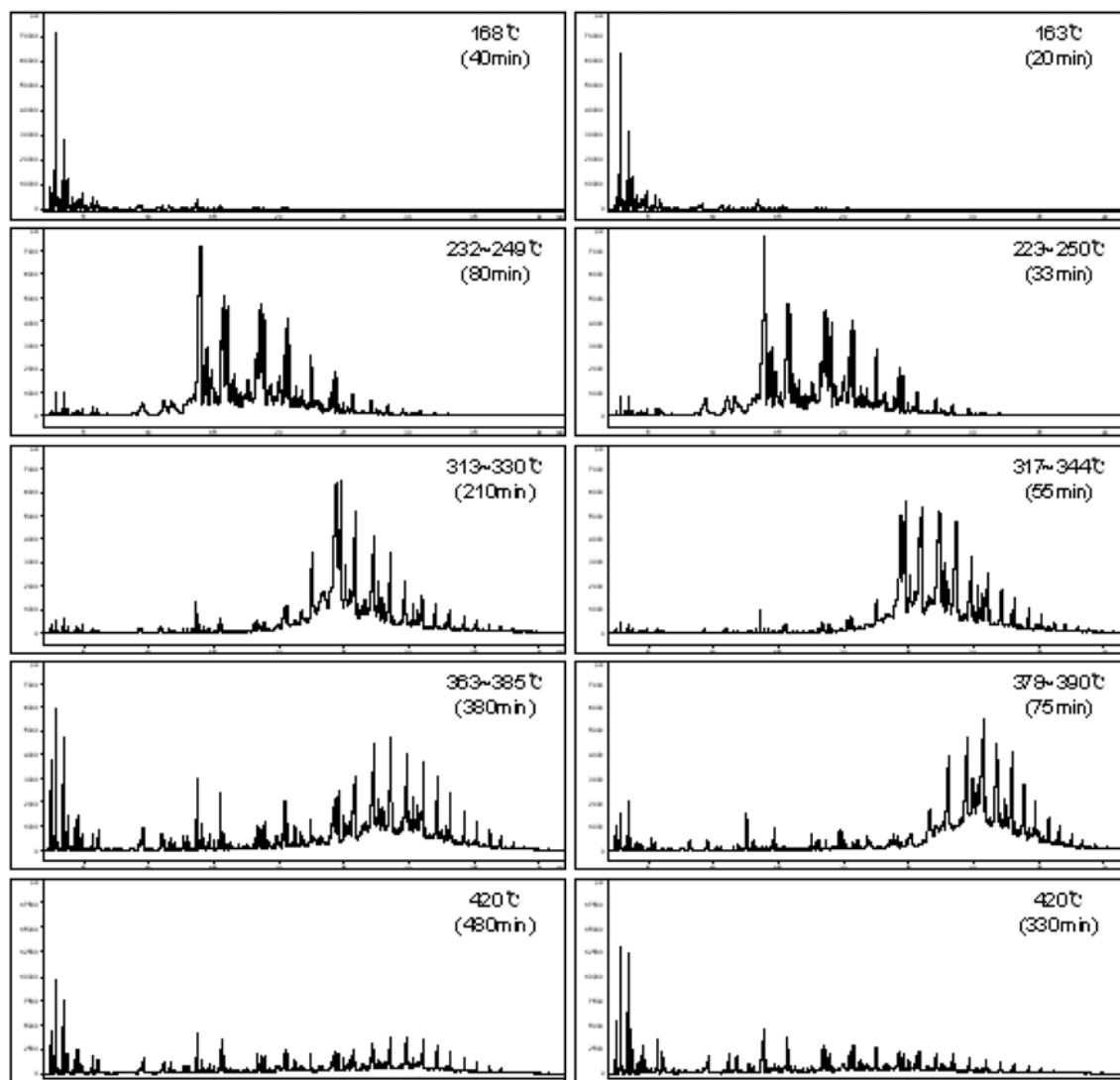


Fig. 4. Comparison of GC peaks of product oils at different reaction temperature (A: Low heating rate, B: High heating rate).

low holding times. Moreover, at even higher reaction temperature of 420 °C the high boiling point materials were much less produced while the low boiling point products were relatively more observed. This result suggests that hydrocarbon products with high boiling points have been transferred to the low boiling point materials by thermal degradation process.

Fig. 5 shows the distribution of carbon number of product oils obtained at different temperatures for two different heating rates. Here, the components of product oils with more than 1% in composition have been considered in this study. As can be seen in Fig. 5, for the temperatures below 170 °C the carbon distribution of product oil ranges between 4 and 9, indicating the gasoline range. Between 313 and 344 °C, and between 363 and 390 °C, the carbon numbers are distributed from 8 to 23, showing the presence of kerosene and diesel, respectively. But for the highest temperature of 420 °C the thermal degradation of high molecular materials to low molecular materials took place, resulting in the reduction of carbon number (between 4 and 20) and the abundant production of low molecular materials.

While the GC peak characteristics were obviously observed for

different heating rates at the same temperatures as shown in Fig. 4, the carbon distribution in Fig. 5 shows different trends for two different heating rates. For the low reaction temperature ranges between 163 and 167 °C a similar carbon distribution appeared irrespective of heating rates. For the high reaction temperature ranges between 300 and 400 °C low molecular materials were more produced at low heating rate than at high heating rate. In the meantime, high molecular materials were more produced at high heating rate. This kind of trend is more explicit for the higher temperatures between 363 and 390 °C. In the case of 420 °C the thermal degradation proceeded more actively, resulting in the appearance of inverse trend with temperature between 300 and 400 °C. In other words, with increasing the temperature the high molecular materials decomposed to low molecular ones, and the yield of low molecular products was higher at high heating rate than low heating rate.

CONCLUSION

This study is aimed at obtaining information for characteristics of raw pyrolytic oils produced by a thermal degradation of municipi-

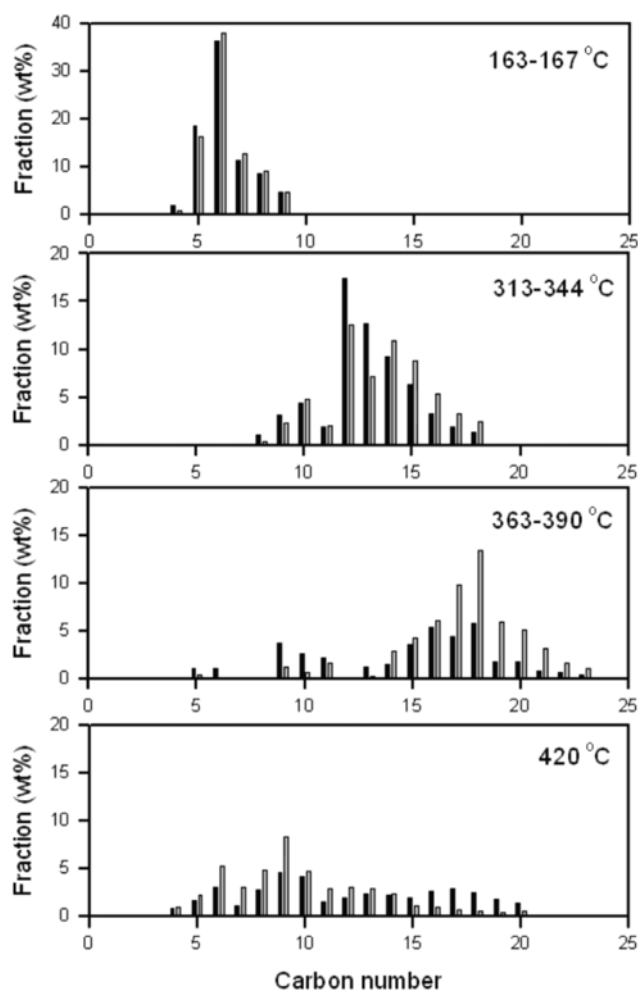


Fig. 5. Carbon number distribution of product oils obtained at different reaction temperature (■: Low heating rate, □: High heating rate).

pal plastic wastes using a commercial rotary kiln reactor, and at comparing the characteristics of products oils obtained by using two different heating rates. About 0.2 of H/C ratio for raw pyrolytic oil was higher than that for gasoline, kerosene, and diesel, and the heating value for raw pyrolytic oil was a little higher than 10,000 kcal/kg. As shown in GC analyses, the carbon numbers ranged from 5 to 30 (indicating the gasoline, kerosene, and diesel ranges) and the wax was also included. These gave rise to difficulties in direct usage for the industrial applications.

For the purpose of upgrading the raw pyrolytic oils, two different heating rates were used for product oils at increasing the temperature from room temperature to 420 °C. The cumulative amount of

liquid products was definitely influenced by heating rates and reaction temperatures. When compared to raw pyrolytic oils, the H/C ratio and heating value of product oils obtained at different temperature segments were high, and comparable, respectively.

The increase of reaction temperature to 390 °C caused the high molecular materials to be produced. For higher reaction temperatures than 380 °C the thermal degradation of high boiling point materials changed to low molecular ones. Based on carbon number distribution data, the carbon numbers were less than 10 (gasoline range) for the reaction temperatures less than 170 °C. For temperatures less than 390 °C the kerosene and diesel were mostly produced. However, for higher temperatures than 420 °C the thermal degradation of high boiling point materials actively took place and transferred to low boiling point materials in the gasoline range.

At low reaction temperatures, the carbon number distribution for product oils obtained at different temperatures showed no explicit difference for two heating rates. Meanwhile, for middle range of reaction temperatures between 300 and 400 °C, low boiling point products were obtained at low heating rate, and high boiling point materials were produced at high heating rate. These results were contrary to those observed at high temperature of 420 °C.

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