

Degradation of High Density Polyethylene, Polypropylene and Their Mixtures in Supercritical Acetone

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(Received 5 March 2001 • accepted 4 April 2001)

Abstract—The degradation of high density polyethylene (HDPE), polypropylene (PP) and their mixtures was carried out in supercritical acetone under the reaction temperature ranging from 450 °C to 470 °C, pressure ranging from 60 atm to 100 atm and reaction duration time as 60 min. The yields of gas, oil and wax components and the compositions and distributions of liquid-like products were measured by means of gas chromatography and gas chromatography/mass spectrometer. In every run, the reaction was completed in 30 min after reaching the prescribed temperature. The yields of oil and gas degraded from PP were not greatly influenced by the temperature, whereas in HDPE, the yields of oil decreased and that of gas increased, respectively, with rising temperature. The yields of oil from HDPE and PP increased with increasing pressure up to 7 atm and the values under higher pressure remained almost constant, i.e., 88% for HDPE and 96% for PP. Correspondingly, the yields of wax from HDPE and PP decreased with increasing pressure below 75 atm and above the value they remained almost constant, especially zero with PP. Generally, the degradation performance was influenced by the temperature rather than applied pressure. For the degradation of mixtures of HDPE and PP, with increasing PP composition, the yield of oil increased, whereas that of wax decreased, and above 80% of PP composition, it decreased to zero. For example, the yields of oil, wax and gas from a 52 wt% HDPE–48 wt% PP mixture, amounted to 90 wt%, 1 wt% and 9 wt%, respectively. The yield of wax decreased with increasing PP percentage.

Key words: Degradation, Supercritical Acetone, High Density Polyethylene, Polypropylene

INTRODUCTION

The use of plastics as commodities continues to grow, the increasing amount of waste plastics causes serious environmental hazards. Waste plastics occupy a large volume, when buried in a landfill, due to low density; moreover, they are hardly degraded biologically in the soil. Incinerating waste plastics also generates toxic gases, and is not a viable option. These are the reasons why new technologies are needed in the waste plastic treatment. Research on thermal degradation of waste plastics has been conducted where source materials and reusable oil are recovered, leaving some problems to be tackled such as excessively long degradation time, generation of toxic gases and the coking of reactants [Hwang et al., 1998; Oh et al., 1999].

Supercritical fluids have recently been used in waste plastic treatments to address the difficulties in thermal degradation of waste plastics. A supercritical fluid is one whose temperature and pressure are higher than its critical temperature and pressure. The hydrodynamic characteristics of supercritical fluids can be summarized as follows.

1. The density of a supercritical fluid is near that of the liquid phase fluid.
2. The viscosity of the supercritical fluid is near that of the gas phase fluid.

3. The diffusivity of a supercritical fluid is in between that of liquid phase fluid and that of gas phase fluid

The characteristics of supercritical fluids greatly enhance the reaction rate.

Koll and Metzger [1978] studied the degradation of cellulose and chitin with supercritical acetone. After Modell [1985] developed a process in which supercritical water was used to degrade organic materials, a number of researchers began to apply supercritical fluids to waste treatments. Dhawan et al. [1993] used supercritical toluene in the degradation of polyisoprene and waste rubber. Koehler et al. [1993] used supercritical water in the degradation of polyvinyl chloride. Jung et al. [1999] studied the recovery of oil from waste scrap tires. Research on recovery of monomer from PET and PS were performed by Kim et al. [2001] and Hwang et al. [1999].

In this study supercritical acetone was used in the degradation of high density polyethylene, polypropylene and their mixture. The relation between yields and the reaction condition is discussed.

EXPERIMENTAL

The schematic diagram of experimental apparatus is shown in Fig. 1. The reactor for the process was fabricated by Autoclave Company (U.S.A.). The reactor temperature was controlled by a PID controller (Sinko Co. PC600, Japan) with the maximum discrepancy of 1 °C. The rising pressure in the heated reactor was controlled by a back pressure regulator, which keeps the pressure in the

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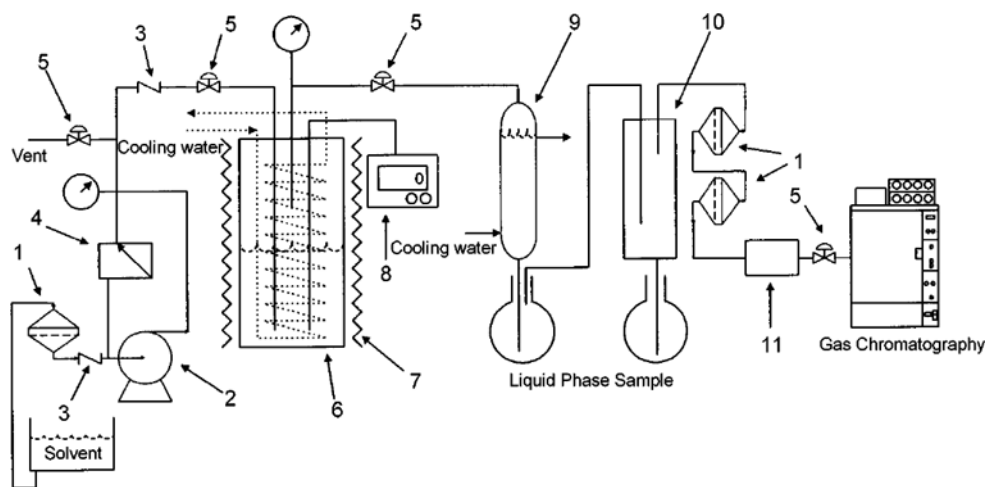


Fig. 1. Schematic diagram of experimental apparatus.

- | | | |
|----------------------------|-------------------|-----------------------|
| 1. Line filter | 5. Shut-off valve | 9. Water condenser |
| 2. Metering pump | 6. Reactor | 10. Separator |
| 3. o-ring check valve | 7. Furnace | 11. Turbing flowmeter |
| 4. Back pressure regulator | 8. Thermocouple | |

reactor constant.

The high density polyethylene (which is in a cylindrical shape and whose molecular weight, diameter, height and weight are 222,000, 2.3-2.6 mm, 2.8-3.3 mm and 14-18 mg respectively) produced by Honam Petrochemical Co. (Korea) was fed to the process. Polypropylene (Samsung Chemical Co, Korea) used in the experiment is also in a cylindrical shape and its molecular weight, diameter, height and weight are 115,000, 4.1-4.3 mm, 2.1-2.3 mm and 19.3-19.9 mg respectively. First reagent grade acetone (Ducksan chemical Co, Korea) was used.

A gas chromatograph (GC14A, Shimadzu, Japan) and GC/MS (Hewlett-Packard, 6890 GC, 5973 MSD) were used for the analysis of the products. The 25 meter long capillary column is packed with DB-WAX. The operation conditions of GC/MS are shown in Table 1.

The reactant was washed by ultrasonic washer (Soniclean 160HT) and dried at 50 °C for one day before use. Then the reactor was heated at the rate of 10 °C per minute. The weight ratio of acetone and reactants was 10 to 1. We set the time as the starting point of reaction

when the temperature and pressure reached the prescribed values of supercritical temperature and pressure.

RESULTS AND DISCUSSION

1. Variations of the Yields of Gas, Oil and Wax Components from HDPE and PP with Temperature

The variations of the yields of gas, oil and wax components with temperature were observed to identify the dependencies of HDPE and PP degradation with supercritical acetone on the reaction temperature. The reaction temperature was raised from 450 to 470 °C by 5 °C and the reaction pressure and time were 85 atm and 30 minutes respectively.

Fig. 2 shows the dependences of the yields of gas, oil and wax components from HDPE and PP on the reaction temperature. It is apparent that in the low temperature region, a small amount of wax is generated from HDPE, whereas no wax is generated from PP even at lower temperatures. As the temperature rises, the wax component from HDPE decreases, which results in an increasing yield

Table 1. Operating conditions of GC and GC/MS

	GC	GC/MS
System	Simadzu 14B SPL-14 split/splitless	HP 6890 series GC system HP 5973 Mass Selective Detector
Col. ini. temp.	40 °C	40 °C
Col. ini. time	5 min	5 min
Col. fin. temp.	250 °C	250 °C
Col. fin. time	10 min	10 min
Heating rate 1 (5-32 min)	5 °C/min	5 °C/min
Heating rate 2 (3-37 min)	10 °C/min	10 °C/min
Split ratio	1:100	1:50
Mass range		15-600 m/z
Prog. time	47 min	47 min

Column: DB-Wax (I.D.: 0.2, L: 25 m).

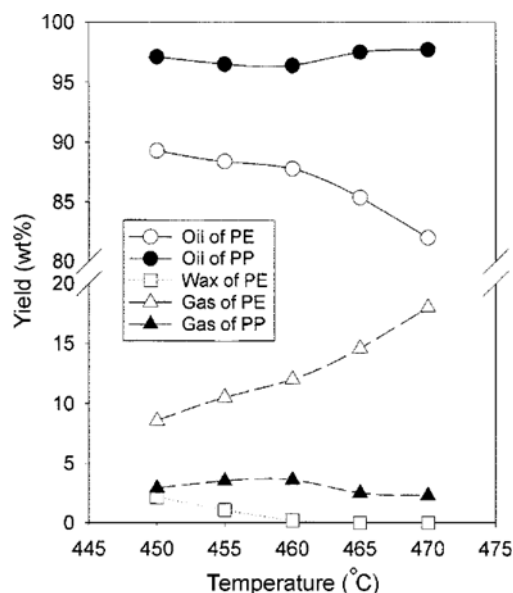


Fig. 2. Dependences of yields of gas, oil and wax from HDPE and PP on temperature ($p=85$ atm, reaction time=30 min).

of gaseous component. The yield of oil from PP is proven to be higher than that from HDPE. Besides, regarding PP, the yields of oil and gas were not so much influenced by the temperature covered in this study, whereas with respect to HDPE, the yields of oil and gas decreased and increased, respectively, with rising temperature.

2. Variations of the Yields of Gas, Oil and Wax Components from HDPE and PP with Pressure

The variations of the yields of gas, oil and wax components with pressure were observed to see how the degradation reaction depends on pressure. The experiment was conducted under the pressures of 60, 75, 85 and 100 atm, when the reaction temperature and the reaction time was set to 450 °C and 30 minutes respectively.

The variations of the yields of gas, oil and wax components from

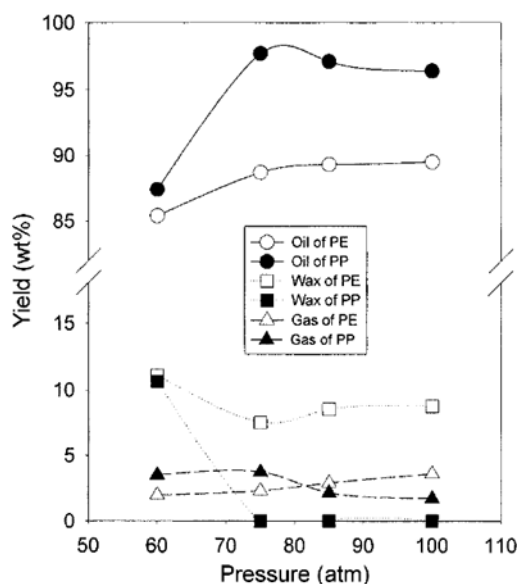


Fig. 3. Dependences of yields of gas, oil and wax from HDPE and PP on pressure ($T=450$ °C, reaction time=30 min).

HDPE and PP with applied pressure are indicated in Fig. 3. It is apparent that the yields of oil from HDPE and PP increase with increasing pressure below 75 atm, and above the value (75 atm) they remain almost unchanged. Correspondingly, the yields of wax from HDPE and PP decrease with increasing pressure below 75 atm and above the value they remain almost constant, especially zero with PP. The yields of gaseous component from HDPE and PP were not affected much by pressure. Generally, it is apparent from Figs. 2 and 3 that the degradation performance is influenced by the temperature rather than the pressure.

3. Variations of the Yields of Gas, Oil and Wax Components from HDPE-PP Mixtures with Weight Percents of PP

The variations of the yields of gas, oil and wax components with weight percent of PP were observed to see how the degradation reaction depends on the weight percent of PP. Oil is well recovered from PP and Wax is well recovered from HDPE. The experiment was conducted with the weight ratio of PE and PP set to 100 : 0, 75 : 25, 50 : 50, 25 : 75 and 0 : 100, when the reaction temperature, applied pressure and the reaction time were set to 450 °C, 85 atm and 30 minutes respectively.

Fig. 4 shows the variations of the yields of gas, oil and wax components from different HDPE-PP mixtures with the weight percents of PP. The yield of oil increased with increasing PP composition. Actually, wax was generated in PE-rich region.

The weight percents of PE, PP, PET, PS and others (eg., PVC, ABS etc.) in the plastic waste in Korea have been found to amount to 26%, 24%, 23%, 15% and 12%, respectively. Thus, the degradation of a mixture of 52 wt% HDPE and 48 wt% PP, was examined. Time dependency of the reaction was observed by conducting the experiment in which reaction temperature and applied pressure were set to 450 °C and 85 atm, respectively, with the reaction time ranging from 0 to 60 minutes. Fig. 5 shows the time dependences

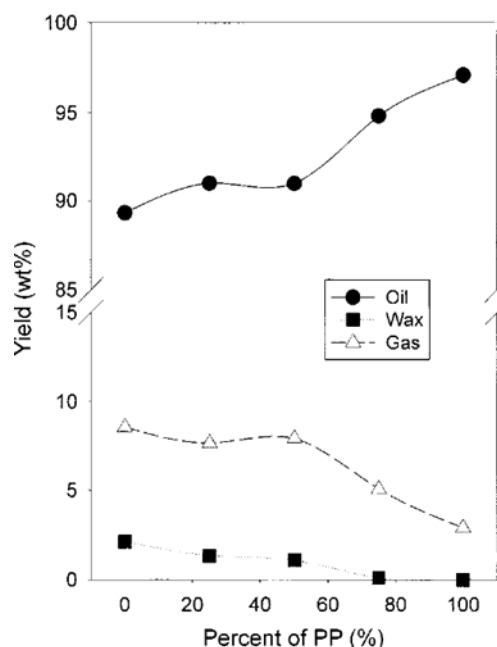


Fig. 4. Variations of yields of gas, oil and wax from HDPE-PP mixtures with the weight percents of PP ($T=450$ °C, $p=85$ atm, reaction time=30 min).

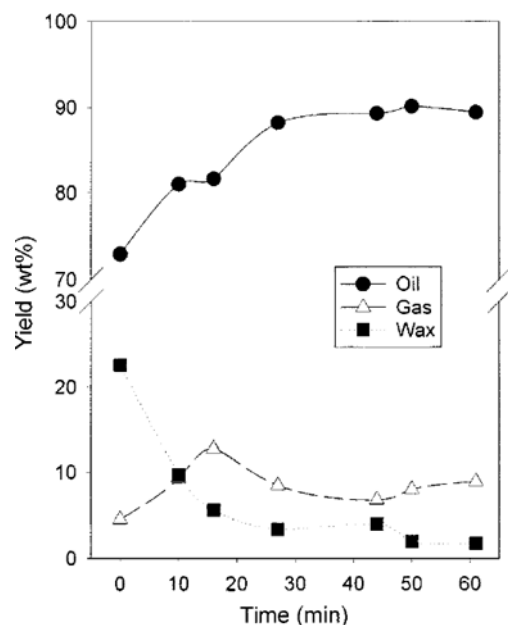


Fig. 5. Time dependences of yields of gas, oil and wax from a 52 wt% HDPE - 48 wt% PP mixture ($T=450^{\circ}\text{C}$, $p=85\text{ atm}$, reaction time=30 min).

Table 2. Compositions of liquid-like products degraded from HDPE at different temperatures

Temp. ($^{\circ}\text{C}$)	Alkanes	Alkenes	Ketones	Aromatics
450	73.1	0	19.3	7.6
460	56.8	8	23	12.2
470	53	13.9	18.1	15

of the yields of gas, oil and wax components from the mixture. At reaction time zero, the yield of wax amounted to more than 20%. After 10 min had passed, the yield of wax decreased to less than 10%. The reaction was found to go to completion in 30 min. Even though the reaction was further continued, a small amount of wax was detected.

4. Analysis of Products

The compositions of liquid-like products degraded from HDPE in supercritical acetone at different temperatures are listed in Table 2. The composition of alkanes decreased with rising temperature, and ranged from 53% at 470°C to 73% at 450°C . The composition of alkenes at 450°C remained zero. And it increased with temperature and approached 14% at 470°C . The composition of ketone, which is supposed to be formed by the reaction with acetone, amounted to ca. 20%. The composition of aromatics was varied from 7.6% at 450°C to 15% at 470°C . The fact that the composition of aromatics increased with temperature may be attributed to

Table 3. Compositions of $\text{C}_4\text{-C}_8$, $\text{C}_9\text{-C}_{12}$, $\text{C}_{13}\text{-}$ products degraded from HDPE at different temperatures

Temp. ($^{\circ}\text{C}$)	$\text{C}_4\text{-C}_8$	$\text{C}_9\text{-C}_{12}$	$\text{C}_{13}\text{-}$	Aromatics
450	74.36	20.2	5.44	7.32
460	81.82	16.05	2.13	12.2
470	77.45	19.96	2.59	15

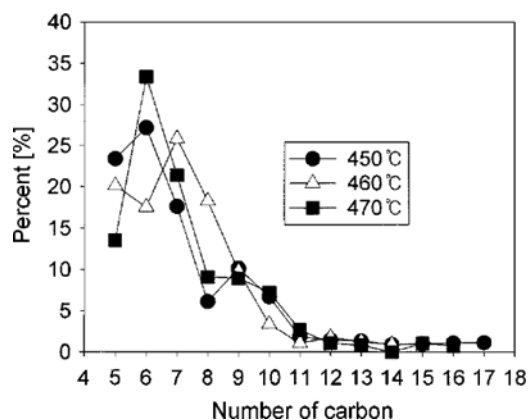


Fig. 6. Distribution of numbers of carbon in the constituents degraded from HDPE.

Table 4. Compositions of liquid-like products degraded from PP at different temperatures

Temp. ($^{\circ}\text{C}$)	Alkanes	Alkenes	Ketones	Aromatics
450	50.4	14.1	20.9	14.6
460	41	17.6	21.6	19.8
470	49.7	18.8	17.3	14.2

the trend of easier recombination of degraded components with benzene at higher temperatures. The numbers of carbon in the constituents degraded from PE are listed in Table 3, and the distribution of carbon numbers is demonstrated in Fig. 6.

The compositions of liquid-like products degraded from PP at different temperatures are listed in Table 4. The composition of alkanes amounted to 40-50%, which was lower than that from HDPE. The yield of alkenes, with increased with rising temperature, ranged from 14% to 19%, a considerably large value as compared to that from HDPE especially at lower temperatures (i.e., 450°C and 460°C). The composition of ketones ranged from 17% to 22%, similar to that from HDPE. The composition of aromatics was varied from 14% to 20%, being larger than that from HDPE especially at lower temperatures. Regarding PP, the numbers of carbon in the degraded products are listed in Table 5, and the distribution is drawn in Fig. 7. The compositions of the liquid-like products with carbon numbers ranging from 8 to 10 are shown to be much higher than those degraded from HDPE.

Similar results concerning the degradation of mixtures of HDPE and PP at 450°C , are listed in Table 6. The composition of alkanes ranged from 60% to 70%. The composition of alkenes amounted to more or less than 10%. The composition of ketones was varied from 15% to 22%. The composition of aromatics amounted to more or less than 6%. The compositions of such liquid-like products are

Table 5. Compositions of $\text{C}_4\text{-C}_8$, $\text{C}_9\text{-C}_{12}$, $\text{C}_{13}\text{-}$ products degraded from PP at different temperatures

Temp. ($^{\circ}\text{C}$)	$\text{C}_4\text{-C}_8$	$\text{C}_9\text{-C}_{12}$	$\text{C}_{13}\text{-}$	Aromatics
450	78.48	21.52	0	14.6
460	82.14	17.86	0	19.8
470	81.42	18.58	0	14.3

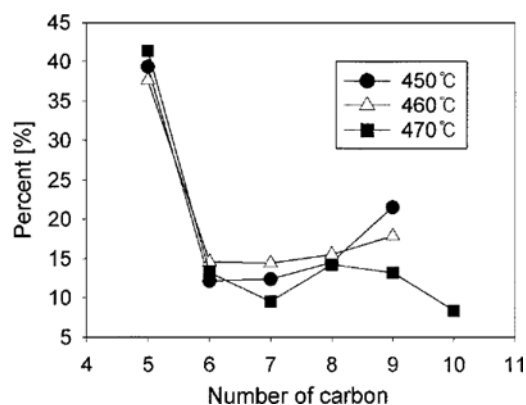


Fig. 7. Distribution of numbers of carbon in the constituents degraded from PP.

Table 6. Compositions of liquid-like products degraded from different HDPE-PP mixtures at 450 °C

HDPE	PP	Alkanes	Alkenes	Ketones	Aromatics
100	0	73.1	0	19.3	7.6
75	25	70.9	6.9	15.4	6.8
50	50	65.4	6.9	22.2	5.5
25	75	61.7	10.7	21.3	6.3
0	100	50.4	14.1	20.9	14.6

Table 7. Compositions of C₄-C₈, C₉-C₁₂, C₁₃-products degraded from different HDPE-PP mixtures at 450 °C

HDPE	PP	C ₄ -C ₈	C ₉ -C ₁₂	C ₁₃ -	Aromatics
100	0	74.36	20.2	5.44	7.32
75	25	79.19	19.06	1.75	6.75
50	50	80.52	18.4	1.08	5.52
25	17	83.23	16.77	0	6.36
0	100	78.48	21.52	0	14.6

not so much influenced by the composition of the mixtures over the range of PP composition of 25% to 75%. The numbers of carbon in the degraded products from HDPE-PP mixtures are listed in Table 7. The distributions are drawn in Fig. 8, which are shown to be much affected by the weight percents of PP.

The degradation of HDPE, PP and their mixtures in supercritical acetone within the experimental conditions covered here had the features that no reactants remained, only a trace amount of char was produced, and the reaction residual was less than 0.001 wt%.

Table 9. Yields of products by thermal degradation of pure HDPE and PP

	HDPE				PP			
	400 °C	430 °C	460 °C	500 °C	370 °C	400 °C	430 °C	460 °C
Gas	3.8	13.7	12.4	13.4	12.8	12.4	12.4	15.5
Oil	11.0	64.3	81.3	84.2	10.9	66.9	78.6	80.1
HBP*	85.2	22.0	6.4	2.4	76.3	20.7	9.0	0
Oil/Gas	2.89	4.69	6.50	6.28	0.85	5.39	6.30	5.16

*High-boiling product

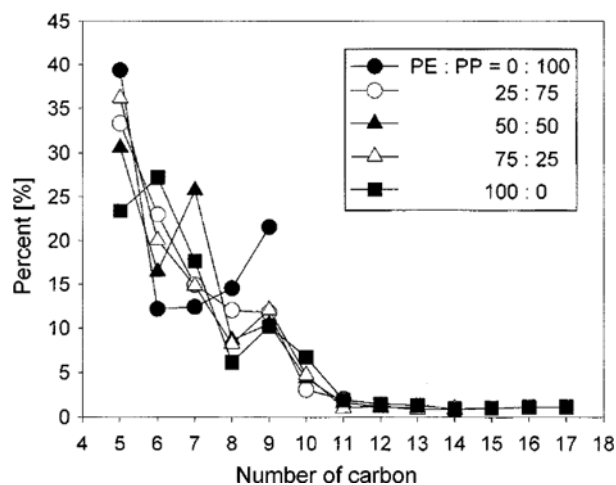


Fig. 8. Distribution of numbers of carbon in the constituents degraded from different HDPE-PP mixtures.

Table 8. Comparisons of results on degradation of HDPE in supercritical acetone with those of pyrolysis of HDPE

Degradation method	Temp. (°C)	Gas (%)	Oil (%)	Residue (%)	Wax (%)
Pyrolysis 1	450	8	82.5	9.5	-
Pyrolysis 2	600	24.12	75.78	0	-
	640	54.77	45.23	0	-
	680	67.12	32.49	0.39	-
This study	450	8.56	89.3	-	2.14

5. Comparison of Degradation in Supercritical Acetone with Thermal Degradation

The comparison of the results from the degradation in supercritical acetone with those of pyrolysis (i.e., thermal degradation) is presented in Table 8. For the pyrolysis of LLDPE at 450 °C, the yield of oil was reported to reach more than 80% [McCaffrey et al., 1995], but no mention was made on the generation of wax. As the pyrolysis temperature rises, the yield of gaseous components increases, and subsequently the yield of oil decreases [Choi, 1997]. No wax was detected at temperatures ranging from 600 °C to 680 °C [Choi, 1997].

Table 9 shows the yields of products from the pyrolysis of pure PE and PP [Jung et al., 1998]. It is apparent that the yield of oil increases with rising temperature for pyrolysis of both PE and PP. The yields of oil from the pyrolysis of PE and PP attained 84.2% at 500 °C and 80.1% at 460 °C, respectively. Table 10 shows simi-

Table 10. Yields of products by thermal degradation of mixtures of HDPE and PP

	HDPE-PP (1:2)		HDPE-PP(1:1)			HDPE-PP (2 : 1) HDPE-PP (5 : 1)	
	430 °C	370 °C	400 °C	430 °C	460 °C	430 °C	
Gas	11.8	4.2	14.7	19.3	20.6	19.2	15.6
Oil	76.8	3.1	27.5	65.3	75.2	61.8	57.8
HBP*	11.5	92.7	57.8	15.4	4.2	19.0	26.6
Oil/Gas	6.50	0.73	1.87	3.38	3.65	3.22	3.71

*High-boiling product.

lar results by pyrolysis of mixtures of PE and PP [Jung et al., 1998]. For the pyrolysis of a 50% PE-50% PP mixture, the yield of oil increased to 75.2% at 460 °C.

Nevertheless, the yield of oil from the pyrolysis of PE and PP has been found to be lower than that from the degradation in supercritical acetone. In addition, the reaction completion time for the former (pyrolysis) is longer than that for the latter, i.e., 100 min vs. 30 min.

CONCLUSION

The degradation of HDPE, PP and their mixtures in supercritical acetone was carried out at reaction temperatures of 450 °C to 470 °C and applied pressure of 60 atm to 100 atm. The reaction was continued till 60 min. The following findings were obtained.

1. A small amount of wax is generated for the degradation of HDPE. The yield of aromatics is higher for the PP degradation than for the HDPE degradation.
2. The yield of wax degraded from HDPE decreases with rising temperature, and subsequently, the gaseous components are increased.
3. Regarding PP, the reaction temperature does not have so much influence on the yields of oil and gas components.
4. The yields of gaseous component from HDPE and PP are not much affected by the pressure.
5. With reference to the degradation of mixtures of HDPE and PP, the generation of aromatics is reduced much even with a small amount of HDPE contained, whereas the generation of wax and gaseous components was retarded much with a small amount of PP contained.
6. The reaction is completed in 30 min after reaching a pre-scribed temperature.
7. In the degradation of a 52 wt% HDPE-48 wt% PP mixture, the yield of oil attained 88 wt% under the following reaction conditions; temperature=450 °C, pressure=85 atm, and weight ratio of acetone to reactants=10.
8. The degradation in supercritical acetone has the favorable features of low temperature, short reaction time and high oil yield as compared to the pyrolysis (i.e., thermal degradation).

ACKNOWLEDGEMENT

The authors thank the Korea Energy Management Corporation for the financial support.

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