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PYROLYSIS CHARACTERIZATION OF MSWS AT THERMAL DECOMPOSITION CONDITIONS

Jong-In Dong†, and Tae-Heun Kim
Department of Environmental Engineering, University of Seoul, Korea
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Abstract : The purpose of this study is to understand the characteristics of pyrolysis products through lab-scale pyrolysis tests of MSW (Municipal Solid Waste) at different operating conditions and to get optimum conditions for desirable products. Target samples were recomposed of each component based on dry compositions of MSWs directly collected from S city. Isothermal pyrolysis experiments were performed at different conditions for 45g of MSW samples in a batch reactor. The temperature was varied from 400°C to 700°C. Oxygen concentration was varied as 5%, 10% and 15% with 60cc/min inflow rate of O_2. Pyrolysis products such as char, oil, tar, gas obtained at each pyrolysis condition were analyzed in terms of yield, composition and heat values. The results of this studies indicated that decomposition reaction at low oxygen concentration is much faster than nitrogen atmosphere. Gaseous products (CO, H_2, CH_4) were obtained more effectively at higher temperature but the amount of gaseous product suitable for auxiliary fuel was relatively small. Tar and wax were the main components of liquid products. Since the amount of oil is small and it is mostly hydrophilic, it is considered not feasible to use as a main fuel. It was found that char product has a value of fuel due to its high calorific value. From this fact, it would be one option to try to obtain more char as a target product from MSWs pyrolysis process. From the results of experiments done at different pyrolysis conditions, most of reactions occur in initial 10~15 minutes. Therefore, the reaction of initial stage could be considered as the most important step of total pyrolysis process.

Key Words : MSWs, Isothermal pyrolysis, Fuel, Batch reactor, Pyrolysis products

INTRODUCTION

Since 1970s, Germany and Japan have had development experiences of the pyrolysis of MSWs. Now the technology has reached a considerable position. However, this technology cannot be directly applied to Korean situations, due to the differences of MSWs compositions and heat values.

Most of pyrolysis studies have been performed in terms of heating-rate conditions of a very small amount of single component, with limited application of pyrolysis system like a pilot plant. Therefore process-based study applicable to actual MSWs is required for technology development[1]. The purpose of this study is to understand the characteristics of pyrolysis products through pyrolysis characterization tests of MSWs at different operating conditions and to get optimum conditions for desirable products.

Compositions and characteristics of pyrolysis products at N_2 atmosphere and low O_2 concentrations have been investigated. Furthermore several tests have been done to obtain the optimum thermal decomposition conditions.[2]

† Corresponding author
E-mail: jidong@uos.ac.kr
Tel: 02-2210-2532, Fax: 02-2244-2245

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples with size of 3～4 cm was recomposed of each component based on dry compositions of MSWs that are directly collected from S city during May 2001. These samples consisted of flammables about 86.51%, inflammables about 13.49%. Paper & vinyls were 74.50% of the whole flammables. Moisture was about 30.70% in the flammables. Foods contained the highest moisture in the flammables. Isothermal pyrolysis experiments were performed at different conditions for 45g MSWs samples in the batch reactor.

Equipments

The batch type pyrolysis system is shown schematically in Figure. 1. The reactor is externally heated by an electric furnace and is composed of the 1st gas heating furnace and 2nd furnace reactor. The 2nd furnace has a 10cm×10cm×10cm stainless steel reactor[3]. Carrier gas preheated to 800°C in the 1st furnace is introduced to the reactor and heat is supplied from the walls. Oxygen-nitrogen ratio of the carrier gas varied by adjusting the flowrate of the gases. The gases were mixed at the required concentrations through sufficient mixing before they flowed into the reactor. The flow rate of the carrier gas was controlled by MFC (Mass Flow Controller). Water bath was connected to the end of the reactor. The temperature of the condenser was maintained at 3°C. Glass wool filter was installed to remove the particulate in the end of the condenser. The gaseous products were collected after dry gas meter and was analyzed using gas chromatography.

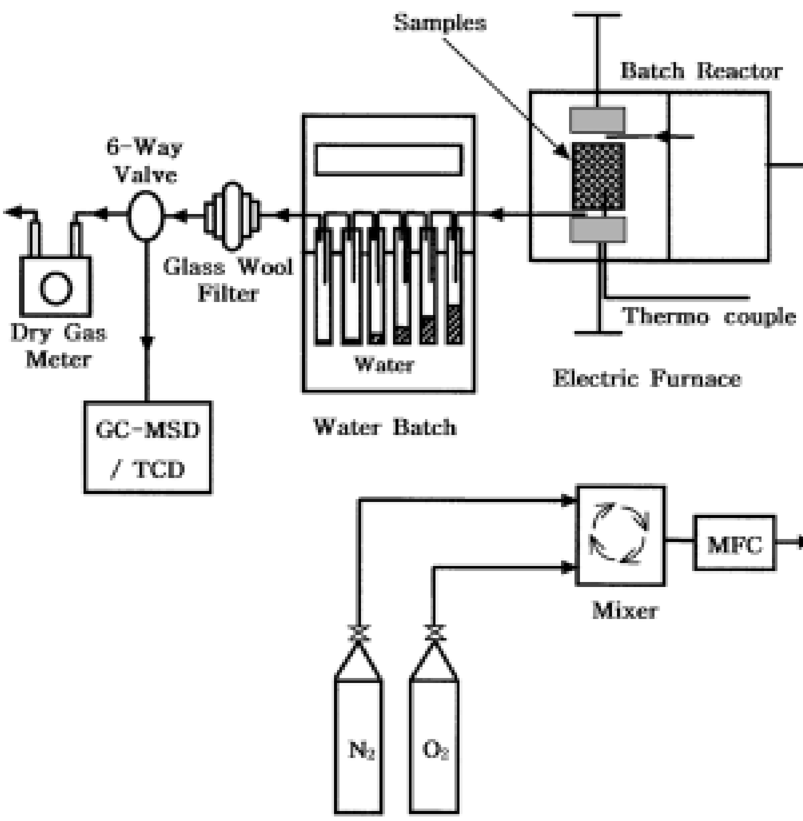


Figure 1. Schematic diagram of batch type pyrolysis system.

Experimental Methods

Isothermal pyrolysis

The temperature of pyrolysis was varied from 400°C to 700°C. When the temperature of the reactor was stabilized to the set temperature, sample was introduced from the upper part of the reactor. Order of the reaction, activation energy and pre-exponential factor over total reaction time of isothermal pyrolysis were calculated. The kinetics of the reaction was assumed to be the 1st order then activation energy and pre-exponential factor were calculated.[4)]

Pyrolysis at N_2 condition & low oxygen concentrations

Oxygen concentration was set to 5%, 10%, 15% O_2, and the inflow rate was set at 60 cc/min. Nitrogen and pure oxygen was sufficiently mixed in the mixing zone before the inflow to the reactor.

Analysis Methods

Pyrolysis products such as char, oil, tar and gas at each condition were analyzed to get yield, composition and heat values.

Yield analysis of gaseous products

Gaseous products obtained in the pyrolysis reaction were collected in a sample bag, and total amount of recovered gas was assumed by subtracting the amount of carrier gas passed during the reaction from total amount of samples. Yields were calculated by applying the concentration of each gas composition to total amount of produced gas.

Yield analysis of liquid (oil & tar) products

Liquid products were divided into "oil" and "tar". Generally product recovered in condensation bottles is considered as "oil", and product recovered in the wall of reactor is considered as "tar". But tar contains various high molecular weight organic compounds, which are wax type at normal temperature. So, in this study, wax type product could be obtained in condensation bottles. Therefore we considered fluid contents recovered in condensation bottles as "oil", and the other product of wax type as "tar".

Yield analysis of char products

After the reaction ended, the internal temperature of reactor was reduced below 300°C, and solid residues remaining inside the reactor were recovered and cooled. The residue thus obtained was weighed to get the yield of char.

RESULTS AND DISCUSSION

Analysis Results of Waste Samples

Physical characteristics, proximate analysis results and chemical compositions of target MSWs are listed in Table 1~3.

Table 1. The Physical Characteristics of Target MSWs

Apparent Density(kg/m^3)			170.15
Physical Characteristics on Wet Basis (%)	Flammables	food	15.01
		paper	34.91
		wood	0.41
		leather/rubber	6.88
		textile	3.6
		vinyl/plastic	7.37
		others	18.33
		total	86.51
	Inflammables	metal	6.20
		glass	6.46
		stone/pottery	N.D
		used briquet	N.D
		others	0.83
		total	13.49

Table 2. The Result of Proximate Analysis

Proximate Analysis (%)	Flammables	Moisture	30.70
		Combustible Material	60.10
		Ash	9.20
	Whole Waste	Moisture	27.70
		Combustible Material	61.30
		Ash	11.00

Table 3. Chemical Composition of Flammables in Target MSWs

(unit : %)

C	H	O	N	Cl	S	Ash	Total
40.61	6.22	36.50	1.27	0.38	0.01	15.00	100.00

Isothermal Pyrolysis of MSWs

45g MSWs sample was pyrolyzed at 100% nitrogen atmosphere, and 5%, 10%, 15% oxygen concentrations, at 400°C, 500°C, 600°C and 700°C. So, isothermal pyrolysis was conducted in each experiment to calculate the rate of weight reduction at different time intervals. The flow rate of the carrier gas was maintained at 60 cc/min.

Pyrolysis for thermal decomposition conditions

Rate of weight reduction and degradation is shown in Figure. 2 and 3. As appeared in Figure. 2, the rate of weight reduction at different temperatures has nearly similar trends. Rate of degradation of MSWs sample for isothermal pyrolysis at various O_2 concentration is shown in Figure. 3. It is found that at oxidation conditions rate of the weight reduction increases as oxygen

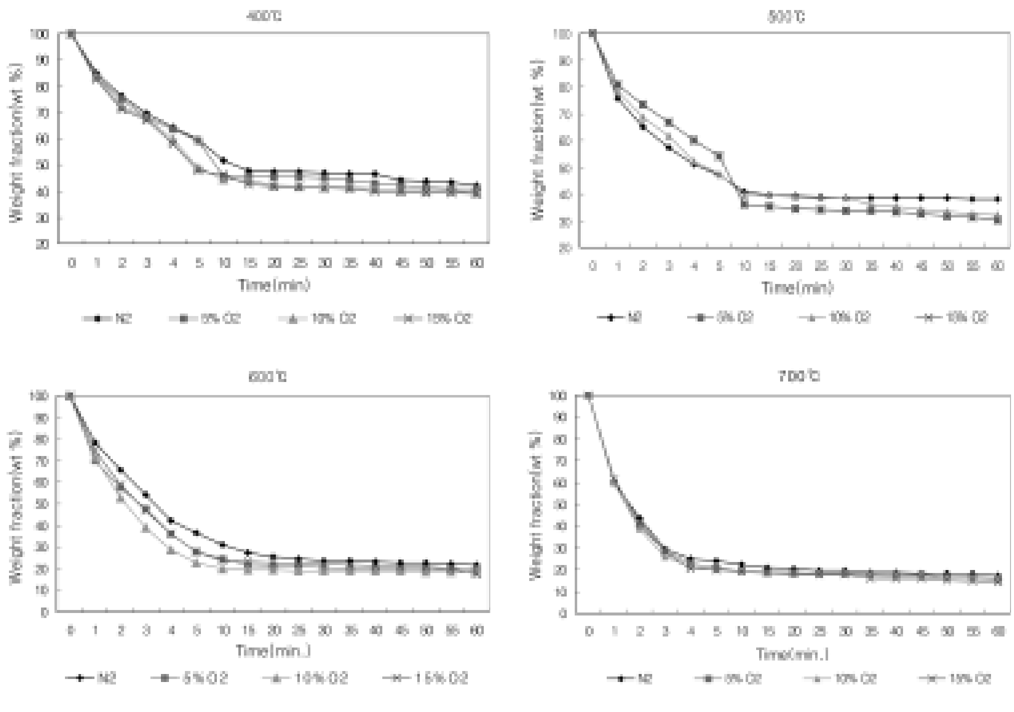
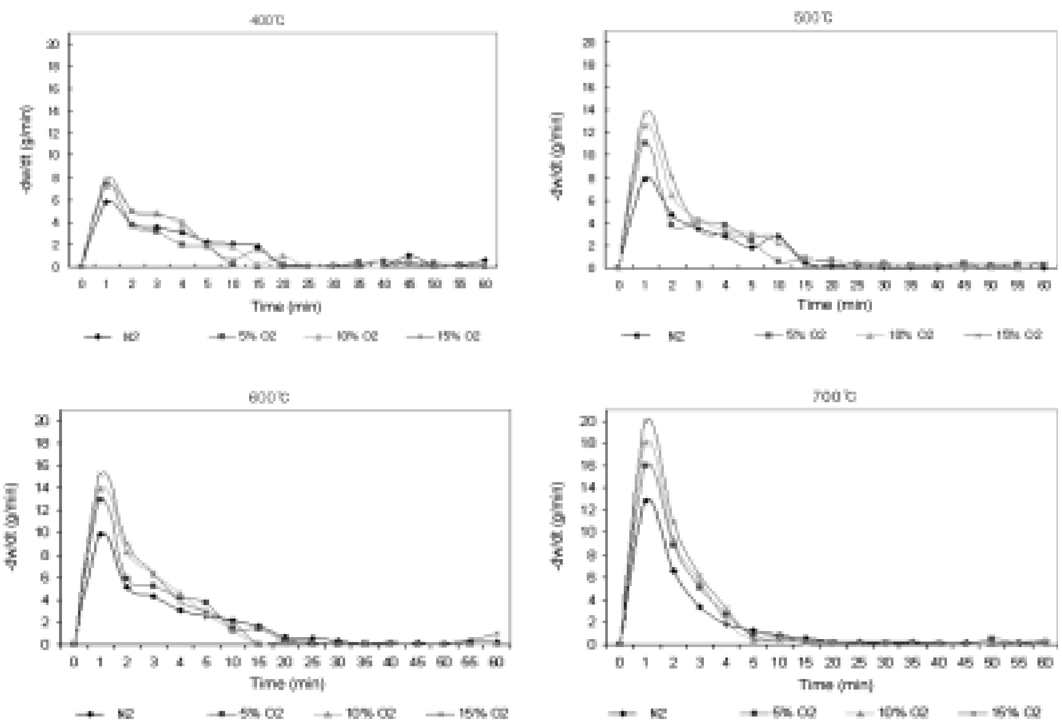


Figure 2. Weight change profiles at various O_2 concentrations.



Figrue 3. Rates of degradation of MSW samples for isothermal pyrolysis at various O_2 concentration

concentration increases. But, there is not much difference at the same temperature. At higher temperatures, the effect of rate of the weight reduction on oxygen concentration is negligible. Most of reaction was observed to occur in initial 5 min. and there is no significant change in the rate of weight reduction after this time.

Isothermal Pyrolysis Kinetics of MSWs

The order of the reaction and rate constants were calculated by using the following equation nonlinear regression. The activation energy and pre-exponential factors were determined by Arrhenius equation. The results are summarized in Table 4.

$$\frac{dX}{dt} = A\,(1-X)^n \exp[-\frac{E_a}{RT}]$$

It is found that order of reaction at each degradation condition has the value of about 1. As the temperature of pyrolysis increases, order of the reaction approaches nearly to the 1st order. The activation energy, 15.31 kJ/mol is the highest for N_2, and 13.92 kJ/mol, 13.84 kJ/mol, and 13.09 kJ/mol are for 5% O_2, 10% O_2 and 15% O_2, respectively. As oxygen concentration increases, activation energy decreases but with little difference. Pre-exponential factor has the highest value of 5.2096 hr^{-1} at the nitrogen atmosphere.

In isothermal pyrolysis, most of MSWs degradation occurs in initial 5 min. Pyrolysis reaction behavior for this initial 5 min. could be assumed of the 1st order reaction. The kinetic parameters, activation energy, and pre-exponential factor for decomposition condition at initial 5 min. are shown in Table 5. Also, it is found that the kinetic constants become higher, as the temperature of the condition increases. In the initial stage of pyrolysis, activation energy has the highest value of 19.45 kJ/mol for N_2, and the

Table 4. The kinetic parameters of MSWs at different atmospheres

Atmosphere	Temp.(°C)	Kinetic constant(k)	n	$A(hr^{-1})$	E_a(kJ/mol)
Nitrogen	400	0.3348	1.6264	5.2096	15.31
	500	0.5398	1.3674		
	600	0.6182	1.2990		
	700	0.7944	1.2769		
5% O_2	400	0.3962	1.0266	4.7974	13.92
	500	0.4056	1.0642		
	600	0.4276	1.3485		
	700	0.7897	1.2009		
10% O_2	400	0.3036	1.0817	4.3842	13.84
	500	0..3929	1.4972		
	600	0.4093	0.7813		
	700	0.7868	1.1614		
15% O_2	400	0.3236	1.1206	2.8699	13.09
	500	0.3385	1.0850		
	600	0.3912	1.1467		
	700	0.7049	1.1727		

Table 5. The kinetic parameters of MSWs at different conditions during initial 5 min

Condition	Temp.(°C)	Kinetic constant(k)	$A(hr^{-1})$	E_a(kJ/mol)
Nitrogen	400	0.0875	2.6179	19.45
	500	0.1202		
	600	0.1955		
	700	0.2390		
5% O_2	400	0.1310	2.4655	18.61
	500	0.1372		
	600	0.2288		
	700	0.2674		
10% O_2	400	0.1274	2.2150	18.47
	500	0.1289		
	600	0.2629		
	700	0.2758		
15% O_2	400	0.1305	2.0045	15.60
	500	0.1722		
	600	0.2473		
	700	0.2947		

lowest of 15.60 kJ/mol for 15% O_2.

Characteristics of Product for Thermal Decomposition Conditions

Yield of solid, liquid and gaseous products recovered by isothermal pyrolysis tests at 400～700°C are shown in Table 6. It can be found that yield of char is about 23.00～42.22% at nitrogen condition, but at low oxygen levels, yield of char decreases to about 14.44～40.98%, and yield of oil, tar and gases increase.

Effect of temperature on pyrolysis products yield

Distributions of gas, oil, tar, and char recovered at each temperature are shown in Fig. 4. Generally more gaseous products were generated at elevated degradation temperature, and yield of gaseous products increases rapidly at temperatures higher than 500°C. The amount of gaseous products actually generated is considered more than that recovered, but yield of gas is not so high due to polymerization to tar or char. In the case of char, its yield decreases as the

Table 6. Product yields from pyrolysis tests

Condition	Temp.(°C)	Char(%)	Oil(%)	Tar(%)	Gas(%)
Nitrogen	400	42.22	19.11	9.33	3.39
	500	38.16	18.67	17.78	3.93
	600	21.56	11.86	30.23	7.62
	700	23.00	11.22	26.67	14.11
5% O_2	400	40.98	20.67	8.67	3.64
	500	35.12	16.67	19.11	4.23
	600	19.78	5.33	46.00	8.20
	700	15.33	17.33	25.48	15.72
10% O_2	400	39.56	17.78	11.78	4.15
	500	32.22	14.90	13.11	4.51
	600	18.61	5.56	41.33	9.43
	700	16.00	16.67	27.11	16.13
15% O_2	400	39.11	18.44	13.33	4.50
	500	30.22	15.56	28.67	6.63
	600	17.56	8.44	40.89	15.70
	700	14.44	20.44	26.44	21.41

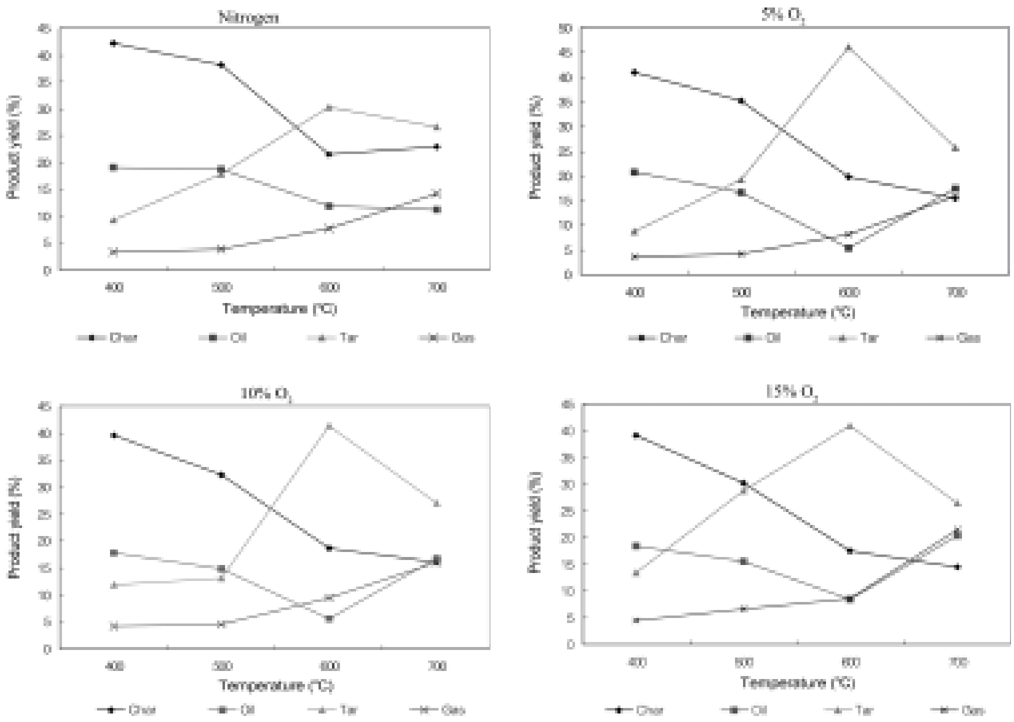


Figure 4. Pyrolysis products yield at different temperatures.

temperature increases, and then shows not much change at temperatures higher than 600°C. The yield of char at nitrogen atmosphere at 400°C is 42.22%.

The yield of tar increases continuously to 600°C, and then decreases, but the yield of oil decreases gradually up to 600°C, and then increases rapidly.

Effect of oxidative condition on pyrolysis products yield

The products yield at different temperatures

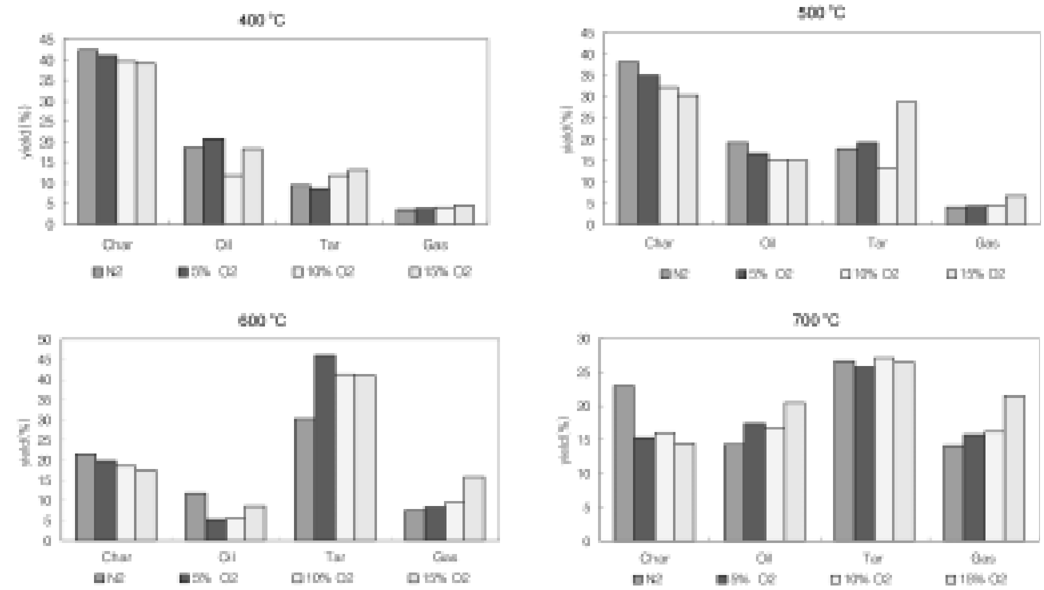


Figure 5. Pyrolysis product yields at different oxidative conditions.

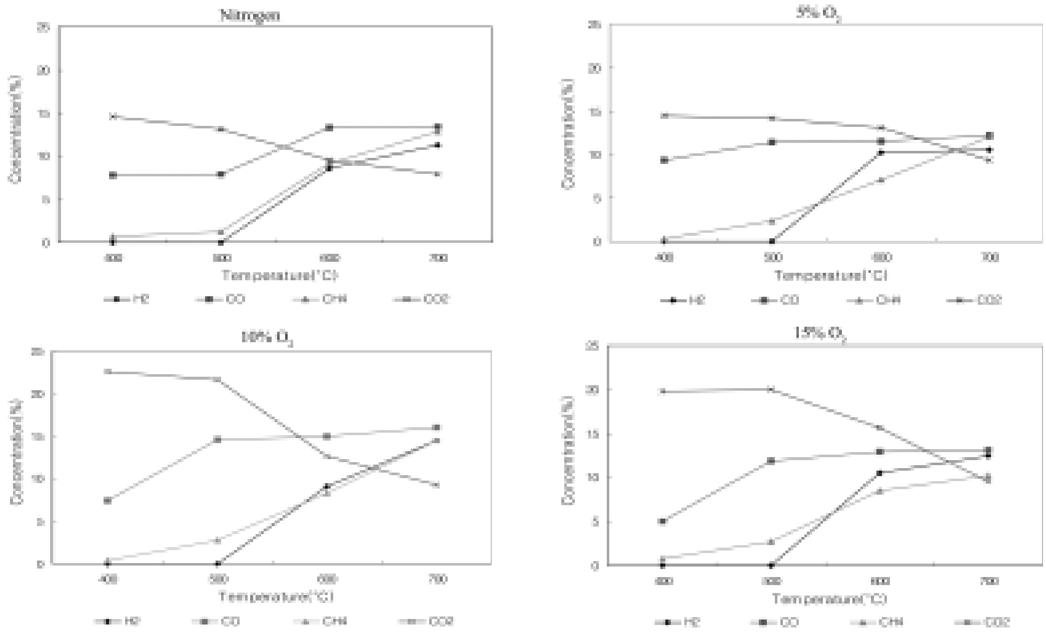


Figure 6. Composition of gas after pyrolysis at different temperature conditions.

and oxidation conditions is shown in Figure. 5. Yield of char is relatively lower in the presence of oxygen than at nitrogen atmosphere. It seems that yield of gas, tar and oil shows great difference with the change in oxygen concentration, and as the pyrolysis temperature increases, this tendency is more remarkable. However, there is only a little difference in terms of gas yield in the temperature range of 400～600°C.

Distributions of gas products

As shown in Figure. 6, it is found that the concentration of CO_2 degreases as the pyrolysis temperature increase. However, H_2, CO and CH_4 increases as the temperature increases. Specially, CO is generated at the temperatures higher than 500°C.

CONCLUSION

The results of this study indicate that decomposition reaction rate of MSWs at low oxygen concentration is faster than at nitrogen atmosphere. Generally yield of gaseous products is higher as oxygen concentration becomes higher, and the production of CO and H_2 is higher in the presence of oxygen than at nitrogen. It is also found that as the degradation temperature increases, more CH_4 is obtained. So it seems that high temperature and low oxygen concentration would be suitable to obtain gas as the major product used for main fuel. Char is considered to have characteristics of fuel due to the high heat value. From this point of view, in pyrolysis of MSWs, it would be advisable to try char as a target product. Also, from the results of experiments with different pyrolysis conditions, it is found that most of reaction occurs in initial 5 min. Therefore, the reaction of initial 5 min. could be considered as the most important step of total pyrolysis process.

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REFERENCES

1. Kim, J.-S., Kaminsky, W., Schlesselmann, B., "Pyrolysis of a fraction of mixed plastic wastes depleted in PVC," J. Anal. Appl. Pyrolysis 40-41, pp. 365～372 (1997).
2. Horne, P. and Williams, P., "Influence of temperature on the products from the flash pyrolysis of biomass," Fuel, Vol. 75, No. 9, pp. 1051～1059 (1996).
3. Li. A., Cen, K. F., Li, S.Q., Ren, Y., "Pyrolysis of solid waste in a rotary kiln : influence of final pyrolysis temperature on the pyrolysis products," J. Anal. Appl. Pyrolysis 50, pp. 149～162 (1999).
4. Pinto, F., Costa, P., Gulyurtlu, I., Cabrita, I., "Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield," J. Anal. Appl. Pyrolysis, 51, pp. 39～55 (1999).