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Decomposition Characteristics of Residue from the Pyrolysis of Polystyrene Waste in a Fluidized-Bed Reactor

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Abstract−Effective treatment of residue generated from the pyrolysis of polystyrene wastes has been one of the important factors in the recovery of styrene monomer and oil from polystyrene wastes. Depending on the experimental conditions, the yields of oil and styrene monomer are considerably decreased in the presence of residue. Here the residue was decomposed effectively in a catalytic fluidized-bed reactor. Nitrogen and silica sand were used as a fluidizing gas and a bed material, respectively. Effects of catalyst, temperature and gas velocity on the characteristics of decomposition of the residue were examined. It was found that the residue could be decomposed to oil or chemicals effectively by means of a catalytic fluidized-bed reacting system. The yields of oil and individual chemicals and the composition of the products were dependent upon the operating variables such as reaction temperature, catalyst and gas velocity.

Key words: Residue Decomposition, Polystyrene Waste, Fluidized Bed, Catalyst

INTRODUCTION

A promising alternative to dumping or incineration for the treatment of plastic waste such as polystyrene waste can be pyrolysis to recover the monomer or other valuable chemicals. The recycling to fuel oils from the waste polymers has been attractive and sometimes commercially operated. However, the fuel oils thus recovered produce large amounts of carbon dioxide when burned as fuels. Therefore, several investigations have focused on the recovery of monomers from polymers [Hirose et al., 1998; Sasse and Emig, 1998; Mertin et al., 1999]. However, a considerable amount of residue has been generated in the process of monomer recovery. The residue has to be treated effectively to increase the recovery of oil and monomer in the continuous stirred tank reactor. Therefore, the effective treatment of residue generated from the pyrolysis of polystyrene waste has been one of the important factors in the recovery of styrene monomer from the polystyrene wastes [Puente et al., 1997; Lim et al., 2000; Masuda et al., 2001].

The temperature distribution and heat transfer in the reactor are important factors in determining the reactor performance as well as the yields of oil and monomer in the pyrolysis reactor, since the pyrolysis of polymer plastic waste has to be carried out at high temperature. In addition, the residence time and its distribution of polymers in the reactor can affect the product distribution recovered [Kim et al., 1999; Song et al., 1999; Cha et al., 2002]. A more uniform temperature distribution can be achieved by using a fluidized-bed reactor [Shun et al., 1993; Cho et al., 1996; Lee et al., 1999; Liu et al., 2000].

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‡This paper is dedicated to Professor Dong Sup Doh on the occasion of his retirement from Korea University.

In the present study, thus, the decomposition characteristics of residue from the pyrolysis of polystyrene waste have been investigated in a catalytic fluidized-bed reactor. Effects of catalyst, temperature and gas velocity on the yields of oil and chemicals and on the selectivities of oil and chemicals have been discussed.

EXPERIMENTAL

Experiments were performed in a stainless steel fluidized-bed reactor whose diameter was 0.0508 m and 1.5 m in height, respectively, as can be seen in Fig. 1 [Kim et al., 2001; Lee et al., 2002]. The freeboard region was made of 0.102 m ID stainless steel tube. Dried, filtered and compressed nitrogen gas was injected into the reactor through the perforated-type distributor installed between the main column section and the distributor box, after preheating by means of preheater installed in the main gas feed line. The distributor contained 27 holes with triangular pitches and was covered with 400 mesh screen for preventing from bed material weeping. The diameter of each hole was 6 mm.

Sand particles whose density and mean diameter were 2,500 kg/m^3 and 240 μm, respectively, were used as the bed materials. Catalyst such as CBV28014 or CBV3024E (ZSM-5 type Zeolite product of Zeloyst International) was used to enhance the conversion of the thermal decomposition of residue. The properties of the catalysts are summarized in Table 1. The residue waste generated from the continuous stirred tank reactor was used as a feed material. The results of the ultimate analysis of the polystyrene waste and its residue generated after pyrolysis are summarized in Table 2.

The residue waste was melted at 100 °C prior to being injected into the reactor, to be formed as solid beads with a mean diameter of 1 mm. The catalyst was mixed with the feed material during this process in a given amount [Kim et al., 2001; Lee et al., 2002].

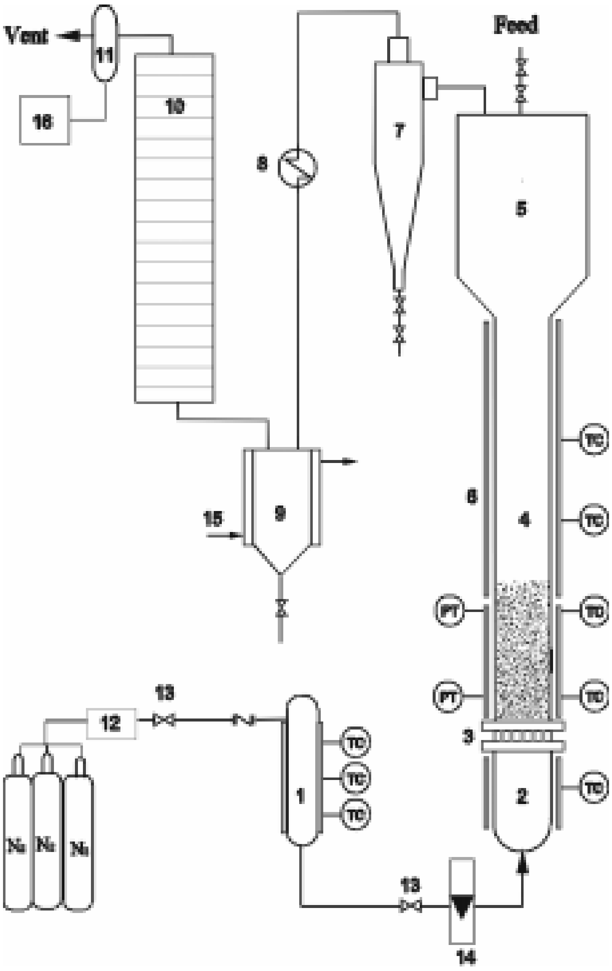

Fig. 1. Experimental apparatus.

1. Pre-heater
2. Distributor box
3. Distributor
4. F-bed reactor
5. Freeboard
6. Electric heater
7. Cyclone
8. Heat exchanger
9. Condenser
10. Mist filter
11. Gas sample bag
12. Regulator
13. Control valve
14. Flowmeter
15. Water jacket
16. GC

Table 1. Property of catalysts

Catalyst	SiO_2/Al_2O_3 mole ratio	Na_2O	Surface Area (m^2/g)	Nominal cation form
CBV 3024E	30	0.05	400	Ammonium
CBV 28014	280	0.05	400	Ammonium

Fifty grams of feed material was fed to the reactor at a given operating condition. The oil product or styrene monomer was obtained by means of a condenser. The yield of oil product or styrene monomer was determined by the following equations [Kim et al., 2001].

$$\text{Yield of oil : } Y_{oil}=\frac{W_o}{W_f}\times 100 \quad (1)$$

$$\text{Yield of styrene monomer : } Y_{SM}=\frac{W_{SM}}{W_f}\times 100=\frac{W_{SM}\times Y_{oil}}{W_o}\times 100 \quad (2)$$

Table 2. Ultimate analysis of residue waste

Feed material	Element [wt%]				
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Polystyrene waste	91.50	7.62	0.04	0.03	0.81
Residue after pyrolysis of PSW	93.44	5.41	0.13		1.02

The outlet gas which was obtained at the gas detection port was analyzed by means of on-line gas analyzer (GC-MS, HP-5890 plus, column; DB-1HT; GC-TCD; GC-FID). The yield of gas product was determined by the following equation:

$$\text{Yield of gas : } Y_{Gas}=\frac{W_{Gas}}{W_f}\times 100=\frac{C_{Gas}\times Q_{N2}\times \text{time}}{W_f}\times 100 \quad (3)$$

RESULTS AND DISCUSSION

Effects of reaction temperature on the yield of oil can be seen in Fig. 2. In this figure, the increase of reaction temperature from 450 to 550 °C can increase the values of oil yield (Y_{oil}) in all the cases studied. However, the further increase of reaction temperature from 550 to 600 °C leads to the considerable decrease of oil yield. That is, the increase of reaction temperature leads to the increase of gas phase products instead of liquid phase. It can be concluded that the optimum reaction temperature is 550 °C for the recovery of oil from residue waste within these experimental conditions. This figure also shows that the addition of catalyst can effectively increase the yield of oil. It is interesting to note that the catalyst of CBV 28014 is more effective at a relatively lower temperature (less than 500 °C), while the catalyst of CBV 3024E is more effective at a higher temperature (higher than 550 °C). This can be due to the selectivity characteristics of each catalyst [Kim et al., 2001; Lee et al., 2002a, b].

Effects of gas velocity (U_G) on the yields of oil product can be seen in Fig. 3. Note in this figure that the values of oil yield increase with U_G at the relatively lower gas velocity, but decrease gradually with a further increase in the gas velocity from 0.2 to 0.5 m/s. This can be due to the time of thermal decomposition of residue waste decreasing with increasing gas velocity in the reactor. Since the minimum fluidization velocity of bed materials is 0.09 m/s, the bed material cannot be fully fluidized at the gas velocity of 0.15 m/s; thus, the increase of gas velocity can lead to more effective fluidization conditions for a higher value of oil yield. Therefore, the value of oil yield exhibits a local maximum value with the variation of gas velocity in the fluidized-bed reactor. The optimum gas velocity for the maximum oil yield is 0.2 m/s within these experimental conditions. It has been understood that, in the relatively lower range of U_G, the fluidization motion of bed materials becomes more vigorous with increasing U_G, but in the higher range of U_G, the increase of U_G leads to the further higher bed expansion, which results in the significant decrease of holdup of bed materials. These can directly decrease the heat transfer coefficient and mixing intensity in the fluidized-bed reactor [Kang et al., 2000; Kim et al., 2001; Lee et al., 2002a, b].

As can be seen in Fig. 3, the value of oil yield increases up to 15-

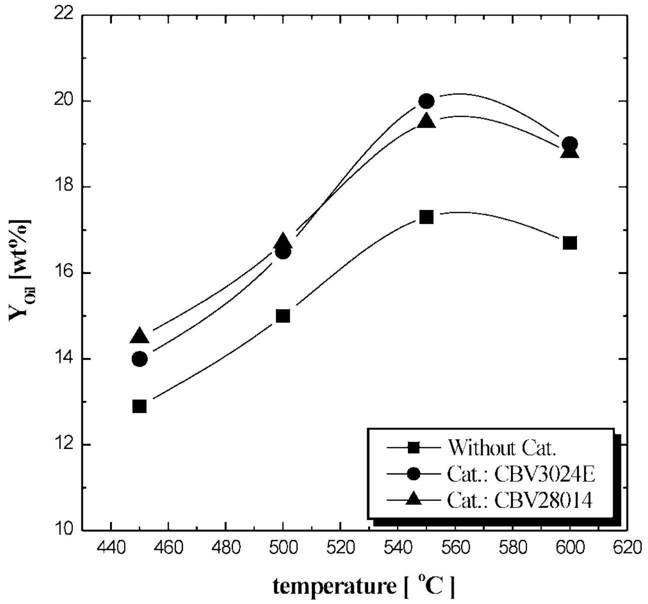

Fig. 2. Effects of temperature on the yield of oil in a catalytic fluidized-bed reactor (U_G=0.2 m/s).

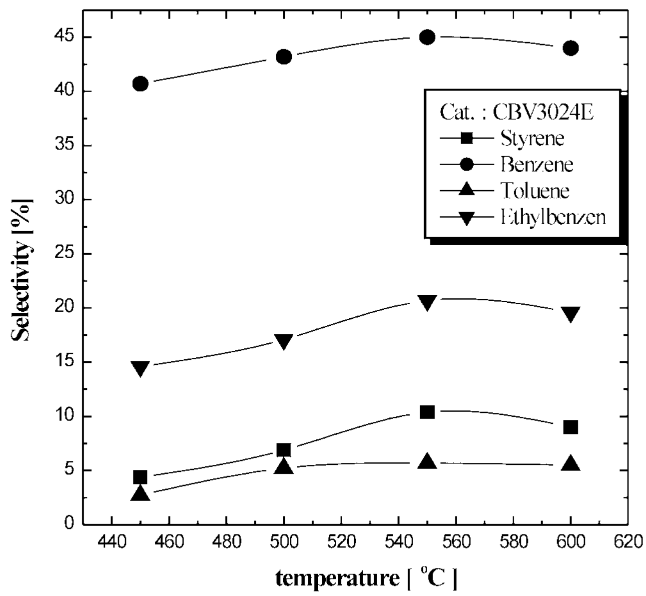

Fig. 4. Effects of temperature on the selectivity of oil in a catalytic fluidized-bed reactor (U_G=0.2 m/s).

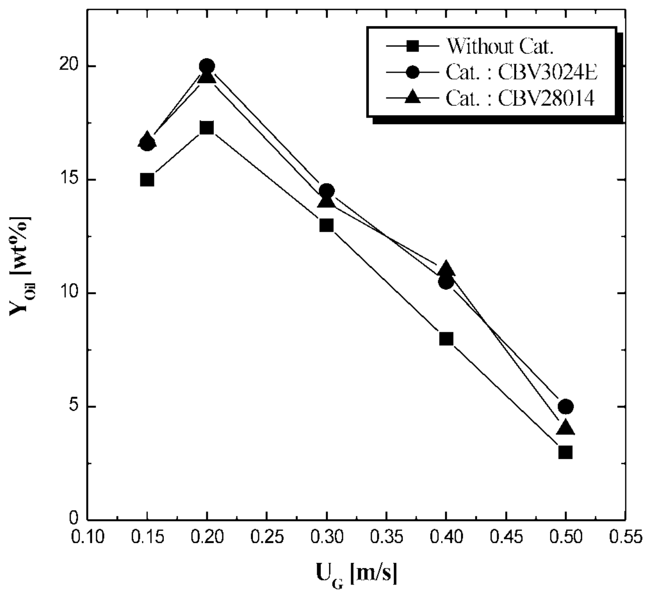

Fig. 3. Effects of gas velocity on the yield of oil in a catalytic fluidized-bed reactor (T=550 °C).

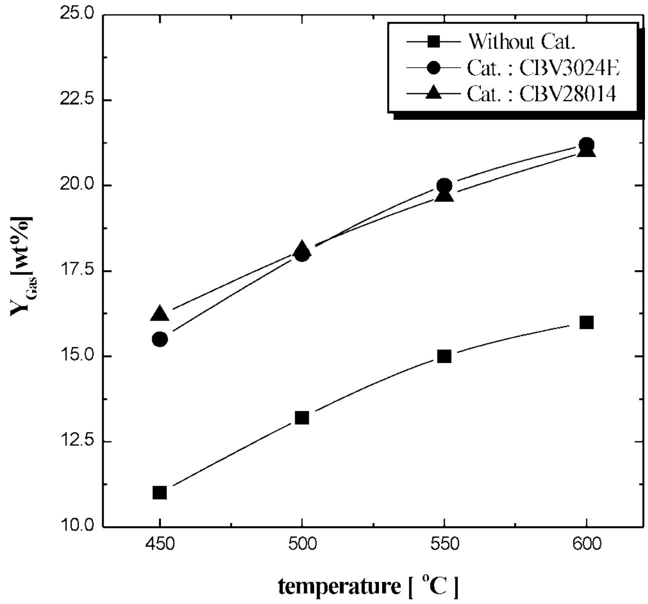

Fig. 5. Effects of temperature on the yield of gas product in a catalytic fluidized-bed reactor (T=550 °C).

30 wt% with the addition of catalyst, CBV3024E or CBV28014, but the effects of catalyst kind on the oil yield cannot be found within this experiment.

Effects of reaction temperature on the selectivity of oil component can be seen in Fig. 4. From the chromatography analysis of the liquid products generated from the pyrolysis of residue waste, it has been found that the main components are styrene monomer, benzene, toluene and ethylbenzene. It is interesting to note that 5-10 wt% of styrene monomer can be obtained from the residue waste by using the catalyst of CBV 3024E. As can be seen in Fig. 4, the selectivities of these four components show slight maximum values with increasing reaction temperature. It is understood that the yield of oil products decreases at the higher reaction temperature, compensating for the increase of gas products. The optimum temperature for the maximum recovery of styrene monomer and other chemicals is 550 °C.

Effects of decomposition temperature on the yields of gas products can be seen in Fig. 5. In this figure, the yields of gas products increase with increasing reaction temperature from 450 °C to 600 °C. As mentioned before, this can be due to the fact that the residue waste could be decomposed into gas phase more easily, with increasing reaction temperature. The addition of catalyst in the reactor can also increase the yield of gas phase products up to 14-30 wt%; however, considerable effects of catalyst kind on the yield of gas

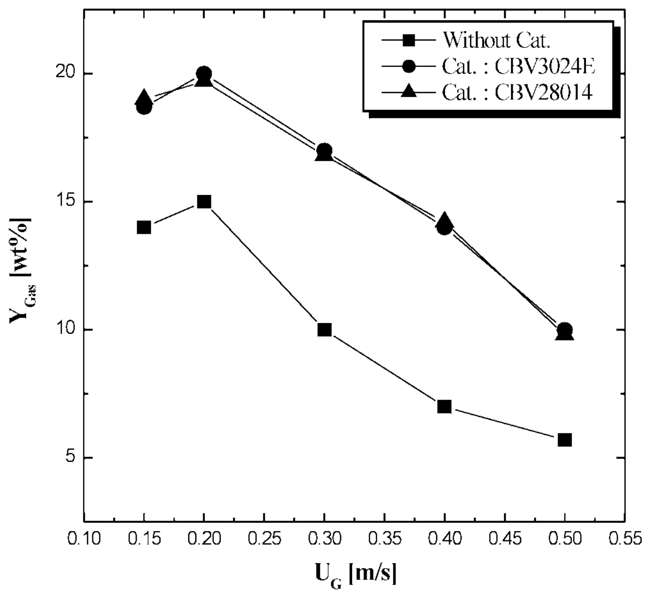

Fig. 6. Effects of gas velocity on the yield of gas product in a catalytic fluidized-bed reactor (T=550 °C).

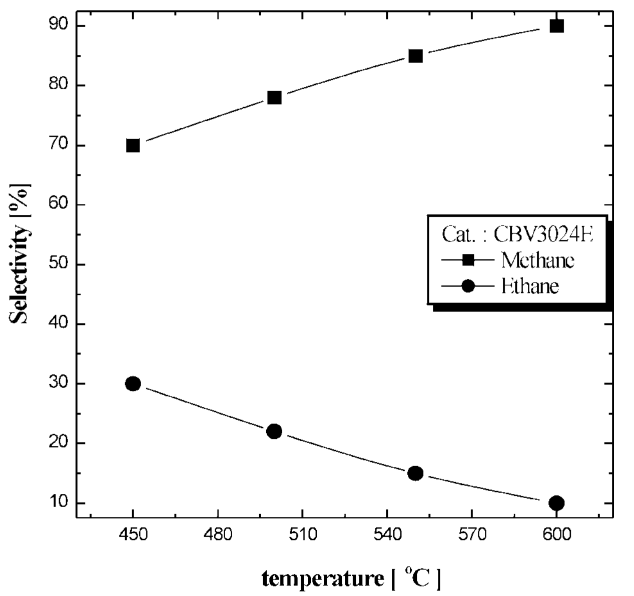

Fig. 7. Effects of temperature on the selectivity of gas product in a catalytic fluidized-bed reactor (U_G=0.2 m/s).

products cannot be found within these experimental conditions, as in the case of oil products.

Effects of gas velocity (U_G) on the yields of gas product can be seen in Fig. 6. The yield of gas product decreases gradually with increasing gas velocity, at the higher range of U_G. But, as can be expected, at the relatively lower range of U_G, the yield of gas product increases with increasing U_G. This can be due to the same reason why the yield of oil product exhibits a local maximum value at the intermediate gas velocity (U_G=0.2 m/s).

Effects of reaction temperature on the selectivity of gas product can be seen in Fig. 7. It has been found that the main components of gas product are methane and ethane. The amount of methane compared to that of ethane increases profoundly with increasing reaction temperature up to 600 °C.

Table 3. Comparison of selectivity and product between the thermal and the catalytic pyrolysis of residue at 550 °C

Catalyst	CBV 3024E	CBV 28014	Without Cat.
Feed	Residue	Residue	Residue
Oil [wt%]	20	19.5	17.3
Gas [wt%]	20	19.7	15
Char	57.6	59.8	65.6
	Selectivity [%]		
Styrene monomer	10.4	11	6
Toluene	5.7	5.0	3.0
Benzene	45	44	32
Ethyl benzene	20.7	20	14
α-methylstyrene	17	18.3	15
Methane	85	86	80
Ethane	15	14	20

A comparison of the selectivity and products between the catalytic and the thermal pyrolysis has been summarized in Table 3. The value of selectivity of oil component and gas product such as styrene monomer, benzene, toluene, ethlybenzene, α-methylstyrene, methane and ethane shows higher values in using catalyst than those without catalyst. Especially, 10-11 wt% of styrene monomer and 19-20 wt% of oil and gas products can be recovered by using catalyst in a fluidized-bed reactor [Carniti et al., 1995; Zang et al., 1995].

CONCLUSION

The residue waste generated from the pyrolysis of polystyrene waste was effectively decomposed in a catalytic fluidized-bed reactor. The optimum temperature for the maximum oil yields and styrene monomer recovery was found to be 550 °C. The optimum gas velocity was 0.2 m/s within these experimental conditions. The yield of gas product increases with increasing reaction temperature, but decreases with increasing gas velocity over 0.2 m/s, exhibiting a maximum value at 0.2 m/s. As a result of this study, 10-11 wt% of styrene monomer and 19-20 wt% of oil and gas products can be recovered by using catalyst of CBV3024E or CBV28014 in a fluidized-bed reactor.

NOMENCLATURE

C_{Gas} : concentration of gas [g/*l*]
Q_{N_2} : flow rate of N_2 [*l*/min]
Y_{Gas} : yield of gas [wt%]
Y_{oil} : yield of oil [wt%]
Y_{SM} : yield of styrene monomer [wt%]
W_{Gas} : weight of gas obtained [g]
W_o : weight of oil obtained [g]
W_f : weight of feed material [g]
W_{SM} : weight of styrene monomer obtained [g]

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