POLY(METHYL METHACRYLATE) PYROLYSIS BY TWO FLUIDIZED BED PROCESS

Akinobu Sasaki,*[1] Toshiro Tsuji[2]

[1]*Mitsubishi Rayon, Otake, Hiroshima, Japan.*
[2]*Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido, Japan.*
E-mail: sasaki_ak@mrc.co.jp

Abstract: PMMA was continuously pyrolyzed by our new process consisting of pyrolyzer and regenerator and crude MMA of purity 94-95% was recovered with a yield 95%. Transparent MMA of purity 99.8% was obtained by distillation of the crude MMA. The characteristics of this process are 1) PMMA is pyrolyzed by sensible heat of circulating sand between the two fluidized beds, 2) residual oil of distillation is used as a fuel at regenerator where sand is heated up and soot derived from PMMA is incinerated, 3) at pyrolyzer, nitrogen is used as fluidization gas which is separated from pyrolysis product and reused. This process was successfully scaled up from bench plant(15kg/hr) to demonstration plant(300kg/hr). In comparison with MMA synthesis by natural resources, MMA production by PMMA pyrolysis can reduce energy usage.

1. Introduction

PMMA pyrolysis has been intensively studied by many researchers1). PMMA pyrolysis by fluidized bed is relatively new method. Kaminsky2) carried out experiments at a laboratory-scale plant with a capacity 3kg/h. The fluidized bed was heated indirectly from outside to temperatures between from 600 to 900 C. Because of the heating system, this method can not be done in large-scale plant. We invented a new process consisting of pyrolyzer and regenerator. In this process, pyrolyzer is not heated from outside. Instead, hot sand is continuously circulating between pyrolyzer and regenerator. PMMA is pyrolyzed only by the sensible heat of the circulating hot sand. This enables the new process to be up-scaled.

2. Experiments

Experiments were conducted both at bench plant and demonstration plant. Each plant consists of pyrolyzer, regenerator, condenser, mist-separator and distillation column.

2.1 Apparatus

Fig.1 shows apparatus. Tab. 1 summarizes the dimensions of pyrolyzer and regenerator of bench plant. Hot sand is discharged out of pyrolyzer by screw and fed to regenerator. The discharge rate is controlled by the speed of screw rotation. Between the two reactors, two automatic valves exist, and these valves open and close by turns so that nitrogen in pyrolyzer and air in regenerator will not mix with each other. Residue of PMMA discharged out of pyrolyzer with sand is burned out in regenerator. Residue-free hot sand out of regenerator is fed to pyrolyzer.

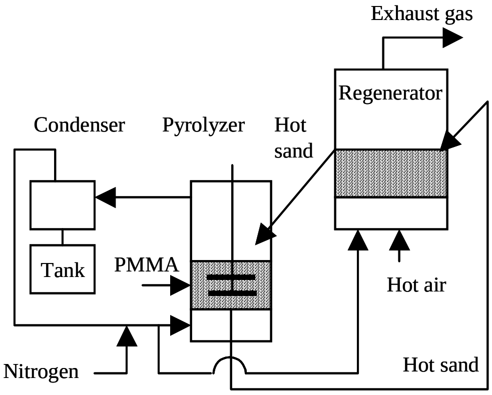

Fig.1 Apparatus

Tab.1 Dimensions

	Pyrolyzer			Regenerator		
	Shape	Diameter	Height	Shape	Diameter	Height
Bench Plant	tube	0.35m	1.5m	tube	0.9m	2m

The mixed gas of pyrolysis gas and nitrogen is cooled and condensed by multi tube heat exchanger. This heat exchanger is followed by two mist-separators. The first mist-separator is cyclone type and the second one is wire-mesh type. Nitrogen separated from pyrolysis product is pumped up by a blower and fed to pyrolyzer again. A part of the mixed gas which contains volatile organic compounds is fed to regenerator and incinerated.

2.2 Material

Homo PMMA was supplied by Mitsubishi Rayon. Its size was 5mm in diameter. Sand used was river sand and its mean size was 0.3mm in diameter. Minimum fluidization gas velocity is estimated to be approximately 5cm/s.

2.3 Standard conditions

Tab. 2 shows standard conditions employed at bench plant.

Tab.2 Standard and Conditions

	Qp kg/s	Qs kg/s	Ws kg	θs s	Ts.in C	T C	Qn2 Nm3/s	Tn2.in C	F1 -	F2 -
Bench plant	0.004	0.04	85	2.1E+03	580	400	0.005	30	0.002	0.02

3. Result and Discussion

3.1 Analysis of Pyrolyzer

In this analysis, we define two important factors F1 and F2. F1 is weight ratio of polymer to sand in the pyrolyzer and defined by Equation 1. For stable operation, low F1 value is preferred because polymer melt is viscous and may deteriorate the fluidity of sand bed.

$$F1 = \frac{Wp}{Ws} \tag{1}$$

Wp under stationary condition in pyrolyzer can be estimated by Equation 2.

$$\frac{dWp}{dt} = Qp - k \times Wp = 0 \tag{2}$$

k is rate constant of polymer pyrolysis at temperature T.k is estimated by thermogravimetric analysis.

$$\frac{dW}{dt} = -k \times W \tag{3}$$

Then, F1 can be expressed by Equation 4.

$$F1 = \frac{Wp}{Ws} = \frac{Qp}{k \times Ws} \tag{4}$$

In TGA experiments, we found k to be 0.02(1/s) at 400(degree C). In the case of bench plant, F1 is estimated to be 0.002.

Sand was fed and discharged at the same speed to hold constant Ws. Mean residence time of sand is defined by Equation 5.

$$\theta s = \frac{Ws}{Qs} \tag{5}$$

As hot sand is circulating between the two reactors, a part of PMMA does not pyrolyze in pyrolyzer and is discharged out of it. F2 is the weight ratio of unpyrolyzed polymer to polymer fed to the reactor and defined by Equation 6.

$$F2 = \frac{Qs \times \frac{Wp}{Ws}}{Qp} = \frac{Qs}{Qp} \times F1 = \frac{1}{k \times \theta s} \tag{6}$$

For higher yield of PMMA pyrolysis product, F2 must be kept very small. Small F2 value means that most part of PMMA pyrolyzes in the reactor.

θ s is 2100(s) at bench plant. Then, F2 is calculated to be 0.02. It is apparent that lower F2 value can be obtained at larger rate constant k (higher temperature T) or longer residence time θ s. As stated by Kaminsky[2)], MMA purity of the crude MMA inevitably decreases at higher temperature T. Preferable T is around 400 degree C in terms of relatively large rate constant k and high MMA purity.

Scaling-up of pyrolyzer was carried out so that F1 and F2 at demonstration plant are almost the same as those at bench plant.

3.2 Heat balance in Pyrolyzer

Heat balance in pyrolyzer is expressed by Equation 7.

$$\begin{aligned} &Qp \times \left[H1 + H2 + Cp \cdot p \times (T - Tp \cdot in) \right] = \\ &Cp \cdot s \times Qs \times (Ts \cdot in - T) + Cp \cdot n2 \times Qn2 \times (Tn2 \cdot in - T) \ - EnergyLoss \end{aligned} \tag{7}$$

At bench plant, approximately 80% of sensible heat of hot sand was consumed to pyrolyze PMMA. The value at demonstration plant increases to approximately 90% because the ratio Qn2/Qp decreases from 1.2 at bench plant to 0.6 at demonstration plant. In our process, nitrogen was not heated up before being fed to pyrolyzer. By using hot nitrogen, the energy efficiency can be increased.

3.3 Properties of recovered crude MMA and distilled MMA

Tab. 3 shows the properties of crude MMA and distilled MMA at bench plant and demonstration plant. The yield of crude MMA was the same, however its MMA purity deteriorated by 1%.

Tab.3 Properties of crude MMA and ditilled MMA

		Bench Plant	Demonstration Plant
Crude MMA	Yield	95%	95%
	Purity	95%	94%
Distilled MMA	Purity	99.8%	99.8%

3.4 Comparison between MMA synthesis and PMMA pyrolysis

There are two major MMA synthesis methods, namely ACH method and C4 method. According to published books[3-4)], ACH method and C4 method consume 72MJ/kg-MMA and 53MJ/kg-MMA to synthesize MMA, respectively. Based on our experiments at demonstration plant, the energy consumption is estimated to be 10-13 MJ/kg-MMA when the total yield from PMMA to distilled MMA is 90-70%. The total yield greatly depends on the MMA purity of distilled MMA being aimed at.

4. Conclusion

PMMA was successfully pyrolyzed and very pure MMA was obtained at relatively large-scale plant. By taking into consideration the two important factors, namely F1 and F2, preferable mean residence time of sand θ s turned out to be 30min or longer at 400C. PMMA pyrolysis is advantageous in comparison with other MMA synthesis methods in terms of energy usage.

5. Nomenclatures

Qp : feed rate of polymer [kg/s]
Qs : feed rate of sand [kg/s]
Qn2 : feed rate of nitrogen [$\mathrm{Nm^3/s}$]
Wp : weight of polymer in pyrolyzer [kg]
Ws : weight of sand in pyrolyzer [kg]
θs : mean residence time of sand in pyrolyzer [s]
k : rate constant of pyrolysis [1/s]
H1 : heat of depolymerization [J/kg]
H2 : heat of vaporization [J/kg]
Cp.p : specific heat of polymer [J/(kg.K)]
Cp.s : specific heat of sand [J/(kg.K)]
Cp.n2 : specific heat of nitrogen [$\mathrm{J/(Nm^3.K)}$]
Tp.in : temperature of polymer fed to pyrolyzer [C]
Ts.in : temperature of sand fed to pyrolyzer [C]
Tn2.in : temperature of nitrogen fed to pyrolyzer [C]
T : temperature in pyrolyzer [C]

References

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