

# Air bubble-assisted tar removal in polyvinylchloride pyrolysis

Yanlei Chen<sup>1</sup>, Hao Xu<sup>1</sup>, and Fumitake Takahashi<sup>1</sup>

<sup>1</sup> Department of Transdisciplinary Science and Engineering, School of Environment and Society, Tokyo Institute of Technology, G5-601, Tokyo Institute of Technology, Suzukake, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

## INTRODUCTION

With increase of social and industrial importance of plastic-based products, plastic waste recycles have been concerned more seriously. According to the Ministry of the Environment Japan, the cumulative plastic waste generation in the world is expected to increase 5 times larger than that in 2020. 70% of collected plastic wastes were actually exported to China and other ASEAN countries before legal regulation of plastic waste import by China government. In real recycle processes, the 67% of plastic processing residues were incinerated and 8% of the residue was landfilled. Only 25% was used for direct recycles.

Of three major pathways of plastic waste recycles, chemical recycle is considered the best way owing to its large potential to generate energy resources such as syngas, oil and activated carbon products comparing to serious limitations of material recycle and relatively low efficiency of thermal recovery.

However, tar, which is by-products produced from chemical recycle processes like pyrolysis-oil generation and gasification for syngas production, will cause serious problems due to its high toxicity and damages to process equipment, human bodies, and the environment. The purpose of the study is to develop a new tar removal method using air bubble assistance for plastic pyrolysis.

## MATERIALS AND METHODS

### Materials

Polyvinylchloride (PVC) was used as feedstock in this study according to its high market-share, high contents of the additives and plasticizers. PVC and magnesium sulfate made by Fujifilm Wako Pure Chemical Corporation, Japan were used. Distilled water were from Monota RO,Co.,Ltd.(Japan). Nitrogen (G3 grade: purity=99.9995%) was used as pyrolysis medium gas purchased from TAIYO NIPPON SANSO Corporation, Japan. Air stone GX-63 was purchased from AS ONE Corporation, Japan. All reagents were used as received.

### Methods

Proximate analysis and ultimate analysis for PVC sample were performed using a muffle furnace TMF-3000 (TOKYO RIKAKIKAI Co.,Ltd. Japan), constant temperature dryer (EIP-600B, AS ONE Corporation, Japan) and CHN corder JM10 (J-Science Lab Co.,Ltd. Japan). The contents of hydrogen, oxygen,

carbon, sulfur and contents of moisture, volatiles, ash and fixed carbon were measured. Lab-scale fixed bed pyrolysis experiments were performed with the air bubble-assisted tar removal. Temperature controller AGC-1P and tubular furnace ARF series (Asahi Rika Factory, Ltd. Japan.) and Multi Air Station MSA-1 (AS ONE Corporation, Japan) were used for all pyrolysis experiments. Air flow rate ranged from 0 to 10L/min in the pyrolysis experiments for air bubble injection. Tar collected from the pyrolysis experiments was analyzed by Gas Chromatograph Mass Spectrometer QP2010 (Shimadzu Corporation, Japan) in order to identify the composition of organic compounds in collected tar. Before the analysis, tar needed dehydration treatment using magnesium sulfate. Octanol-Water partition coefficients and diffusion coefficients of these common organic compounds analyzed in this study were used to discuss the trend of hydrophilicity and hydrophobicity among the tar collected at different air flow rates.

## RESULTS AND DISCUSSIONS

The results of proximate analysis and ultimate analysis were listed in Table 1. The results of collected tar at different air flow rates are shown in Fig. 1. As shown in Fig.1, when air flow rate is 5 L/min or less, the amount of tar collection decreased compared with that without air injection. On the other hand, when air flow rate increases to 6 L/min or more, tar collection increased with increase of air flow rate. When air flow rate is 10 L/min, tar collection exceeds that without air injection. It should be noted that tar collection was partially affected by air stone for bubble generation.

Table.1 Proximate analysis and ultimate analysis (wt%)

Sample/ Contents	Moisture	Volatile	Ash	Fixed Carbon
PVC	NA	92.33	1.20	6.47
	H	C	N	O
PVC	4.54	38.37	0.07	0.64

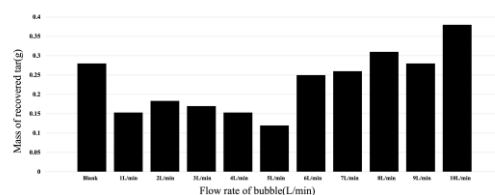


Fig.1 Tar recovery assisted by air bubble injection

The amount of tar adsorbed onto air stone might reach to 0.15 to 0.22 g. Further experiments are necessary to evaluate the impact of tar adsorption onto the air stone.

The compositions of tar are shown in Fig. 2 and 3. Fig.2 shows the compositions of organic groups like aliphatic, monocyclic aromatics, PAHs, and others. Fig.3 shows the compositions of tar categorized by carbon numbers like C6-9, C10-13, C14-17, and C18-more. Fig 2 shows that aliphatic tars were collected more with increase of air injection rate. On the other hand, PAHs tars were collected less at higher air injection rate. Fig.3 shows that more amount of small carbon tars (C6-9 fractions) was also trapped with increase of air injection. On the other hand, tars with larger carbon numbers was collected less with increase of air injection. Therefore, air injection affected not only tar removal efficiency but also collected tar characteristics.

The effects of air injection rate on tar collection performance and tar characteristics are discussed focusing on tar hydrophobicity and hydrophilicity. Fig.4 shows the average of Octanol-Water partition coefficients of major tar components. Fig.5 shows the average of gaseous diffusion coefficients of the major tar components. Fig.4 shows negative correlation between air flow rates and the average Octanol-Water partition coefficients. As shown in Fig.2 and Fig.3, higher air injection increased the collection of aliphatic tars and small carbon-number tars dramatically. These results are consistent with negative correlation between

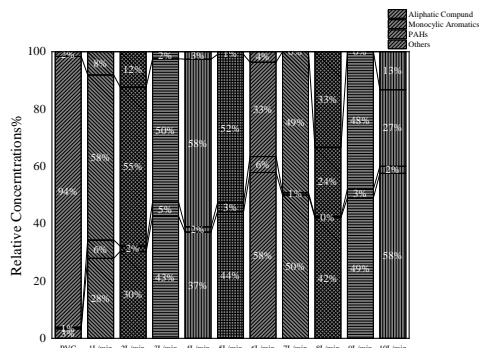


Fig.2 Tar compositions categorized by organic groups

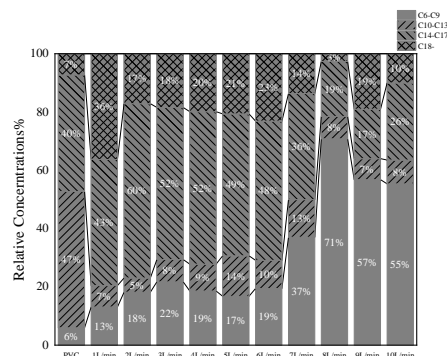


Fig.3 Tar compositions categorized by carbon number

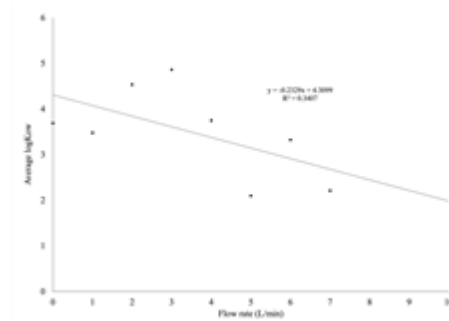


Fig.4 Comparison between air flow rate and average Octanol-Water partition coefficients

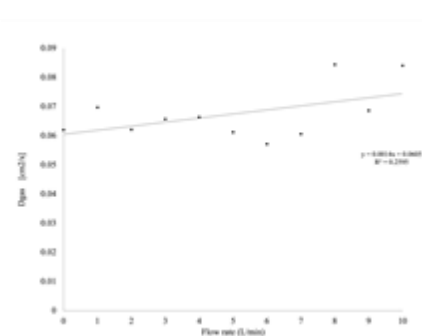


Fig.5 Comparison between air flow rate and average gaseous diffusion coefficients

air flow rate and the average Octanol-Water partition coefficients. Higher air flow rate helped the collection of hydrophilic, aliphatic, and small carbon number tars. The increase of tar collection at 6 L/min or larger injection rate is derived from promoted collection of aliphatic tars. A positive correlation between air flow rates and the average diffusion coefficients is also consistent with the other results. In general, smaller molecule tars will have larger diffusion coefficient. When air is injected at higher flow rate, more amount of air bubbles would be generated. It means that syngas bubble would have more contacts with air bubbles at water scrubbing stage (tar collection). When tar has larger diffusion coefficient, tar would transfer from syngas bubble to air bubble more and it results in more efficient transfer of tars to the scrubbing water. It would result in larger tar collection.

## CONCLUSIONS

This study found that air bubble-assistance was helpful to promote tar collection in PVC pyrolysis when air flow rate exceeded 10 L/min. The promotion effect of air injection on tar collection was derived from the increase of hydrophilic, aliphatic, and small carbon-number tars. Further researches are necessary to investigate tar removal mechanisms. Gaseous tar transfer from syngas to air bubble might play an important role.