A Study on Pyrolysis of Brominated Flame Retardant Plastics for Oil Utilization

Janaury 2014

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Graduate School of Engineering

CHIBA UNIVERSITY

（千葉大学審査学位論文）

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Chapter 1

General Introduction

1.1. Introduction

Replacement of metal material by plastics for weight and cost reduction is now one of the strategies of many engineering fields. For example, various parts of vehicle were changed from metal to plastic. Since CO_2 emission from vehicle must be reduced, it is necessary to reduce the weight of vehicle for improving fuel economy and for suppressing the CO_2 emission. The utilization of plastic in vehicle is very effective for these purposes. Then, thermal recovery from plastic material becomes one of the new engineering issues in the final material recycle system of vehicles. The utilization of plastic material is increasing every year. In order to increase the volume of plastics and use plastics more safety, flame retardant is usually added in plastics. Several kinds of flame retardant have been developed according to various principles. Role of flame retardant is mainly expected to suppress rapid combustion. Up to now, many kinds of halide type flame retardant have been used well. However, there are many problems for the flame retardant to be solved. For example, a flame retardant with halide has possibility to generate dioxins through combustion process. Then other types flame retardant with non-halide are now developing. Further, addition of flame retardant is

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now considered as a new method to control mechanical characteristics of plastic compounds. There are many kinds of positive effect of flame retardant as generally considered, but are some negative effects of it. For example, flame retardant added in a plastics suppresses a complete combustion of plastics, and it deteriorates thermal recovery efficiency of plastics.

1.1.1. Waste plastic treatment

In most of countries, specific information on waste plastics might be limited and the waste plastics management system might fall within the overall solid waste management so that no specific regulations, economic tools, institutions or services are developed as a separate management system for this specific waste stream. Hence, all the information regarding solid waste management such as policies/laws, institutions, financing mechanism and technologies for all the waste generating sources (domestic, commercial, industrial, agriculture, healthcare facilities, E- waste, etc.) should be collected, analyzed and any direct or indirect implications on waste plastics should be identified.

Some local issues may also be of interest such as to confirm the existence of pollution related regulations which may, directly or indirectly, have an impact on waste plastics

or its treatment. For example pollution due to plastic bags, and related laws if any, would be of interest 50 for developing this information. Another example could be of air pollution act to address incineration of waste containing waste plastics and its emissions.

Additionally, as a local issue it is important to identify the informal sector involved in the management of the waste/plastic waste since they have a big impact on the waste plastics pathways.

Most of the countries do not have a separate system for waste plastics management and it is usually managed under an umbrella system for solid waste management. Hence it is recommended to assess the current solid waste management system and find the gaps with reference to waste plastics management for making recommendations to make improvements in the solid waste management covering waste plastics. Solid waste management may vary from country to country and from city to city. In most of the countries, the local governments are responsible for municipal solid waste management; however industrial solid waste and hazardous waste is the responsibility of national governments. In some places, the local governments are responsible for all types of waste; however, there may be different departments to manage municipal waste, industrial waste and hazardous waste. There could be fewer or more systems. The

systems may be classified with respect to the responsible institution. If there is only one institution or department that is responsible for all types of solid waste management, then it may be considered that there is a single management system. However, if there is more than one institution responsible for different types of solid waste or waste generated by different sources then it is considered as a separate management systems. Therefore, it is recommended to collect the data and information separately for different types of systems even if there is some overlapping in terms of regulations and laws, financial mechanisms, technology and infrastructure and stakeholder participation.

There are many kinds of final treatment of waste plastics. There are

1. Material recycling

(Raw material for plastic and commercialization and recycling)

2. Chemical recycling

(Chemical materials and fuels by liquefaction and gasification)

3. Thermal recycling

(Waste power generation, RDF, RPF)

1.1.2. Recycling technology of various general-purpose plastic

Production of plastic in Japan is about 15 million tons in 2012. Almost half of account

is for polyethylene (PE) and, the others are polypropylene (PP), polystyrene (PS). This

is because of the sheet for packaging materials such as plastic wrap and bags, such as

civil engineering construction, production of polyethylene and polypropylene, which is

suitable as a material is more about 40% of the use of plastic.

In a simple thermal decomposition without using any solvent or catalyst, the oil rate is

80% or more thermoplastic resin PE, PP, PS, etc. As the pyrolysis oil recycling

technology were operated at food factories of KAMEDA Co., Ltd and TORASHO

industry Co., Ltd, recycling has been put into practical use relatively (3P) packaging

material or the like discharged from factories [2-3][27-3]. However, the thermal

decomposition oil of PE without catalyst is impossible to be used as fuel yet, because of

mixed waxes in produced oil at present condition regarding PE.

In many cases, chemical recycling and material recycling have been made of ABS

resin and PET resin. For example, in the case of PET resin, film or fiber is material

recycling but , in terms of smell and hygiene, PET bottles can not be used for drinking

PET bottle itself . In the decomposition method of its own with methanol in

combination with ethylene glycol, return DMT of raw materials to (dimethyl

terephthalate) waste PET resin, the raw material for fibers and films, to develop this technology, Teijin is used PET bottle We have developed a technology to produce PET resin back TPA to (terephthalic acid) further from DMT, Teijin Fibers in the Corporation, running a facility of approximately 62,000 tons of annual capacity from 2003 [1] . For ABS resin, that in spite of a resin brominated flame retardants are contained, and have held high the characteristics of the original and hydrolysis test and after heating, has been reported [4].However, the flame retardant plastic of acrylonitrile-styrene-butadiene (FR-ABS) is heated in an inert atmosphere and the volatile products are condensed, the molecular weight distribution of the product oil is very wide. Moreover, this product has poor low properties, very waxy, high halogen compound and unusable as a liquid fuel.

1.1.3. Recycling situation of used electrical and electronic equipment

  Japan is relies on imports for more resources for extremely low output of metal resources and fossil fuels. Study of recycling has been actively carried out in many institutions in terms of securing resources. Further, we consider rare metal or plastic and which is produced from petroleum resources, such as copper and iron are electronic materials have been often used in the used electrical and electronic equipment, thus, the development of recycling become to be essential for these techniques.

  Used electrical and electronic equipment are discharged approximately 2.5 million tons per every year, but the product was actually recovered Home Appliance Recycling Law is only about 50 million tons (2008) as a whole, a lot of precious metals contains such as mobile phone. Except for some equipment, the most equipment is not effectively reused resources contained in spent electrical and electronic equipment [7]. These waste electrical and electronic equipments (WEEE) are commonly used of metals and flame retardant plastic materials. The plastic fraction includes high impact polystyrene (HIPS) and acrylonitrile - butadiene - styrene (ABS) copolymer, and the majority of computer housings are manufactured with HIPS, with the next largest fraction being ABS [8]. WEEE plastics also contain antimony trioxide as a synergist to increase the flame retardant properties of brominated additives. However, during

combustion antimony trioxide promotes the release of bromine radicals via the formation of volatile antimony bromides. Since many impurities are mixed in the plastic, to be reused as the material is difficult, largely merely being simple incineration or landfill.

1.2. Previous studies

1.2.1. Recycling technology of flame retardant plastic

Recycling of plastics in electrical and electronic (E&E) equipment E&E and appliances containing brominated flame retardants is possible and already a reality, delivering satisfactory results, demonstrating superior recyclability and stability, compared to other flame retardants [24]. The most commonly used brominated flame retardants in E&E equipment, such as TBBPA, are fully compatible with integrated waste management systems [25]. Studies, such as the EU Risk Assessment reports, show that it is possible to handle E&E appliances containing in an environmentally friendly and responsible manner while also complying with the Waste Electrical and Electronic Equipment (WEEE) Directive standards and stringent EU emission regulations [26].

Sometimes recycling of plastics containing brominated flame retardants is not possible.

This is the case when after the separation of the different types of plastics the volume of plastics containing brominated flame retardants is too small to make recycling economical. For these streams there is a range of eco-efficient waste management options available, including incineration with energy recovery.

1.2.2. Existing oil technology

Waste plastic oil technology was expected to be a significant technology for Japan where the first oil crisis (oil shock), the second oil crisis is overlap in the 1970s, relied on imports for most of the energy resources. The Ministry of International Trade and Industry Agency of Industrial Science and Technology Hokkaido Industrial Research Institute, and thermal decomposition of plastic (PE mainly) polyolefin-based high production volume, product oil is oil in a liquid state at room temperature using a catalyst since it exhibits a waxy between continued research to obtain, it has been successful. In the 1990s, along with waste issues and global environmental problems to be serious, technology of liquefaction is reviewed again, to enter the empirical research from basic research, practical facilities are beginning to emerge about the industrial waste. Thus why pyrolysis oil is one of the best methods to recover the material and energy from polymer waste, as only about 10% of the energy content of the waste

plastic is used to convert the scrap into valuable hydrocarbon products. This is obtained by breaking down polymers at high temperatures into petrochemical feedstock components from which they originate, while the additives in the polymer materials (e.g. metals, inorganic fillers and supports) remain in the pyrolysis residue.

Municipal waste plastic (MWP) is a complex mixture of polymers such as polyethylene (PE), polypropylene, (PP) and polystyrene (PS) and heteroatom containing polymers such as polyvinylchloride (PVC), acrylonitrile-butadiene-styrene (ABS) and polyethylene terephthalate (PET). ABS represents about 3-5 wt% of municipal waste plastics [2] and it gives pyrolysis oils that contain more than 50 wt% valuable benzene derivatives [3] that makes the process attractive to obtain hydrocarbons or fuels. However, some nitrogen containing compounds are present in oil that can lead to formation of harmful compounds such as HCN or NOx when this oil is used as fuel. In the waste from electric and electronic equipment (WEEE), ABS-Br is the second major plastic (20%) next to HIPS-Br [2].Moreover, ABS materials usually contain brominated flame retardants that create additional problems because organic halogen compounds in oil can lead to formation of dioxins and/or benzofurans . Therefore it is necessary to develop catalysts that can remove bromine and nitrogen from pyrolysis oils.

There have been many reports on the pyrolysis of MWP or of similar polymer

mixtures [5-9]. However, few researches focused on the polymer materials containing

flame retardants and removal of halogen compounds in oil [10,11]. Bhaskar et al. [12]

reported about developing calcium-, iron-, and potassium-based carbon composite

sorbents for capture of hydrogen chloride gas. Calcium- and iron-based composites

were found to be effective in debromination of polymers mixed with high-impact

polystyrene [13,14] or brominated ABS [15]. Iron oxides and iron carbon composites

also decrease the amount of nitrogen in ABS pyrolysis oil and convert the aromatic

nitriles into light aliphatic ones and gaseous ammonia and hydrogen cyanide [16].

Various pyrolysis processes have been tested for processing plastics which contain

brominated flame retardants (BFRs) including fluidized bed pyrolysis, two-stage

pyrolysis , long residence time pyrolysis , and pyrolysis in the presence of iron and

calcium based catalysts . Recently, William et al. reported that the removal of bromine

content of Br-ABS by using zeolite ZSM-5 and zeolite Y-Zeolite was carried out in a

fixed bed reactor at 440°C. The concentration of bromine in oil was 2.7 wt% without

zeolites, and the contents of bromine in oil contained 2.6 wt% with zeolites. Joo-Sik

Kim et al. also reported that the removal of bromine content of HIPS by using various

Ca-based additives (CaO, Ca(OH)2, Oyster Shell) was carried out in a bench-scale

system equipped with a fluidized bed reactor at 460°C. It was found that the

concentration of bromine in oil was 5 wt% without catalyst, and the contents of bromine

in oil contained 1.6, 1.3, and 2.7 wt% with various Ca-based additives.

1.3. The scope of this thesis

The brominated acrylonitrile - styrene - butadiene (Br-ABS) and polyethylene are

heated in an inert atmosphere and the volatile products are condensed, the molecular

weight distribution of the product oil is very wide. Moreover, this product has poor low

properties, very waxy, high halogen compound and unusable as a liquid fuel [9-23]. By

using the reflux condenser, the larger molecules are condensed and fall back into the

reactor to break into smaller molecules by heating again in order to reduce halogen

compound in product oil to be used as fuel.

In the present study, Br-ABS resins are pyrolyzed with a reflux-condenser at 450ºC,

and the reflux temperature was set up 150°C to 200°C. The additive was used sodium

hydroxide (0 % to 5 %).We investigated that the effect of reflux condenser temperature

and NaOH on the amount of bromine compound in product oil to be used as fuel.

However, we investigated that thermal decomposition of polyethylene plastic by using a

reflux condenser apparatus to removal of waxes from the pyrolysis oil.

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Chapter 2

Reduction of halogen compounds by using charcoal and sodium hydroxide via pyrolysis

2.1. Introduction

Most plastics for electrical and electronic equipment contain various flame-retardant substances. The main components of plastic in waste electrical and electronic equipments (WEEE) are high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS), and these polymers are widely used in TV casings, computers, printers and other office electrical and electronic equipments. These plastics contain brominated flame-retardants (BFRs), such as polybrominated biphenyls, polybrominated diphenyl ethers (PBDE), tetrabromo bisphenol-A (TBBA) or polybrominated epoxy resins, and contribute to extremely toxic, which make it difficult to dispose or recycle these plastics. Plastics containing BFRs need careful processing to either destroy or remove the flame retardant additives (A.Tohka & R.Zevenhoven, 2002). Developing countries will produce at least twice as much WEEE as developed countries by 2030 (Estimate absolute computer, Wendy Koch, Apr 30-2010, USA Today). At present, the annual amount of used personal computer was about 150 millions ton/year in the world and about 100 millions/year in developed countries (Estimate absolute computer, Wendy

Koch, Apr 30-2010, USA Today). In computers, BFRs are used in four main applications; printed circuit boards, components such as connectors, plastic covers, and cables (A.Tohka & R.Zevenhoven, 2002), and the amount of used computers will increase in worldwide. The recycle of the plastics containing BFRs will be important, and the process for this recycle is desired.

As feasible way to recycle WEEE waste, pyrolysis processing of WEEE plastics has been intensively investigated for thermally degrading the toxic flame-retardants and producing fuels or chemical feedstock for the petrochemical industry. Various pyrolysis processes for plastics containing BFRs have been tested, such as fluidized bed pyrolysis (W.J.Hall & P.T. Williams, 2006), two-stage pyrolysis (T. Bhaskar, W.J. Hall, N.M.M. Mitan, A. Muto, P.T. Williams & Y. Sakata, 2007), long residence time pyrolysis and pyrolysis in the presence of iron and calcium based catalysts (M. Brebu, T. Bhaskar, K. Murai, A. Muto, Y. Sakata &M.A. Uddin, 2005). Most recently, it was reported that the reduction of bromine content in oil obtained from Br-ABS in a fixed bed reactor as a final pyrolysis temperature at 440∘C by using ZSM-5 and Y-Zeolite (W.J.Hall & P.T. Williams, 2008). While the concentration of bromine in oil was 2.7 wt% without zeolites, those in oil were 2.6 wt% with zeolites. It was also reported that the reduction of bromine content in product oil from HIPS in a bench-scale system equipped with a

fluidized bed reactor at 460ºC by using various Ca-based additives (CaO, Ca(OH)$_2$,

Shell) (Su-Hwa Jung, Seon-Jin Kim & Joo-Sik Kim, 2012), and it was found that while

the concentration of bromine in oil was 5 wt% without additives, those were 1.6, 1.3,

and 2.7 wt% with CaO, Ca(OH)$_2$ and shell, respectively.

  In this work, we attempted to reduce the halogen contents in the pyrolysis oil by using

NaOH as additive and pine charcoal as capture. NaOH is used to trap as inorganic

halogen (NaBr, etc.) in the pyrolysis reactor to reduce halogen in oil, and the pine

charcoal, which has excellent moisture absorption properties of atmospheric humidity

adsorption and decomposition formal action formaldehyde, ethylene gas, dioxin,

ammonia and chemical odors (P. Nowicki & P.Robert, 2010), was used as capture to

absorb halogen in generating gas. We also estimated the contents of bromide in

produced oil for using as alternative fuel.

2.2. Materials and Methods

2.2.1. Materials

The flame retardant ABS plastics obtained from Asahi Kasei Chemicals Co-Ltd., Japan.

The resin contains acrylonitrile butadiene styrene 65 %, flame retardant 30 %, and

others 5.0%. The elemental composition of acrylonitrile butadiene styrene plastic is

shown in Table 1.

Table 1. Elemental analysis of sample plastics used in the study

Elemental composition (wt%)					
C	H	N	Br	Sb	Cl
71.87	6.64	3.94	10.70	3.50	1.00

2.2.2. Additives

Sodium hydroxide obtained from Wako Pure Chemical Industries, Ltd. was used as additive. The pine charcoal was used as capture to absorb halogen. Pine charcoal used in this work was prepared as follows. The pine shell was pyrolyzed under nitrogen pressure at 550°C for 4 hours by using bed reactor.

2.2.3. Experimental Procedures

The experimental apparatus is shown in figure 1.The pyrolysis of ABS plastic was performed in a glass reactor (length: 300 mm; i.d. 50mm) under nitrogen pressure. The plastic sample (60 g) was put into the reactor, and allowed nitrogen substitution. Using additive, sodium hydroxide (3 g; 5 % of sample weight) was added in the reactor. After nitrogen substitution, tubular electric furnace heated up at 5°C /min to 300°C, and then heating up at 3°C /min to 300°C ~ 450°C. The sample is heated for 2 hours,

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decomposed, separated into the oil, the wax, the char and the gas. In this apparatus, the

air-cooled tube was installed to prevent closing of condenser by rapid cooling and to

collect residue impurities and wax in tube to trap the amount of bromine and chlorine in

the pyrolysis oil. Using capture, pine charcoal was set in the inside of the upper of

reactor and in the air-cooled tube. The product oil was collected through this capture. In

this experiment, the wax was collected by air-cooled tube and condenser. The product

yields of oil, wax and char were analyzed after experiment, and mass balance of oil,

wax, char and gas was calculated. Using capture, the weight of capture before and after
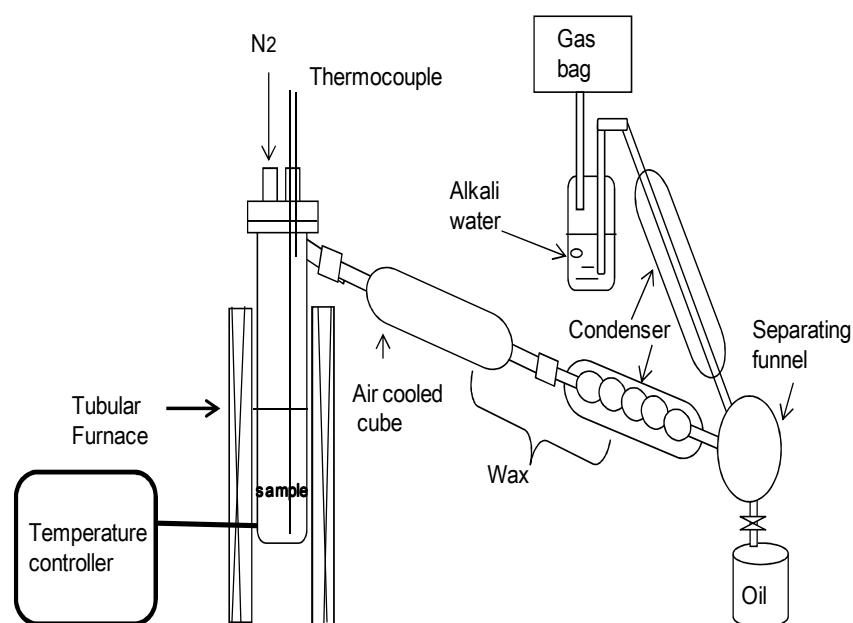
experiments was measured.

Fig. 1.Schematic experimental setup for pyrolysis of ABS at 450°C

2.2.4. Experimental apparatus

The sample plastic was analyzed to determine the decomposition temperature, weight reduction, or grasp of decomposition characteristic by the SHIMADZU Co-Ltd of DTG-60. The amount of samples was analyzed by measuring 10 mg from 5 mg and DTA at 5°C/min to 550°C under a standard pressure of nitrogen atmosphere. Oil and wax were analyzed by gas chromatography/mass spectrometry (GC/MS). Gas chromatography/mass spectrometry (GC/MS) was performed with use of a Hewlett-Packard 5890-II gas chromatograph interfaced with a HP 5972 mass selective detector. GC analysis was carried out on a fused-silica column (60 m x 0.25 mm i.d.) coated with a SPB-5 (1.0 μm film thickness) operated with temperature programming from 40°C up to 250°C at a temperature rate of 3.5°C/min with He as carrier gas (linear velocity = 20 cm/s). EI mass spectra and reconstructed chromatograms were obtained by automatic scanning in the range 35-400 amu. The sample was diluted with methanol before injection. The main compounds were identified by the GC/MS spectrum library (match quality higher than 90%).

The elemental bromine contents of the products (oil, wax and char) are determined as bromide using automatic sample combustion device AQF -2100H (MISTSUBISHI CHEMICAL ANALYTICAL TECH Co.Ltd.), absorbed units GA-210 and ion

chromatograph (ICS-1600 DIONEX Co.Ltd.). In this method, the samples (oil, wax and char) were combusted in the Automatic sample combustion device AQF -2100H. The gaseous bromine species were then capture into the alkali solution (10 mL of H_2O_2) and absorbed by GA-210. The bromine content of the solution was determined using ion chromatograph ICS-1600 for bromide ions.

The combustion experiment of product oil was also conducted to investigate for the calorific value and corrosive of oil. The decomposition of ABS oil, which contains no bromide compounds, and Br-ABS oil are mixed and adjusted to the Br level of 5 mg/L, 20 mg/L, 200 mg/L, 2000 mg/L and 20000 mg/L of each different condition. The combustion tests (each sample is 0.5 g) were performed in a vessel (SUS304) stainless steel under oxygen atmosphere at 3 MPa and investigated the calorific value of oil. After the combustion tests, the stainless steel plate washed with IPA (isopropyl alcohol), ultrasonic for 5 minutes and observed in the range of corrosive surface (1 mm).

2.3. Results & Discussion

2.3.1. Thermogravimetric analysis of ABS

The decomposition of ABS occurs in two separated steps, as shown in figure 2. The weight loss in the first decomposition step (308°C) is 16 wt%, and the second decomposition step (402°C) is 69 wt%. Figure 3 shows the halogen concentration in produced oil at various decomposition temperatures. The chlorine concentration in oil was almost constant at the decomposition temperature 360°C to 450°C, while the bromine in oil was not detected at the decomposition temperature of 360°C, and those was almost constant at the decomposition temperature 375°C to 450°C. The rapidly weight loss between 375 °C to 450°C from the result of TG and DTG curves (Figure 2) was correlated with bromine concentration increase at the decomposition temperature over 375°C. It was considered that halogen compounds in ABS were mostly decomposed and released over the decomposition temperature of 375 °C.

The first valley (308°C) can be roughly attributed to the decomposition of part of halogen and antimony trioxide (Sb2O3). During the thermal decomposition of brominated flame retardant, Sb2O3 as synergist increases the rate of halogen release via the formation of SbBr3 etc. (288° C) (J. Simon, T. Kántor, T. Kozma & E. Pungor, 1982; E. Jakab, Md.A. Uddin, T. Bhaskar &Y. Sakata, 2003; M. Rzyman, M. Grabda, S.

Oleszek-Kudlak, E. Shibata & T. Nakamura,2010). From these results (figure 2 and figure 3), it was considered that a part of Br-ABS was decomposed and chlorine from BFRs decomposed by Sb_2O_3 was mainly released into the gas phase to include the product oil at the first stage (268°C ~ 338°C), and most part of Br-ABS was decomposed, and halogen (chlorine and bromine) decomposed from BFRs by Sb2O3 was released into the gas phase to include the product oil at the second stage (338°C ~ 447°C).
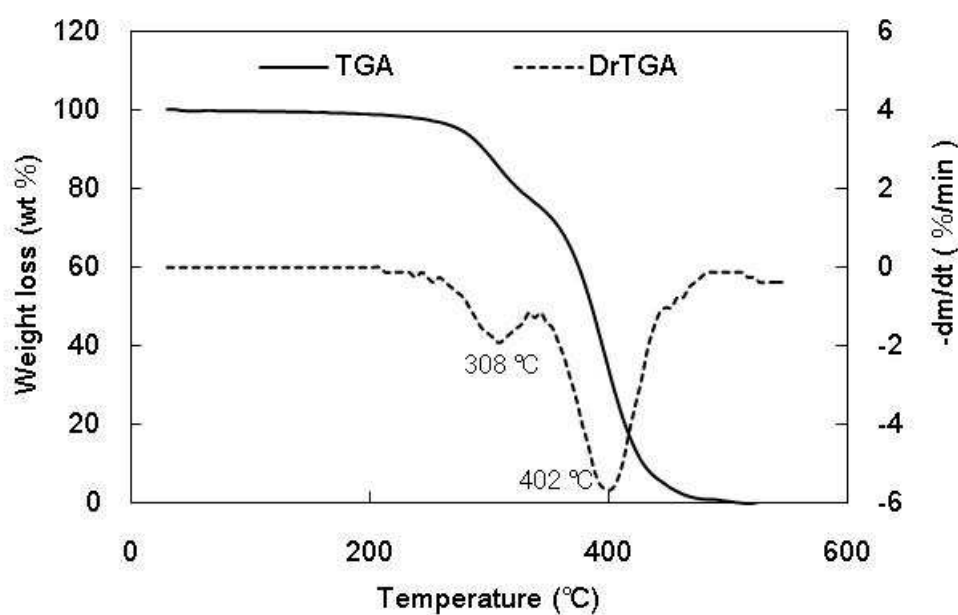
Fig. 2.TG and DTG curves of acrylonitrile butadiene styrene plastics
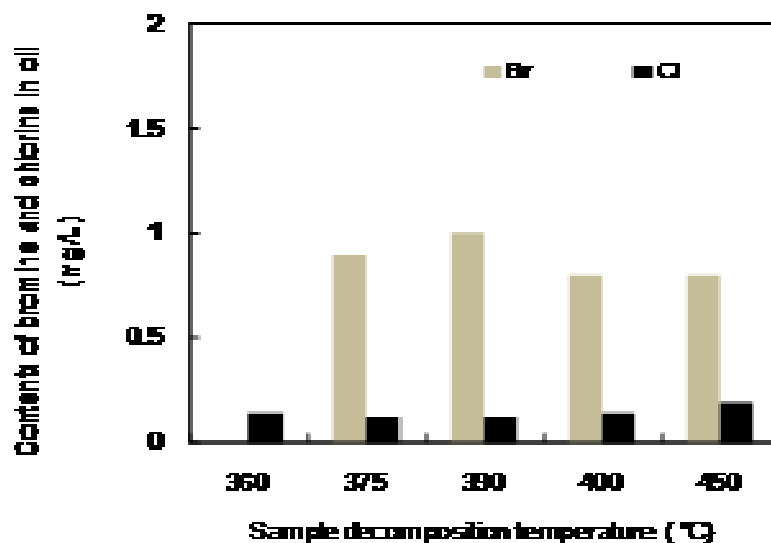
Fig. 3.Halogen concentration in produced oil at various sample decomposition

temperatures

2.3.2. Product Distribution

This work has investigated the effect of NaOH as additive and charcoal as capture on

the yields of pyrolysis products when Br-ABS was pyrolyzed at 450°C. Mass balances

of all experiments are shown in table 2. The individual decomposition of Br-ABS at

450°C was oil: 32.36 wt%, wax: 22.76 wt%, gas: 4.44wt%, and char: 40.44 wt%. It was

reported that the slow pyrolysis of brominated ABS to 450°C at 10°C/ min leads to the

production of oil (34 wt%), gas (5 wt%), and char (61 wt%), and the yield of oil was

almost same as that in this study (M.Brebu, T .Bhaskar , K .Murai, K. Muto, Y. Sakata

& M. Uddin,2004). The yields of product oil using additive and capture were approximately 36 wt %, which are higher than that without additive and capture, while those of char using additive and capture are lower than that without additive and capture. It would be considered that the production of oil promotes using additive and capture. The products by pyrolysis of Br-ABS and Br-ABS with additive were mainly oil (Figure 4 (a)) and wax (Figure 4 (b)), the second was char and the third was gases. Using capture (pine charcoal), the yield of wax decreased and that of capture increased due to the capture of compounds to create wax. These results suggest that the yield of oil is high using sodium hydroxide and capture, and capture can reduce wax production.

Table 2. Mass balances of various pyrolysis experiments

Material	Product of yield (wt %)				
	Oil	Wax	Char	Gas	Capture
Br-ABS	32.36	22.76	40.44	4.44	-
Br-ABS + Charcoal	36.13	8.80	31.19	4.12	19.76
Br-ABS+ NaOH	36.45	24.64	34.91	4.00	-
Br-ABS+ NaOH + Charcoal	36.52	4.47	33.22	3.20	22.59

(a) Oil   (b) Wax

Fig. 4.The images of (a) product oil and (b) wax

2.3.3. Analysis of products

The components in product oil were identified by GC/MS, and GC/MS chromatograms of oils obtained by four ways are shown in figure 5. The major compounds were toluene, ethylbenzene, styrene, cumene, α-methylstyrene, 2-bromophenol, 3-bromophenol, benzenebutanenitrile, 2,8-dimethylquinoline, 3-methylbutyl benzene, 2,4-dibromophenol, 1,3-diphenylpropane, 1,2-diphenylcyclopropane, 4-butyldiphenylmethane,hexadecanenitrile, octadecanenitrile, benzenebutanenitrile and 9-phenylacridine. The bromine compound was detected as 2-bromophenol, 3-bromophenol and 2,4-dibromophenol. It would be considered that Br-ABS sample used in this study contains tetrabromo bisphenol-A (TBBA) flame retardant (it was confirmed by GC/MS component analysis), and TBBA was

decomposed to 2-bromophenol, 3-bromophenol and 2,4-dibromophenol by pyrolysis (Fig. 6).

The halogen contents of the products (oil, wax and char) are determined by using automatic sample combustion device AQF -2100H, absorbed units GA-210 and ion chromatograph ICS-1600.The concentration of halogen in products (oil, wax and char) are shown in Table 3. The contents of bromine and chlorine in oil by pyrolysis of Br-ABS plastic were 3.2 and 0.2 wt%, respectively. Using capture, the contents of bromine and chlorine decrease to 1.7 and 0.9 wt%. Using sodium hydroxide, the contents of bromine and chlorine decreased to 1.3 and 0.004 wt%. Using both of sodium hydroxide and capture, the contents of bromine and chlorine in oil decrease to 0.6 and 0.002 wt%, and the lowest contents among four experiments. The halogen content in char using NaOH and that in capture using capture indicated higher halogen content than others. Therefore, sodium hydroxide can trap halogen in char, and capture can trap gas with halogen in generated gas by pyrolysis.
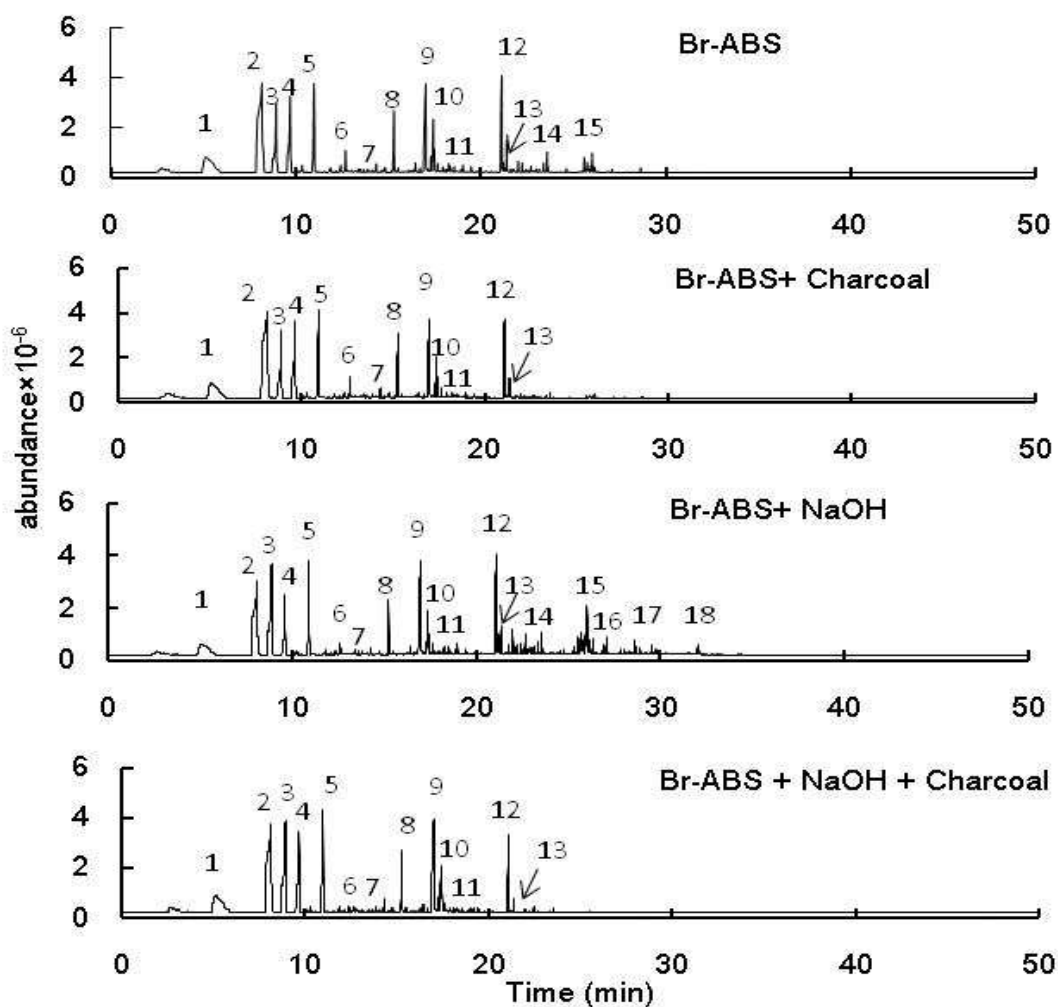
Fig. 5. The GC/MS chromatograms of product oil from Br-ABS by pyrolysis using

additive and charcoal (1: Toruene, 2: Ethylbenzene, 3: styrene, 4:cumene,

5: α-methylstyrene, 6: 2-bromophenol, 7: 3-bromophenol, 8: benzenebutanenitrile, 9:

2,8-dimethylquinoline, 10: 3-methylbutyl benzene, 11: 2,4-dibromophenol, 12:

1,3-diphenylpropane, 13: 1,2-diphenylcyclopropane, 14: 4-butyldiphenylmethane, 15:

hexadecanenitrile,16: octadecanenitrile, 17: benzenebutanenitrile and

18: 9-phenylacridine).
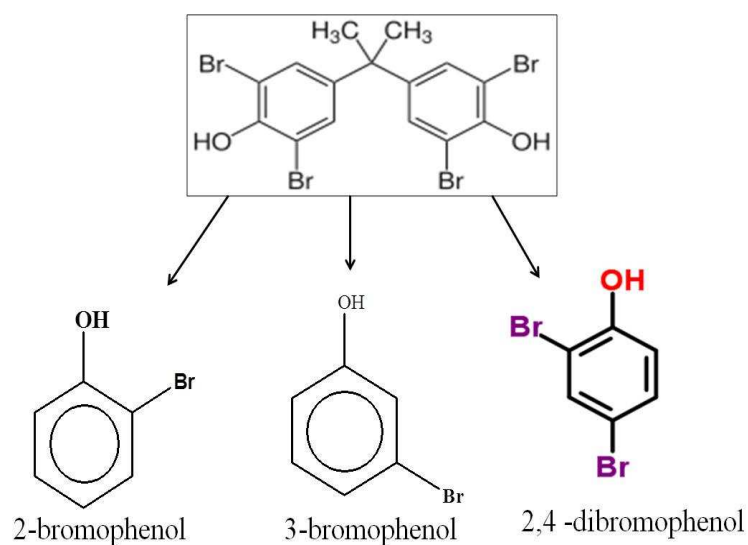
Fig. 6.The decomposition structure of Tetrabromo bisphenol-A (TBBA)

Table 3.Material composition and product distribution

Concentration of halogen (wt %)									
Material	Oil		Wax		Char			Capture	
	Br	Cl	Br	Cl	Br	Cl	F	Br	Cl
Br-ABS	3.2	0.2	41.6	7.3	10.4	2.4	0.6	0.0	0.0
Br-ABS + Charcoal	1.7	0.9	17.8	1.3	8.6	1.5	0.6	43.5	4.8
Br-ABS+ NaOH	1.3	0.0	23.1	1.0	30.2	0.2	0.3	0.0	0.0
Br-ABS+ NaOH + Charcoal	0.6	0.0	6.0	0.5	34.1	5.1	0.9	44.6	5.3

2.3.4. Investigation of the calorific value and corrosive

The calorific value of produced oil by combustion test was shown in figure 7. The calorific value of oil with higher bromine concentration is reduced. The calorific values of product oil with 5 mg/L to 2000 mg/L have 40.0 MJ/kg, 39.5 MJ/kg, 39.2 MJ/kg, 39.0 MJ/kg and 38.0 MJ/kg, respectively, and that of heavy oil is 39.1 MJ/kg, which is almost same as that of product oil with 2000 mg/L of bromine content. After combustion test, stainless steel was observed in the range of corrosive surface (1mm) (Figure 8). The corrosion was confirmed on the surface of stainless steel using the oil with 20,000 mg/L, while no corrosion was observed on the surface of steel using the oil with lower than 2000 mg/L of bromine content. From these result, the bromine concentration in the oil is with lower than 2000 mg/L could be used as alternative fuel.
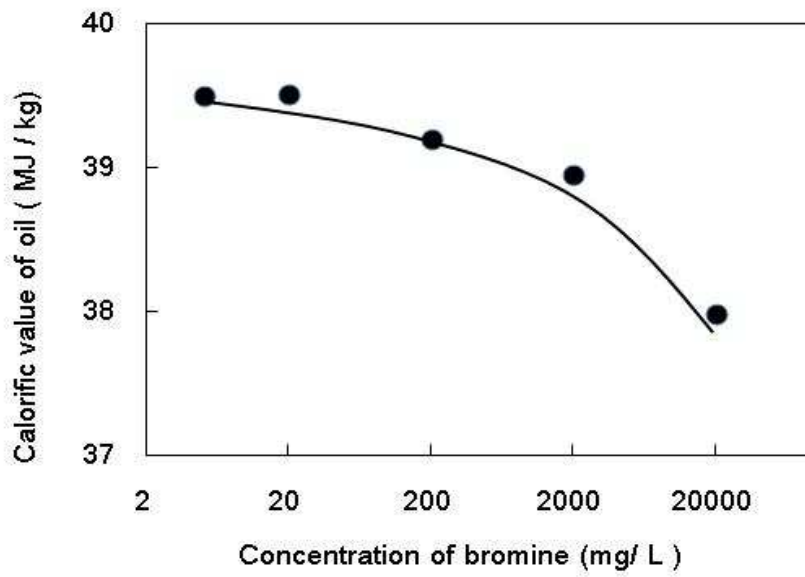
Fig.7. Calorific value by the combustion test of the product oil with various bromine

contents

(a)SUS 304 Before   (b)Br:5 mg/L   (c)Br:20 mg/L

(d) Br:200 mg/L   (e) Br:2000 mg/L   (f) Br:20000 mg/L

corrosion

1mm
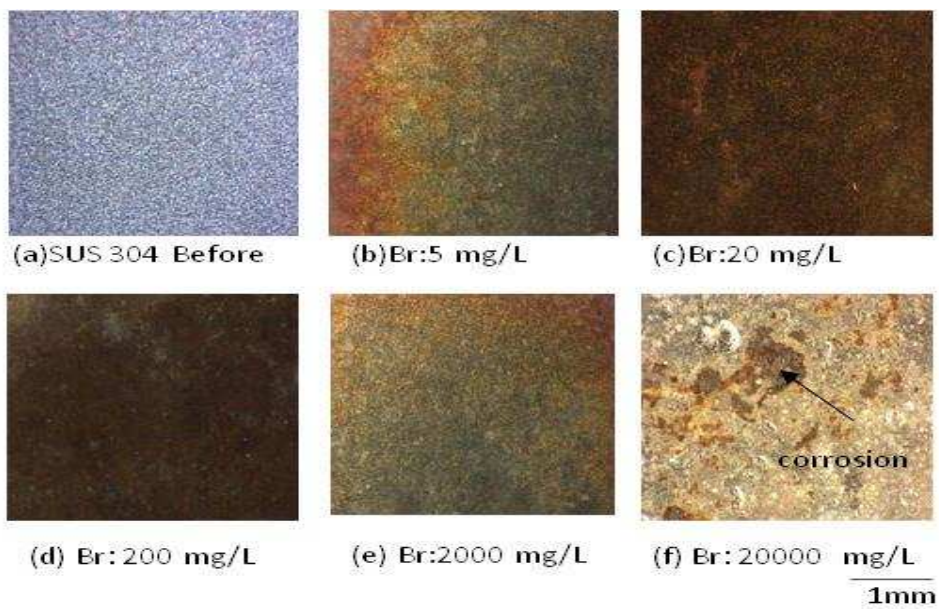
Figure 8.The corrosion on the surface of stainless plate after combustion test

2.4. Conclusions

The acrylonitrile-butadiene-styrene resin containing brominated flame retardant (Br-ABS) was pyrolyzed at 450°C using NaOH and cahrcoal. The yield of pyrolysis oil increased and that of char decrease by using NaOH and charcoal. By using both NaOH and charcoal, the concentration of bromine in pyrolysis oil was reduced from 3.2 wt% to 0.6 wt%. The combustion tests indicate that the pyrolysis oil with the content of bromine in pyrolysis oil could be reduce less than 2000 mg/L can be utilized as fuel without corrosion. These results indicate that NaOH as additive and charcoal as capture are effective to reduce bromine compounds in oil to use as fuel. In this work, the content of bromine in oil was still high for use as fuel. In future, further upgrading of the pyrolysis oil by changing the amount of additive, type of additive and capture and so on would appear to be required.

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Chapter 3

Reduction of halogen compounds by using Scallops shell, Ca(OH)$_2$, and NaOH via pyrolysis using a reflux condenser

3.1. Introduction

 The management and treatment of waste electrical and electronic equipment (WEEE), of which about 50 million tons are annually generated worldwide, is becoming a major concern [1]. The production of WEEE, such as TV housings, computer casings, refrigerator casings and washing machines, consequently results in environmental problems due to the use of harmful materials (e.g. plastic additives, metals). According to the WEEE EU directive, the fraction of major plastics associated with WEEE demands their recovery [2]. WEEE mainly consists of metals and plastic materials. The plastic fraction includes high impact polystyrene (HIPS) and acrylonitrile – butadiene - styrene copolymer (ABS), and more than half of computer housings are made of HIPS, with the next biggest fraction being ABS [3].

 Various pyrolysis processes have been tested for processing plastics which contain brominated flame retardants (BFRs) including fluidized bed pyrolysis [4], two-stage pyrolysis [5], long residence time pyrolysis [6], and pyrolysis in the presence of iron and calcium based catalysts [7]. Recently, William et al. [8] reported that the removal of

bromine content of Br-ABS by using zeolite ZSM-5 and zeolite Y-Zeolite was carried out in a fixed bed reactor at 440°C. The concentration of bromine in oil was 2.7 wt% without zeolites, and the contents of bromine in oil contained 2.6 wt% with zeolites. Joo-Sik Kim et al. [9] also reported that the removal of bromine content of HIPS by using various Ca-based additives (CaO, Ca(OH)2, Oyster Shell) was carried out in a bench-scale system equipped with a fluidized bed reactor at 460℃. It was found that the concentration of bromine in oil was 5 wt% without catalyst, and the contents of bromine in oil contained 1.6, 1.3, and 2.7 wt% with various Ca-based additives.

In the present study, Br-ABS are pyrolyzed with or without NaOH, $Ca(OH)_2$ and scallop shell using a reflux-condenser at 450℃. It is demonstrated that using a reflux-condenser in combination with additives are expected for reducing to trace amounts of bromine compound in product oil.

3.2. Materials and Methods

3.2.1. Materials and additives

Brominated flame retardant of acrylonitrile-butadiene-styrene resin (ABS) used in this study was obtained from Asahi Kasei Chemicals Co. Ltd. (Tokyo, Japan). Raw material contains ABS 65%, flame retardant 30% and others 5 %. The elemental composition of ABS was shown in Table 1.The additives of NaOH and Ca(OH)2 were obtained from Wako Pure Chemical Industries, Ltd. The shell powder was used scallop shell.

3.2.2. Experimental Procedures and apparatus

The experimental apparatus used in this study was shown in Figure 1. The glass reactor (length: 130 mm; i.d. 50 mm) and the glass reflux condenser (length: 350 mm; i.d. 12 mm) were used. The pyrolysis of Br-ABS plastic was performed in a glass reactor under atmospheric pressure in nitrogen gas with a reflux condenser. Approximately, 60 g of Br-ABS were added into the reactor for thermal decomposition. The additives are used to select the amount of each most effective additives (3 g of NaOH, 12 g of $Ca(OH)_2$ and 12 g of shell). In a typical run, the reactor was purged with nitrogen gas at a flow rate of 50 mL/min and held for 60 min to remove oxygen from the reactor. After nitrogen substitution, nitrogen gas flow stopped and the pyrolysis

experiment was performed. The temperature of the plastic bed was measured as the decomposition temperature, and the reactor temperature was increased to the decomposition temperature (450°C) at a heating rate of 5°C/min and held for 30 min. During the experiment, the reflux-condenser (200°C) was heated to the desired temperature. A portion of the hydrocarbon gases condense in reflux condenser and falls back into the reactor. The uncondensed fractions passed through the reflux-condenser, and product oil is collected with cold water condensers. Moreover, the non-condensable gases, which pass through cold water condenser, were collected in an aluminum bag via bubbling in the alkaline water solution. After pyrolysis, the residue was remained in the reactor. All the tests are carried out for a fixed time (2 hours).The pyrolysis products (oil, gas and residue) were calculated mass balance after experiments.
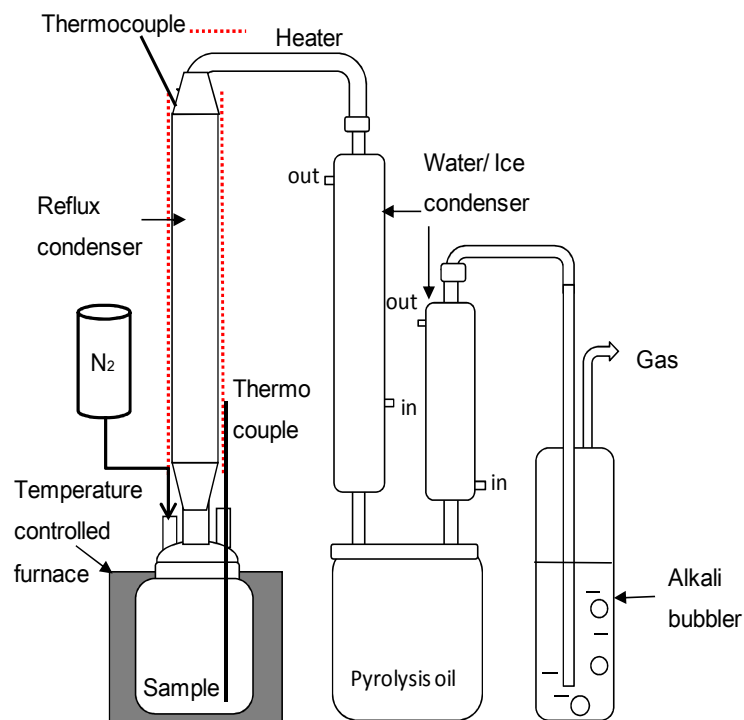
Fig. 1. Schematic diagram of the pyrolysis reactor with a reflux-condenser.

The elemental composition of Br-ABS was determined using a PerkinElmer 2400, EAI CE-440F and Combustion Ion Chromatography. The element of carbon, hydrogen and nitrogen was analyzed by PerkinElmer 2400 and EAI CE-440F. The halogen of bromine and chlorine was determined using Combustion Ion Chromatography and the antimony was determined by JIS K0102 (2010).All oils were diluted with methanol, and quantitatively and qualitatively analyzed by comparing the peaks obtained by Gas chromatography–mass spectrometry (GC/MS). The main compounds were identified by

the GC/MS spectrum library (match quality higher than 90%). All samples were analyzed by 5890 SERIES GC and 5972 SERIES Mass Selective Detector (MS) on an FUSED SILICA capillary column (60 m × 0.25 mm i.d., 1.0 μm film thickness), with pure helium used as the carrier gas. The analysis condition was carried out at a temperature rate of 40°C for 5 minutes, and then increased from 40°C up to 290°C at a temperature rate of 5°C/min. The temperature of injector was set up at 250°C and that of the detector at 280°C. It can identify the substances which have 35-400 m/z.

3.3. Results & Discussion

3.3.1. Mass balance of products

The product yield of Br-ABS and additives (NaOH, Ca(OH)$_2$, Shell) were shown in Table 2. Regardless of additives, the yield of oil is over 60 %, and that of residue is 30-34 %, and that of gas is 5-8 %, which means that oil is the highest yields product via pyrolysis, but the product yield was different depending on additives. Without additive increasing the reflux temperature, the yield of product oils increase, while that of the residue decrease. Therefore, the amount of residue is higher when the additives of shell and Ca(OH)$_2$ other experiments.

Table 1. The product yield of Br-ABS by additives (Shell, Ca(OH)2, NaOH)

Product yield (wt %)	Br-ABS	Shell	Ca(OH)2	NaOH
Oil	64.16	61.27	62.49	62.57
Residue	29.91	33.73	33.13	29.64
Gas	5.93	5.00	4.38	7.79

3.3.2. Analysis of products

The component of product oil was identified by GC/MS. The GC/MS chromatograms of

product oil obtained from Br-ABS and additives are shown in Figure 2. The major

compounds are 1.toluene,   2.ethylbenzene, 3.styrene, 4.cumene, 5. α-methylstyrene,

6.2-bromophenol, 7.3-bromophenol, 8.isopropylphenol, 9.propane, 10.benzene,

11.4-methyl-2,4-diphenyl-1-pentene and other compounds. The bromine compound was

detected as 2-bromophenol, 3-bromophenol and 2,4-dibromophenol. The components of

oil are decreased depending on additives.
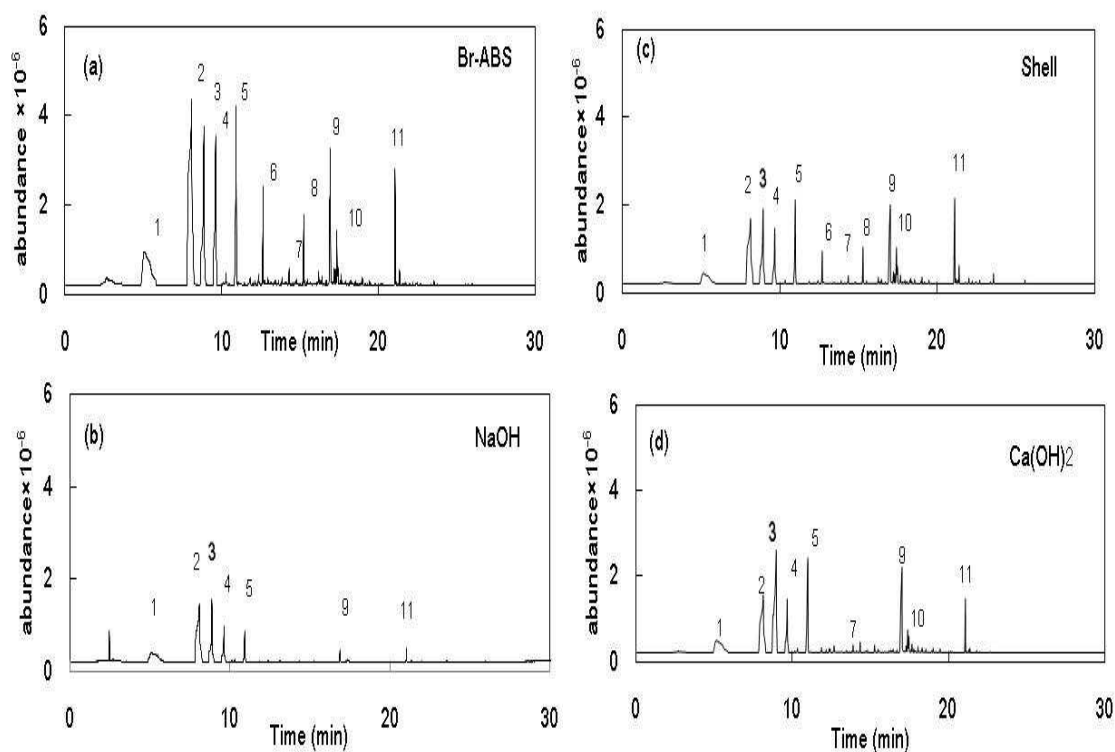
Fig. 2. GC/MS chromatograms of oil products via pyrolysis

(a) Br-ABS (b) Br-ABS+NaOH (c) Br-ABS+Shell (d) Br-ABS+Ca(OH)$_2$

3.3.3. Effect of additives to provide the product oil components

With decreasing depending on additives, the bromine compounds in oil decrease. The total concentration of 2-bromophenol, 3-bromophenol and 2,4-dibromophenol using reflux condenser at 450ºC are 296.46 mg/L,   215.38 mg/L, 116.45mg/L and 27.17 mg/L, respectively(show in Figure 3). These results indicate that the oil containing low bromine compounds can be obtained via pyrolysis using reflux condenser and addition of NaOH.

45
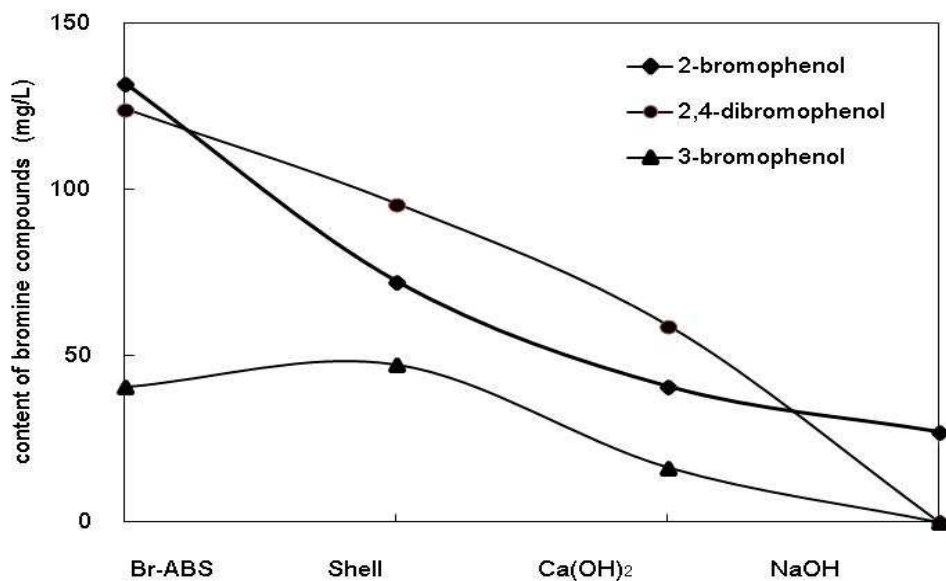
Fig. 3. Concentration of bromine compounds in the product oil of Br-ABS and

additives.

3.4. Conclusions

Br-ABS are pyrolyzed with or without NaOH, Ca(OH)$_2$ and scallop shell using a

reflux-condenser at 450ºC. The pyrolysis oils obtained in all experiments mainly

consisted of isopropyl alcohol, toluene, ethylbenzene, styrene, cumene, propylbenzene

and α-methylstyrene   which are similar to the contents in heavy oil. The bromine

compounds in oil were 2-bromophenol, 3-bromophenol and 2,4-dibromophenol. These

results indicate that NaOH is superior to decrease in the product oil in bromine

compounds other than as an additive effect.

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Chapter 4

Bromine reduction uisng reflux condenser with various temperatures via pyrolysis

4.1. Introduction

Plastic polymer products are widely used in electrical and electronic equipment, and such products generate significant amounts of waste after use. Waste plastic recycling techniques are desirable to protect the environment from non-biodegradable plastics and other toxic substances associated with polymer waste. Among various recycling methods for waste plastics, feedstock recycling has been found to be promising for waste plastics, and pyrolysis is one of the most promising recycling techniques for polymers. By pyrolysis, polymers are converted into gas, oil, and carbon residue for uses such as chemical feedstock and fuel [1].

Plastics from waste electric and electronic equipments (WEEE) contain toxic brominated flame retardants, which present problems particularly for recycling [2–6]. For example, the treatment of brominated compounds from 300°C to 500°C introduces the possible formation of brominated dibenzodioxins and furans [7]. This should be avoided because of the carcinogenic character of these products. Moreover, the production of hazardous by-products reduces the acceptance of recycling processes by the people.

WEEE consists primarily of metals and plastic materials. The plastic fraction includes

high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) copolymer,

and the majority of computer housings are manufactured with HIPS, with the next

largest fraction being ABS [8]. WEEE plastics also contain antimony trioxide as a

synergist to increase the flame retardant properties of brominated additives. However,

during combustion antimony trioxide promotes the release of bromine radicals via the

formation of volatile antimony bromides. Consequently, the bromine radicals quench

the combustion process by aggressively scavenging the other radicals required for flame

propagation [9]. Moreover, some studies indicate that the likelihood of forming

polybrominated dibenzodioxins and dibenzofurans during mechanical and chemical

recycling at certain temperatures is high [3, 10–12]. The flame retardant properties of

WEEE plastics represent a major problem for pyrolysis recycling technologies,

particularly because of the presence of bromine and antimony.

There is abundant literature regarding fundamental investigations of pyrolysis and the

chemical recycling of waste plastics [13–24]. Several investigations have been

performed to assess the effect of antimony trioxide on both the pyrolysis products and

bromine content of plastics during pyrolysis. Bhaskar et al. reported the pyrolysis of

polybrominated HIPS mixed with polypropylene, polyethylene, polystyrene, and

polyvinyl chloride, and debromination was performed using a carbon composite of calcium carbonate (Ca–C) [15]. Vasile et al. investigated improvement of pyrolysis oil quality using the commercial hydrogenation catalyst DHC-8, and they demonstrated that most of the hazardous halogenated compounds were degraded, and halogens were released as gases [25]. Hall and Williams reported on the fast pyrolysis of halogenated plastics from waste computers and showed that the pyrolysis products contained a chemically heterogeneous mixture of hydrocarbons that would need to be treated for the hydrocarbon industry [23]. Blazso et al. studied the analytical pyrolysis of flame retardant polymers in electronic scrap and debromination. They reported that sodium hydroxide enhances bromomethane evolution and depresses the formation of brominated phenol during pyrolysis of brominated epoxy resins [24]. Imai and Hamm have demonstrated the compatibility of brominated flame retardant plastics with feedstock recycling and energy recovery processes [26]. Antos and Sedlar investigated the influence of the flame retardant on thermal decomposition of polypropylene and polymer optical stabilizers [27]. In all these studies, catalysts are mostly used, and the bromine concentration in the produced oil is still high.

Deepyaman and Amitava have studied the effects of a reflux condenser on the molecular weight distribution of products by pyrolysis of polypropylene. They

compared the effects of degradation with and without reflux on the molecular weight

distribution of the product [28]. When brominated acrylonitrile–styrene–butadiene

(Br-ABS) is heated in an inert atmosphere and the volatile products are condensed, the

molecular weight distribution of the product oil is very wide. Moreover, this product has

poor low properties, very waxy, high halogen compound and unusable as a liquid fuel

[15, 29]. By using the reflux condenser, the larger molecules are condensed and fall

back into the reactor to break into smaller molecules by heating again in order to reduce

halogen compound in product oil to be used as fuel.

In the present study, Br-ABS resins are pyrolyzed with a reflux-condenser at 450ºC,

and the reflux temperature was set up 150°C to 200°C. We investigated that the effect

of reflux condenser temperature on the amount of bromine compound in product oil to

be used as fuel.

4.2. Experimental Procedures and apparatus

The brominated flame retardant of ABS resin used in this study was obtained from Asahi Kasei Chemicals Co. Ltd. (Tokyo, Japan). The raw material contains 65% ABS, 30% flame retardant, and 5% other substances.

The experimental apparatus used in this study is shown in Figure 1. A glass reactor (length: 130 mm; i.d. 50 mm) and glass reflux condenser (length: 350 mm; i.d. 12 mm) were used in the experiment. The pyrolysis of Br-ABS plastic was performed in the glass reactor under atmospheric pressure in nitrogen gas with and without reflux condenser. Approximately, 60 g of Br-ABS was added into the reactor for thermal decomposition. In a typical run, the reactor was purged with nitrogen gas at a flow rate of 50 mL/min for 60 min to remove oxygen from the reactor. After oxygen substitution, the nitrogen gas flow was stopped and the pyrolysis experiment was performed. The temperature of the plastic bed was measured as the decomposition temperature, and the reactor temperature was increased to the decomposition temperature (450°C) at a heating rate of 5°C/min for 30 min. During the experiment, the reflux condenser was heated to the desired temperature (from 150°C to 200°C). A portion of the hydrocarbon gases condensed in the reflux condenser and fell back into the reactor. The uncondensed fractions passed through the reflux condenser, and the oil was collected with cold water

condensers. Non-condensable gases, which passed through the cold water condenser, were collected in an aluminum bag via bubbling of the alkaline water solution. After pyrolysis, the residue remained in the reactor. All tests were carried out for a fixed time period (2 h). The mass balance of the pyrolysis products (oil, gas, and residue) was calculated after the experiments. The elemental composition of Br-ABS was determined using PerkinElmer 2400, EAI CE-440F elemental analyzers, and combustion ion chromatography (CIC). Carbon, hydrogen, and nitrogen were analyzed by the PerkinElmer 2400 and EAI CE-440F. Bromine and chlorine were determined using CIC, and antimony was determined by JIS K0102 (2010).

All oils were diluted with methanol, and were quantitatively and qualitatively analyzed by comparing the peaks obtained by gas chromatography–mass spectrometry (GC/MS). The main compounds were identified by the GC/MS spectrum library (match quality higher than 90%). All samples were analyzed by a Hewlett-Packard model 5890 SERIES GC and a 5972 SERIES mass selective detector on a fused silica capillary column (60 mm $\times$ 0.25 mm, i.d.; 1.0 μm film thickness), with pure helium used as the carrier gas. The analysis was carried out at a temperature of 40°C for 5 min, which was then increased to 290°C at a rate of 5°C/min. The temperature of the injector was set at 250°C and that of the detector at 280°C, which could identify substances that have

35-400 m/z.
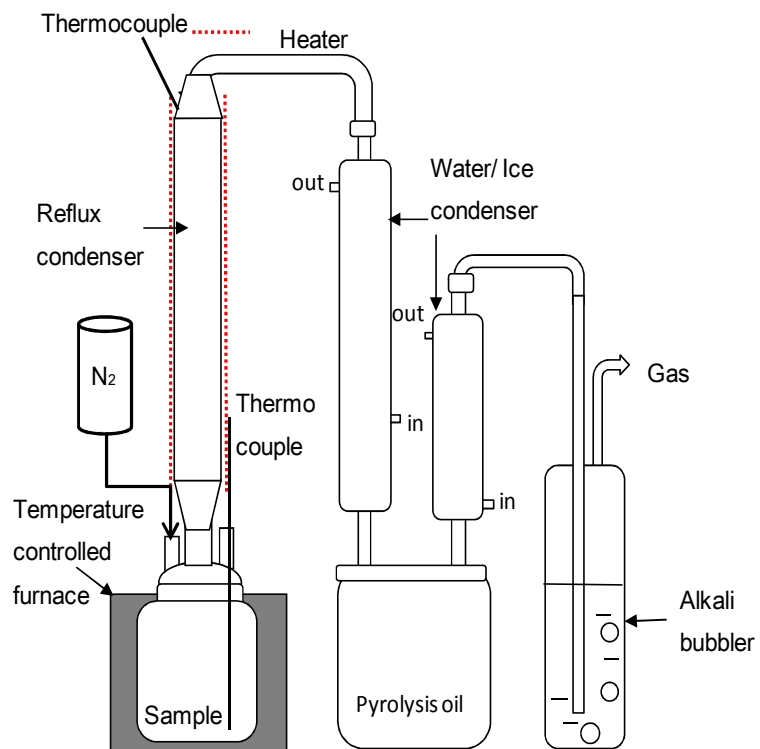
Fig. 1. Schematic diagram of the pyrolysis reactor with a reflux-condenser (reflux

temperature 150 °C to   200°C).

4.3. Results & Discussion

4.3.1. Mass balance of products

The effects of reflux condenser temperature (from 150°C to 200°C) on the product

yields are shown in Table 2. Regardless of reflux temperature, the yields of oil, residue,

and gas were more than 55%, 20%–40%, and 5%–10%, respectively. Hence, the yield

of oil was the highest via pyrolysis; however, the product yield differed depending on

the temperature of the reflux condenser. With increasing reflux temperature, the yield of

product oil increased and that of the residue decreased. Therefore, the amount of

product oil was higher than the residue at higher reflux temperatures.

Table 1.The product yields by the reflux temperature

Product yield (wt %)			
Reflux Temperature (°C)	Oil	Residue	Gas
150	57.8	36.8	5.4
160	63.7	29.4	6.9
170	64.8	27.9	7.3
180	65.5	26.8	7.8
190	68.1	23.3	8.6
200	69.0	22.4	8.6

4.3.2. Analysis of oil products

The components of product oil were identified by GC/MS. The GC/MS chromatograms of the product oil obtained from Br-ABS are shown in Figure 2, and some characteristics for the components of oil decomposition are shown in Table III. The major compounds obtained were similar to the content of heavy oil. The compounds obtained were isopropyl alcohol, toluene, ethylbenzene, styrene, cumene, propylbenzene, α-methylstyrene, and butylbenzene, and the minor components were isopropylphenol, 2-phenylpropan-2-ol, benzenebutanenitrile, 1,3-diphenylpropane, 1,3-diphenylbutane, α-methylstyrene dimer, 1,2-diphenylcyclopropane, 4-cumylphenol, hexadecane- nitrile, and octadecanenitrile. The bromine compounds detected were 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol.

Ethylbenzene was the predominant compound in the oils under all experimental conditions. The peak area of ethylbenzene increased with decreasing reflux condenser temperature. The peak areas of other components with low molecular weight, such as isopropyl alcohol, toluene, styrene, cumene, propylbenzene, α-methylstyrene, and butylbenzene also increased. Moreover, the peak areas of components with high molecular weight diminished. The high molecular weight components return to the

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reactor to decompose into low weight components due to their high boiling/

condensation points.
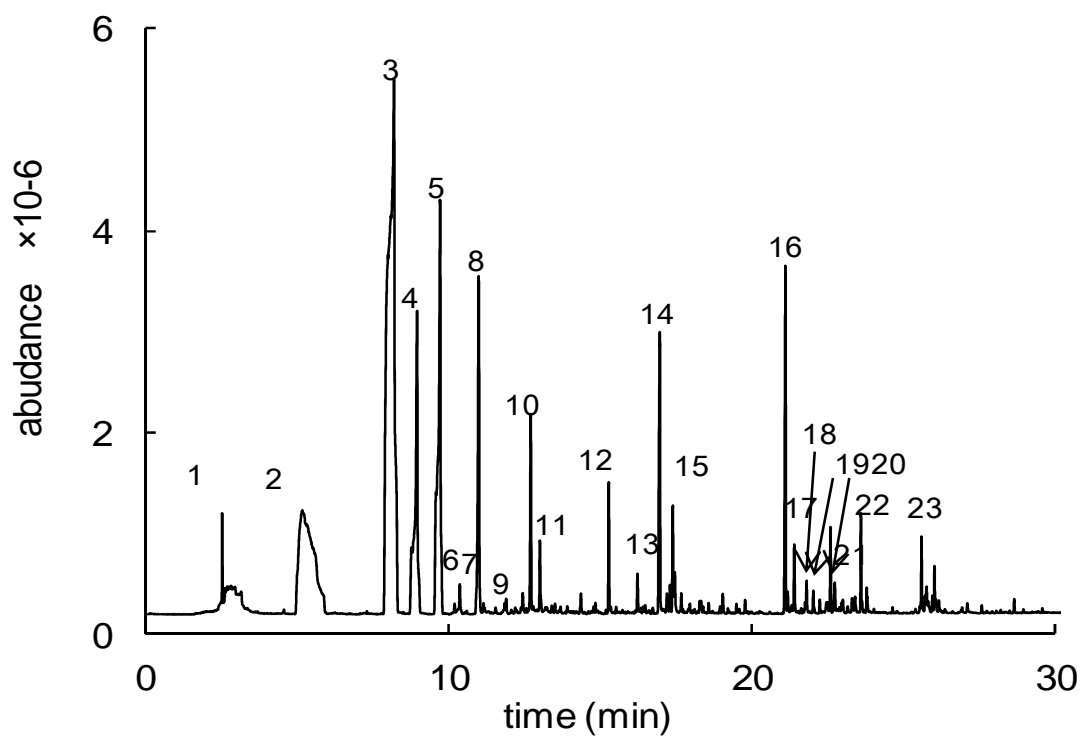
Fig. 2. GC/MS chromatogram of oil products by pyrolysis (reflux temperature at

200°C).

The concentrations of bromine compounds in the oil are shown in Fig. 3. With

decreasing reflux condenser temperature, the bromine compounds in the oil decrease.

The concentration of 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol using the

reflux condenser at 150°C was 42%, 52%, and 38% of the concentration at 200°C,

respectively. These results indicate that the oil containing low bromine compounds can

be obtained via pyrolysis using a reflux condenser at low temperature.
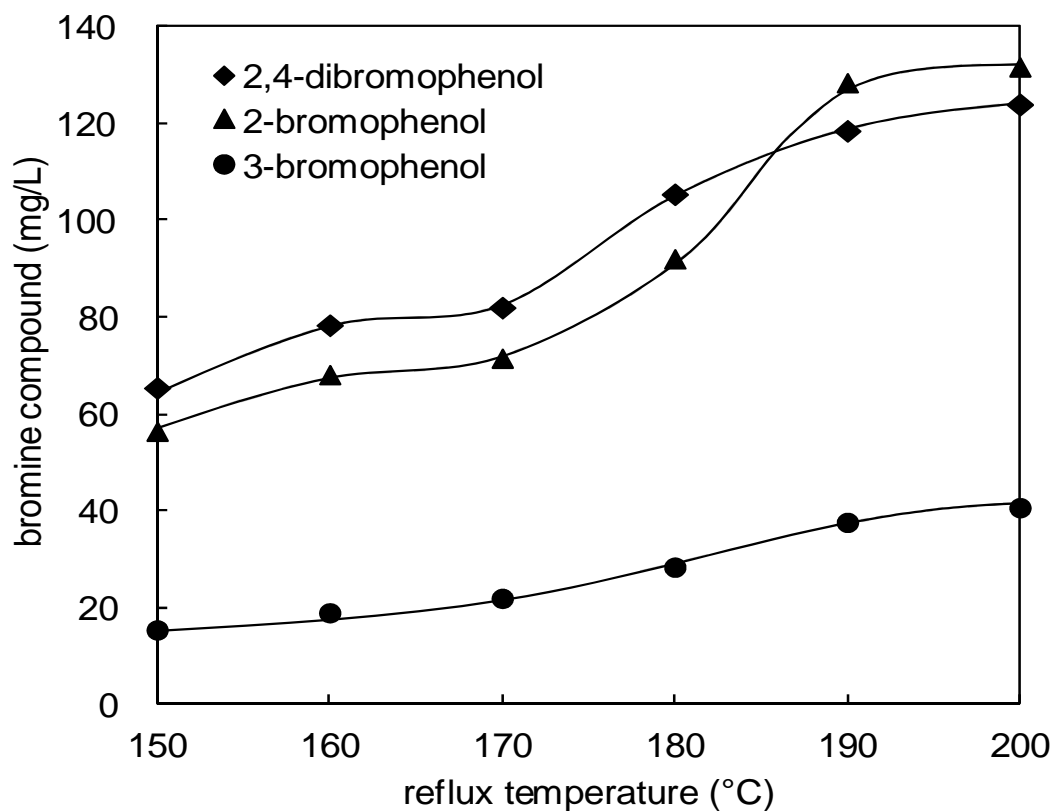
Fig. 3. Concentration of bromine compounds in the product oil using reflux condenser

at various temperatures.

4.3.3. Effect of reflux condenser

The Br-ABS resins were pyrolyzed without a reflux condenser to investigate the effects

of the reflux condenser. Figure 4 shows the concentrations of bromine compounds in

the pyrolysis oil obtained with and without the reflux condenser. The temperature of the

reflux condenser was 200°C. The concentration of the total bromine compounds in the

oil obtained with the reflux condenser was 296 mg/L, while that obtained without the

reflux condenser was 3105 mg/L, which was approximately ten times than that obtained

using the reflux condenser. The concentration of 2-bromophenol, 3-bromophenol, and

2,4-dibromophenol in oil obtained by pyrolysis with the reflux condenser was 6.5%,

11.3%, and 9.5% of the concentration obtained without the reflux condenser,

respectively. The use of the reflux condenser is possible to reduce around one tenth of

bromine compounds in oil obtained via pyrolysis.

Fig.4. Concentration of bromine compounds in the oil obtained via pyrolysis with or without reflux condenser.

Table 2. Component of the decomposition oil, molecular weight and boiling point by
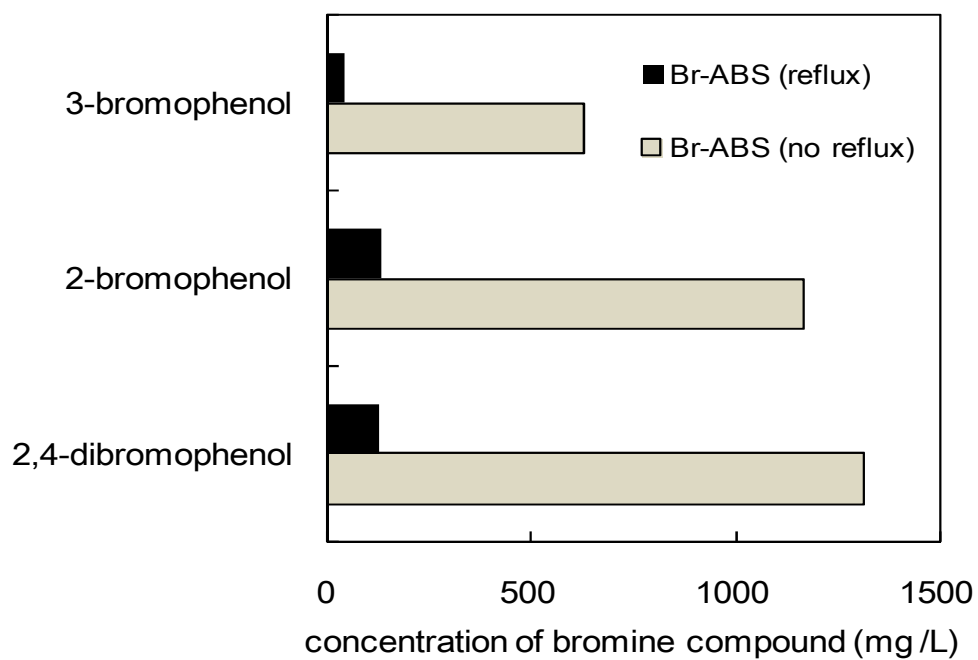
reflux temperature

Peak No.	R.T (min)	Compound	Formula	MW	BP (℃)	Reflux Temperature (%)					
						150℃	160℃	170℃	180℃	190℃	200℃
1	2.5	Isopropyl Alcohol	C_3H_8O	60	83	0.9	0.8	0.7	0.7	0.7	0.6
2	5.3	Toluene	C_7H_8	92	110	16.8	13.3	13.0	10.9	10.6	10.2
3	8.2	Ethylbenzene	C_8H_{10}	106	136	29.0	26.0	24.3	23.5	22.7	21.7
4	8.9	Styrene	C_8H_8	104	145	2.0	1.9	1.9	1.8	1.7	1.5
5	9.7	Cumene	C_9H_{12}	120	152	14.3	11.9	11.6	11.0	10.4	9.2
6	10.3	Propyl Benzene	C_9H_{12}	120	159	9.5	6.9	6.3	7.8	6.7	6.9
7	11.8	2-Propylbenzene	C_9H_{10}	118	152	8.4	7.8	6.9	6.9	6.7	6.3
8	11.9	α-Methylstyrene	C_9H_{10}	118	165	0.6	0.4	0.3	0.1	0.1	0.1
9	12.4	Butylbenzene	$C_{10}H_{14}$	134	183	0.7	0.7	0.5	0.4	0.3	0.2
10	12.7	2-Bromophenol	C_6H_5BrO	172	195	2.3	2.3	2.3	2.4	2.5	2.5
11	12.9	2-phenylpropan-2-ol	$C_9H_{12}O$	136	202	0.3	0.5	0.5	0.6	0.6	0.9
12	15.2	Isopropylphenol	$C_9H_{12}O$	136	212	0.1	0.1	0.2	2.0	2.1	2.1
13	16.2	3-Bromophenol	C_6H_5BrO	172	236	0.2	0.3	0.4	0.4	0.6	0.6
14	17.0	Benzenebutanenitrile	$C_{10}H_{11}N$	145	-	0.2	0.2	0.2	0.2	0.2	0.2
15	17.2	2,4-Dibromophenol	$C_6H_4Br_2O$	250	154	0.2	0.3	0.6	0.8	0.9	1.0
16	21.1	1,3-Diphenylpropane	$C_{15}H_{16}$	196	-	nd	0.1	0.1	0.2	0.1	5.1
17	21.4	1,3-Diphenylbutane	$C_{16}H_{18}$	210	-	nd	0.2	0.2	0.4	0.5	1.0
18	22.0	1,2-Diphenylcyclopropane	$C_{15}H_{14}$	194	-	nd	0.2	0.3	0.1	0.3	0.5
19	22.2	1,4-Diphenylbutane	$C_{16}H_{18}$	210	-	nd	0.1	0.2	0.2	0.3	0.3
20	22.6	α--Methylstyrene dimer	$C_{18}H_{20}$	236	161	nd	0.0	0.1	0.1	0.1	0.2
21	23.3	4-Cumylphenol	$C_{15}H_{16}O$	212	-	nd	0.0	0.1	0.1	0.1	0.2
22	23.6	Hexadecanenitrile	$C_{16}H_{31}N$	237	-	nd	nd	nd	nd	0.7	0.8
23	25.6	Octadecanenitrile	$C_{18}H_{35}N$	265	-	nd	nd	nd	nd	0.5	0.6

R.T: retention time; BP: boiling point; MW: molecular weight; nd: not detected

4.4. Conclusions

ABS resin containing brominated flame retardant was pyrolyzed at 450°C using a reflux condenser to produce oil with low content of bromine compounds. The oil obtained via pyrolysis in all experiments consisted primarily of isopropyl alcohol, toluene, ethylbenzene, styrene, cumene, propylbenzene, α-methylstyrene, and butylbenzene, which are similar to the content of heavy oil. The bromine compounds in the oil were 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol. With increasing reflux condenser temperature, the yield of oil decreased, yield of residue increased, and the yield of bromine compounds decreased. Hence, the bromine content in oil obtained via pyrolysis with the reflux condenser was lower than that obtained without the reflux condenser. These results indicate that the reflux condenser apparatus was effective for reducing bromine compounds in oil.

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Chapter 5

Bromine compounds reduction with addition of NaOH uisng a reflux condenser

5.1. Introduction

Plastics are low-cost materials and widely used because they can be easily processed into light but durable materials with low thermal and electrical conductivity. However, according to the strong increase in plastic consumption more and more plastic waste is accumulated that poses serious problems to the environment due to the unpleasant aspect and the long persistence in landfill. On the other hand, plastic waste has a high content of organic materials and energy that is totally lost by disposal or is recovered only in a very small amount by incineration. Due to the world's limited reserve of coal, crude oil and natural gases, it becomes very urgent to preserve the existing non-renewable materials and to find other carbon sources as feedstock materials or as fuels. Pyrolysis is one of the best methods to recover the material and energy from polymer waste, as only about 10% of the energy content of the waste plastic is used to convert the scrap into valuable hydrocarbon products [1]. These hydrocarbon products are obtained by breaking down polymers at high temperatures into petrochemical feedstock components from which they originate, while the additives in the polymer materials (e.g. metals, inorganic fillers and supports) remain in the pyrolysis residue.

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Waste plastics are divided into two groups of hydrocarbons such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) and hydrocarbons containing heteroatom such as polyvinylchloride (PVC), acrylonitrile-styrene-butadiene resin (ABS) and polyethylene terephthalate (PET).

One of the major components of the waste from electric and electronic equipment is ABS, which usually contains brominated flame retardants. Tetrabromobisphenol A (TBBPA), and brominated epoxy oligomers (TBBPA is built in the oligermer structure) are widely used flame retardants in the plastics of electronic industry, such us epoxy and polycarbonate resins, ABS, high impact polystyrene, phenolic resins and used in textiles as well. Br-ABS and HIPS-Br are commonly found in the waste from electric and electronic equipment (WEEE).Moreover, ABS materials cause additional problems because organic halogen compounds in oil can lead to formation of dioxins and/or benzofurans [2,3]. Therefore it is necessary to remove halogen from pyrolysis oils.

Various pyrolysis processes have been tested for processing plastics which contain brominated flame retardants (BFRs) including fluidized bed pyrolysis [4], two-stage pyrolysis [5], long residence time pyrolysis [6], and pyrolysis in the presence of iron and calcium based catalysts [7]. Recently, William et al. [8] reported that the removal of bromine content of Br-ABS by using zeolite ZSM-5 and zeolite Y-Zeolite was carried

out in a fixed bed reactor at 440°C. The concentration of bromine in oil was 2.7 wt% without zeolites, and the contents of bromine in oil contained 2.6 wt% with zeolites. Joo-Sik Kim et al. [9] also reported that the removal of bromine content of HIPS by using various Ca-based additives (CaO, Ca(OH)$_2$, Shell) was carried out in a bench-scale system equipped with a fluidized bed reactor at 460ºC. It was found that the concentration of bromine in oil was 5 wt% without catalyst, and the contents of bromine in oil contained 1.6, 1.3, and 2.7 wt% with various Ca-based additives.

In the present study, the virgin materials of Br-ABS are pyrolyzed with or without sodium hydroxide by using a reflux-condenser at 450ºC. It is demonstrated that using a reflux-condenser in combination with sodium hydroxide is expected for reducing to trace amounts of bromine compound in product oil. The main objective of this study is to elucidate the influence of a reflux condenser and additive on the debromination of pyrolysis oil.

5.2. Experimental Procedures and apparatus

5.2.1. Material s and additives

Brominated flame retardant of acrylonitrile-butadiene-styrene resin (ABS) was obtained

from Asahi Kasei Chemicals Co. Ltd. (Tokyo, Japan). These virgin material contains

ABS 65%, flame retardant 30%, antimony trioxide (Sb_2O_3) 3.8% and others 1.2%. The

additives of sodium hydroxide (NaOH) are obtained from Wako Pure Chemical

Industries, Ltd.

5.2.2. Apparatus and analysis procedures

 The reactor was used glass reactor (length:130 mm; i.d. 50mm) and, the reflux

condenser (length: 350 mm; i.d. 12 mm) was also made of glass. The pyrolysis of

Br-ABS plastic was performed in a glass reactor under nitrogen pressure with or

without a reflux condenser. The experimental apparatus is shown in Fig. 1.

Approximately, 60 g of plastics were loaded into the reactor for the thermal

decomposition. Sodium hydroxide was used 1% to 5% of plastic weight for the catalytic

tests. In a typical run, the reactor was purged with nitrogen gas at a flow rate of

50 ml /min and held at for 60 min to remove oxygen from plastic sample. The reactor

temperature was increased to the decomposition temperature (450°C) at a heating rate

of 5°C /min and held for 30 min. The temperature of the plastic bed was measured as

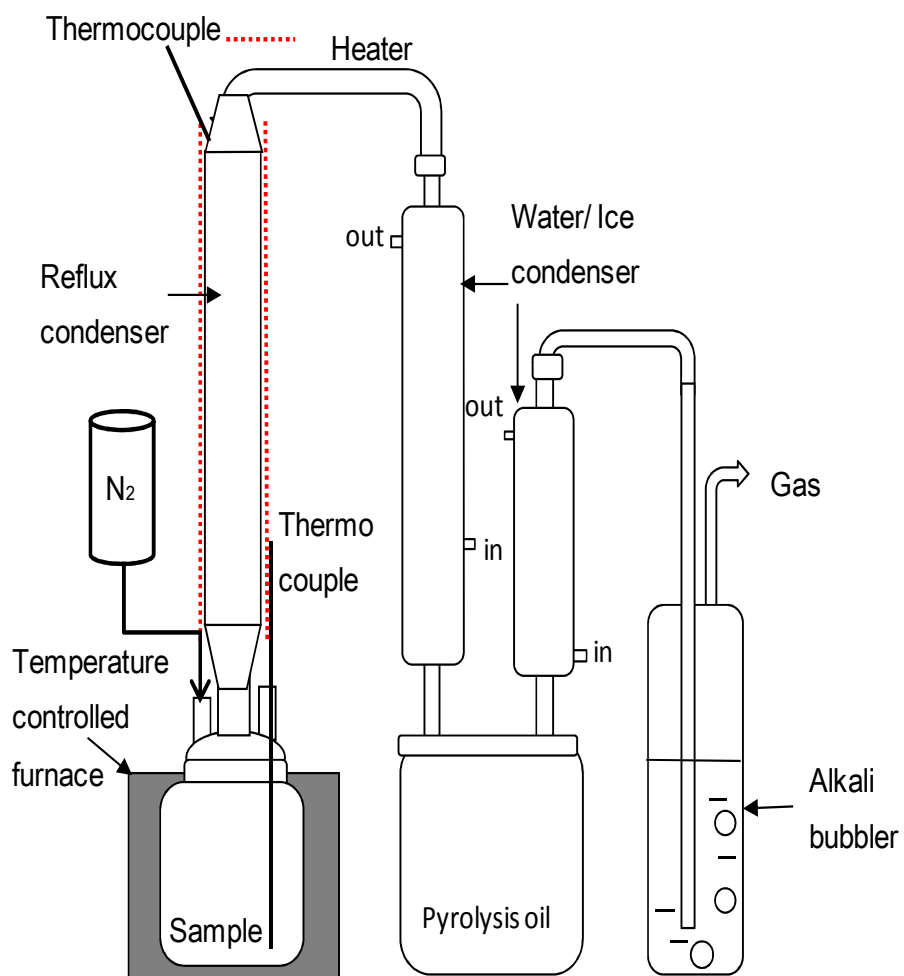the decomposition temperature.

Fig. 1. Schematic diagram of the pyrolysis reactor with a reflux-condenser (with or

without NaOH)

The glass reactor (450°C) and the reflux-condenser (200°C) were heated to the desired temperature. The reflux condenser is setting up to break down the larger molecules break into smaller molecules in the reactor by heating. A portion of the hydrocarbon gases distillates and falls back into the reactor. The uncondensed fractions passed through the reflux-condenser and cold water condenser are collected with separating funnel. Moreover, the non-condensable gases pass through cold water condenser, and finally only the gas is collected in an aluminum bag by bubbling in the alkaline water solution. All the tests are carried out for a fixed time. After pyrolysis, the residue was remained in the reactor. The pyrolysis products (oil, gas and residue) were calculated mass balance after experiments.

The product oils were analyzed by gas chromatography/mass spectrometry (GC/MS). The char and oil were analyzed by using combustion flask followed by ion chromatograph. About 1 g of char and oil sample were combusted in the combustion flask and then washed with ion exchanged water in order to dissolve the gaseous products. The obtained solution was analyzed by a DIONEX DX-120 ion chromatograph that can be anion. And the solid char was also analyzed by scanning electron microscopy (SEM, JSM-6510A) coupled with energy dispersive X-ray

analysis.

Gas chromatography/mass spectrometry (GC/MS) was performed with use of a Hewlett-Packard 5890-II gas chromatograph interfaced with a HP 5972 mass selective detector. GC analysis was carried out on a fused-silica column (60 m x 0.25 mm i.d.) coated with a SPB-5 (1.0 μm film thickness) operated with temperature programming from 40°C up to 250°C at a temperature rate of 3.5°C min-1 with He as carrier gas (linear velocity = 20 cm/s). EI mass spectra and reconstructed chromatograms were obtained by automatic scanning in the range 35-400 m/z. All the oils were quantitatively and qualitatively analyzed by comparing the peaks obtained by GC/MS. The product oil was diluted with methanol. The main compounds were identified by the GC/MS spectrum library (match quality higher than 90%). Ion chromatography was carried on a DX-120 ion chromatograph with an Ion Pac CS12A (4 mm) cation separation column, a guard column and a conductivity detector. Sample was filtered through a 0.45 micro m membrane, diluted with de-ionized H_2O and injected with a mobile phase, flow rate of 1 ml/min. The residue and gas bubble water were analyzed by ion-chromatography DX-120. The solid residue analyzed by SEM/EDX (JSM-6510A) for their elemental contents, including bromine, chlorine, antimony and sodium.

5.3. Results & Discussion

5.3.1. Mass balance of products

This paper has investigated the effect of addition of NaOH (0 to 5 percent) on the yields of pyrolysis products when Br-ABS plastic was pyrolyzed at 450°C.The quantitative results of the decomposition of Br-ABS and addition of NaOH (0 to 5 percent) shown in Fig.2 where it can be seen that the oil was obtained 56 to 63 weight percent. And the residue also was obtained at 27 to 34 weight percent. The gas product was collected 4 to 8 weight percent, respectively. Since NaOH addition of produced oil is low than without NaOH pyrolysis. However, NaOH addition may be increased of residue and gaseous products also a little increased.
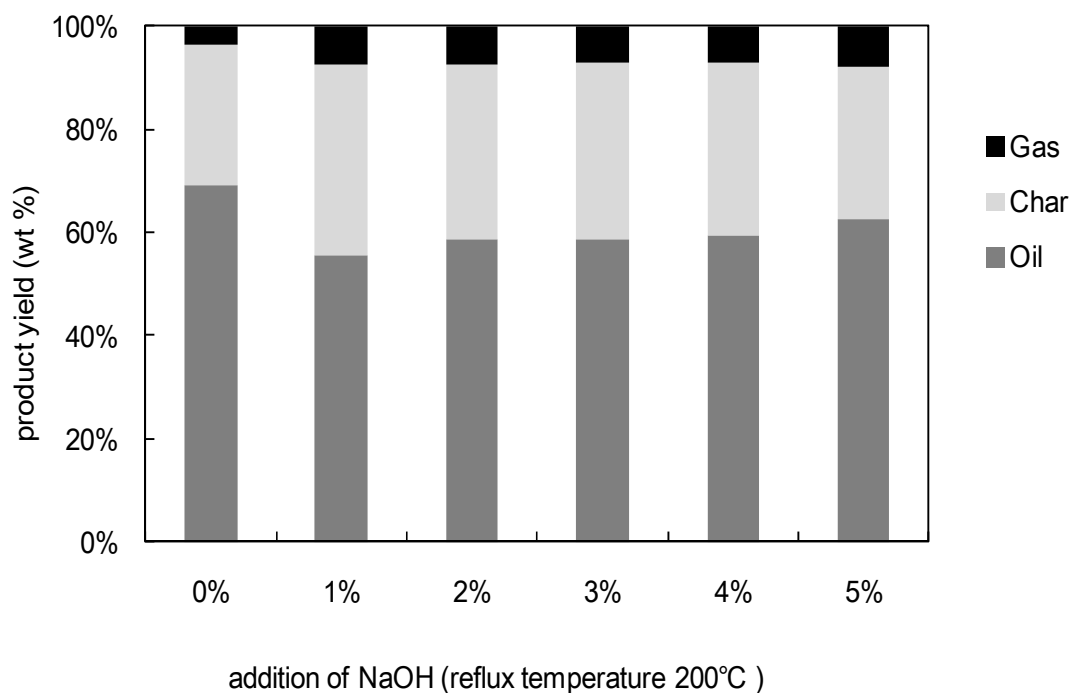
Fig.2.Product yields from the pyrolysis of Br-ABS with NaOH by using reflux

condenser

5.3.2. Analysis of products

 The components of product oil were identified by GC/MS. The GC/MS

chromatograms of the product oil obtained from Br-ABS are shown in figure 3. The

major compounds obtained were similar to the content of heavy oil. The compounds

obtained were isopropyl alcohol, toluene, ethylbenzene, styrene, cumene,

propylbenzene, α-methylstyrene, and butylbenzene, and the minor components were

isopropylphenol, 2-phenylpropan-2-ol, benzenebutanenitrile, 1,3-diphenylpropane,

1,3-diphenylbutane, *α*-methylstyrene dimer, 1,2-diphenylcyclopropane, 4-cumylphenol,

hexadecane- nitrile, and octadecanenitrile. The bromine compounds detected were

2-bromophenol, 3-bromophenol, and 2,4-dobromophenol. The concentrations of

bromine compounds in the oil are shown in figure 4. With decreasing additive of NaOH,

the bromine compounds in the oil increase. The total concentration of 2-bromophenol,

3-bromophenol, and 2,4-dibromophenol using the reflux condenser at 200°C are 296

mg/L, 207 mg/L,143 md/L,127 mg/L,87mg/L and 46 mg/L respectively.

  These results indicate that the oil containing low bromine compounds can be obtained

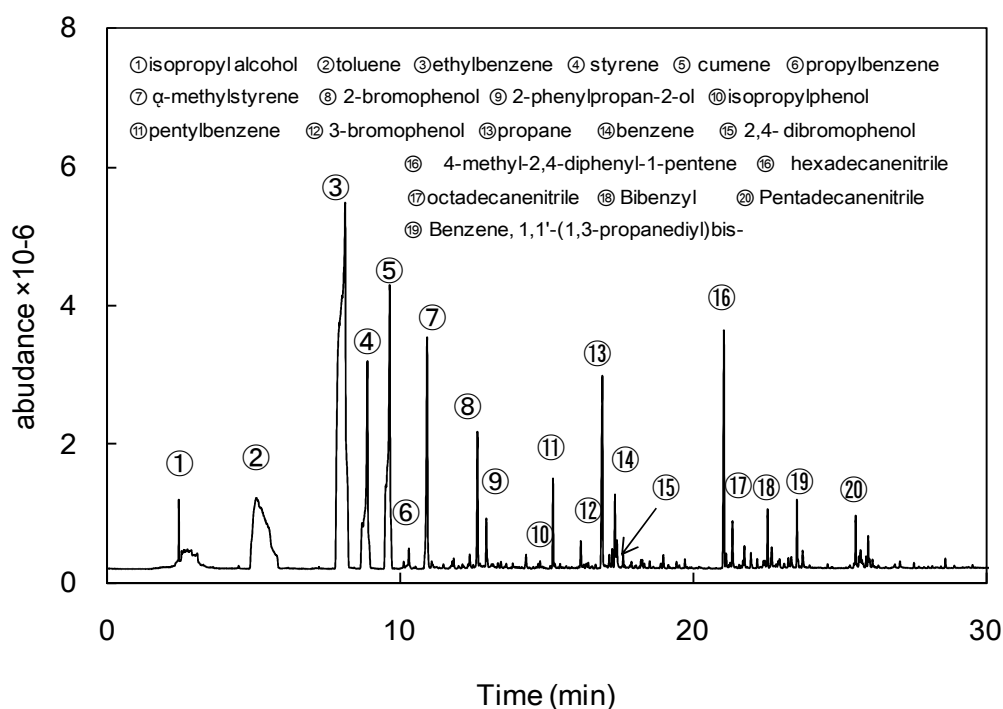via pyrolysis with NaOH and using a reflux condenser.

Fig. 3.GC/MS chromatogram of oil products by pyrolysis (reflux temperature at 200°C)
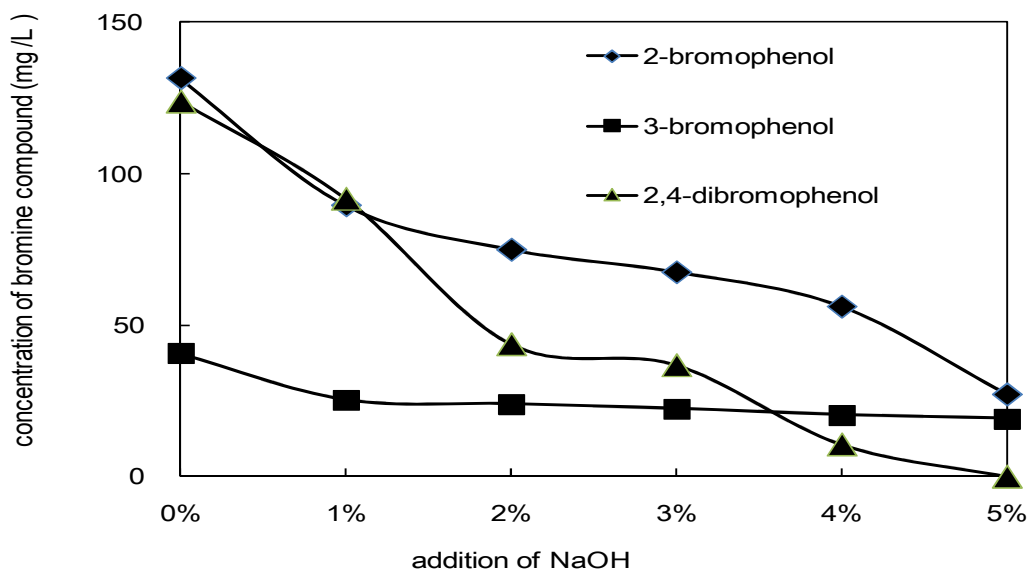
Fig.4. Concentration of bromine compounds in the oil. (Br-ABS and with sodium

hydroxide)

 The halogen concentration in the produced oils is shown in table 1.From this table 1,

we can see that the addition of NaOH was increased, the halogen content in oil was

decreased. The bromine was decreased from 7500 mg/L to 451 mg/L. These result

indicated that the pyrolysis oil was possible use as alternative fuel. The table 2 shows

the analysis of halogen in residue products by ion chromatography. Since NaOH

addition of residue was found that a lot of halogen, it considered that NaOH was

captured halogen compound and leave in residue. However, when addition amount of

NaOH was increased, the residue was a little increased and the content of halogen also

increased.

Table 1.The halogen concentration in the oil

The halogen concentration in the product oil (mg/L)				
		F	Cl	Br
NaOH	0%	450.04±	1598.14±	7504.91±
NaOH	1%	384.59±	826.01±	4581.56±
NaOH	2%	369.75±	416.43±	2683.59±
NaOH	3%	274.77±	263.31±	2395.35±
NaOH	4%	172.17±	231.51±	1454.84±
NaOH	5%	154.76±	129.11±	451.67±

Table 2. The halogen concentration in the residue

The halogen concentration in residue (mg/L)				
		F	Cl	Br
NaOH	0%	69.57±	276.39±	7878.54±
NaOH	1%	195.54±	907.76±	14108.12±
NaOH	2%	1755.62±	1466.34±	22955.67±
NaOH	3%	2830.31±	1961.58±	25109.60±
NaOH	4%	2729.22±	3454.11±	43781.82±
NaOH	5%	1428.34±	7275.69±	48161.58±

The solid residue analyzed by SEM/EDX (JSM-6510A) for their elemental contents,

including bromine, chlorine, antimony and sodium.(show in table 3) The results of table

3 also indicated that the addition amount of NaOH was increased, the content of

halogen and antimony were also increased. Figure 5 is showed analysis of residue of

Br-ABS with NaOH. This figure 5 can be seen bromine and sodium and other elements.

The analysis of residue by ion chromatography are showed   in Fig.6.The situation of

residue are showed in Fig 7 (a) and (b).This figure can be seen that the residue of with

NaOH was found white things on the surface of residue and so hard than without NaOH.

Therefore, it may be considered that NaOH could caught halogen.

Table 3. The elemental composition of residue by SEM-EDC

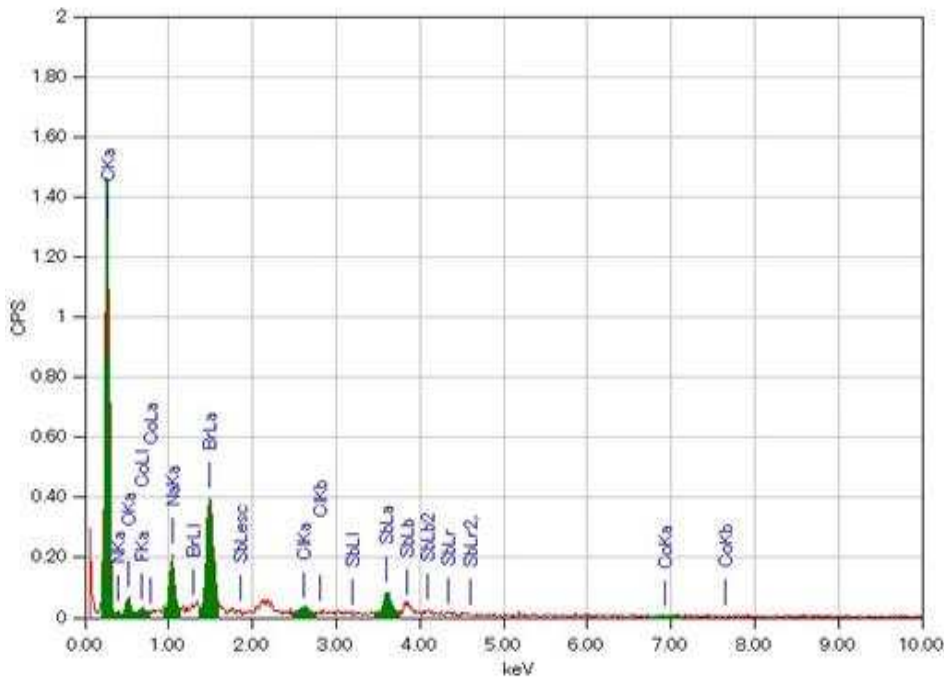| Elemental composition of residue by SEM-EDC (mass %)									
	C	N	O	F	Na	Cl	Co	Br	Sb
NaOH 0%	73.02	13.46	5.67	0.25	nd	0.14	0.07	6.20	1.19
NaOH 1%	66.52	13.78	2.88	0.32	0.87	0.24	nd	12.04	3.35
NaOH 2%	65.13	13.00	3.00	0.49	1.48	0.24	nd	12.59	4.07
NaOH 3%	65.07	7.02	1.55	0.45	2.50	0.37	0.08	17.66	5.30
NaOH 4%	64.22	6.42	1.38	0.79	2.56	0.52	0.09	18.31	5.71
NaOH 5%	61.64	6.58	0.12	1.70	2.61	0.66	0.18	19.40	7.11

Fig.5 Analysis of residue of Br-ABS with NaOH by SEM-ECD
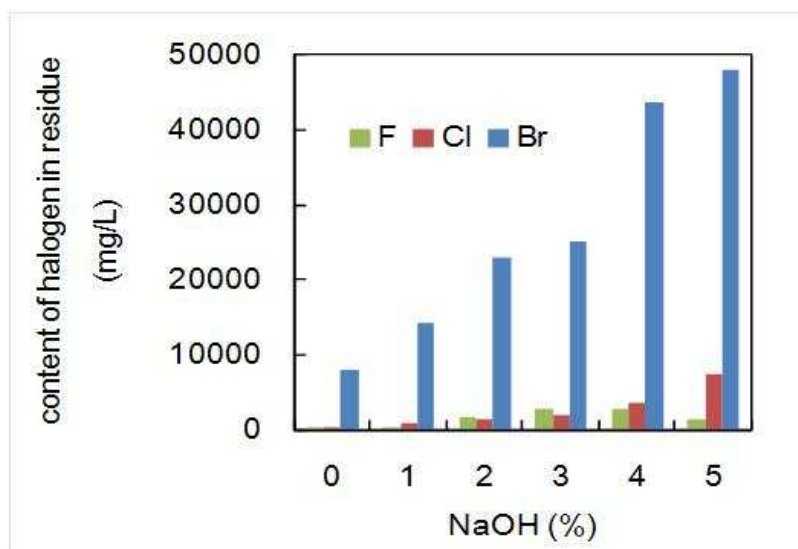
Fig.6. Analysis of residue by ion chromatography

Fig.7.(a) Residue of Br-ABS   (b) Residue of Br-ABS+NaOH

5.4. Conclusions

ABS resin containing brominated flame retardant was pyrolyzed with or without NaOH at 450°C using a reflux condenser to produce oil with low content of bromine compounds. With increasing addition of NaOH, the yield of oil decreased, yield of residue increased, and the yield of bromine compounds decreased. Hence, the bromine

content in oil obtained via pyrolysis using the reflux condenser was lower than that

obtained without NaOH. These results indicate that the addition of NaOH and the reflux

condenser apparatus was more effective for reducing bromine and bromine compounds

in oil. Otherwise, the NaOH addition was may be leave halogen in the residue.

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Chapter 6

Thermal pyrolysis of Polyethylene plastic by using a reflux-condenser apparatus;

Removal of waxes from the pyrolysis oil

6.1 Introduction

High-density polyethylene (HDPE) or Polyethylene high density (PEHD) is a polyethylene thermoplastic made from petroleum. It takes 1.75 kg of petroleum (in terms of energy and raw materials) to make 1 kg of HDPE. HDPE is commonly recycled and has the number "2"as its recycling symbol. (1) High density polyethylene is one of the largest used commodity plastics due to its vast applications in many fields. Due to its non biodegradability and low life, HDPE contributes significantly to the problem of Municipal Waste Management. To avert environment pollution of HDPE wastes, they must be recycled and recovered. On the other hand, steady depletion of fossil fuel and increased energy demand, motivated the researchers and technologists to search and develop different energy sources. Waste to energy has been a significant way to utilize the waste sustainably, simultaneously add to meet the energy demand. Plastics being petrochemical origin have inherently high calorific value. Thus they can be converted back to useful energy. (2) This paper we investigated the reflux condenser temperature and removal of waxes in the pyrolysis oil at 450 ℃.

6.2. Material & Experimental appratus

High Density Polyethylene resin (HDPE) was obtained from Asahi Kasei Chemicals Co.Ltd. (Tokyo, Japan). The amount of samples was analyzed by measuring 10 mg from 5 mg and DTA at 5°C/min to 550°C under a standard pressure of nitrogen atmosphere. The experimental apparatus is shown in Fig. 1.

Approximately, 30 g of plastics were loaded into the reactor for the thermal decomposition. In a typical run, the reactor was purged with nitrogen gas at a flow rate of 50 ml/ min and held at for 60 min to remove oxygen from plastic sample. The reactor temperature was increased to the decomposition temperature (450°C) at a heating rate of 5°C/ min and held for 30 min. The reflux condenser temperature was held 150°C ~ 200 °C. The temperature of the plastic bed was measured as the decomposition temperature. After the decomposition, the product oil was analyzed by GC/MS of Hewlett-Packard 5890-II gas chromatograph.
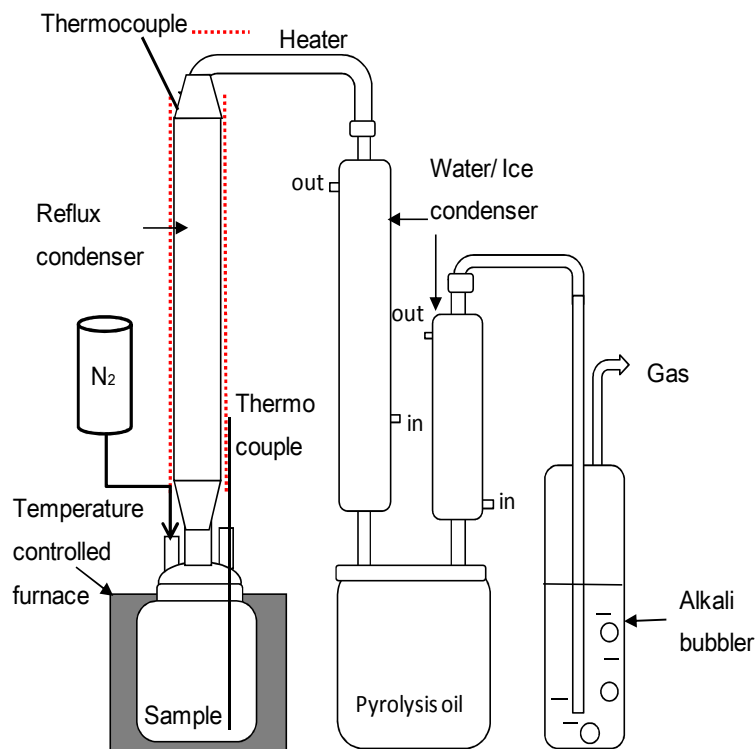
Fig.1.Schematic experimental setup for pyrolysis of HDPE at 450◦C

6.3. Results and Discussion

Figure 2 shows the distribution of reaction products by reflux temperature (150◦C ～ 200 ◦C). In this case of reflux temperature (150 ◦C ~ 200 ◦C), the product oil was collected 26.30, 27.48, 35.22, 37.50 and 44.29 wt%, respectively. The gas product was collected about 6 to 10 wt % .The residue was 64.11, 66.56, 57.28, 65.28, 56.21 and 47.52 wt%. The residue was found waxes. We understand that the product oil decreased slightly from 150°C ~ 160°C of reflux temperature, the residue has also increased than 170°C ~ 190°C of reflux temperature. Also produces oil yield was increased from

170°C ~ 190°C, in the case of 200°C, the residue was decreased and, instead of gas has increased slightly. It considered that if the reflux temperature is low, the oil yield has decreased by polymer decomposed is condensed and gone back into the reactor.
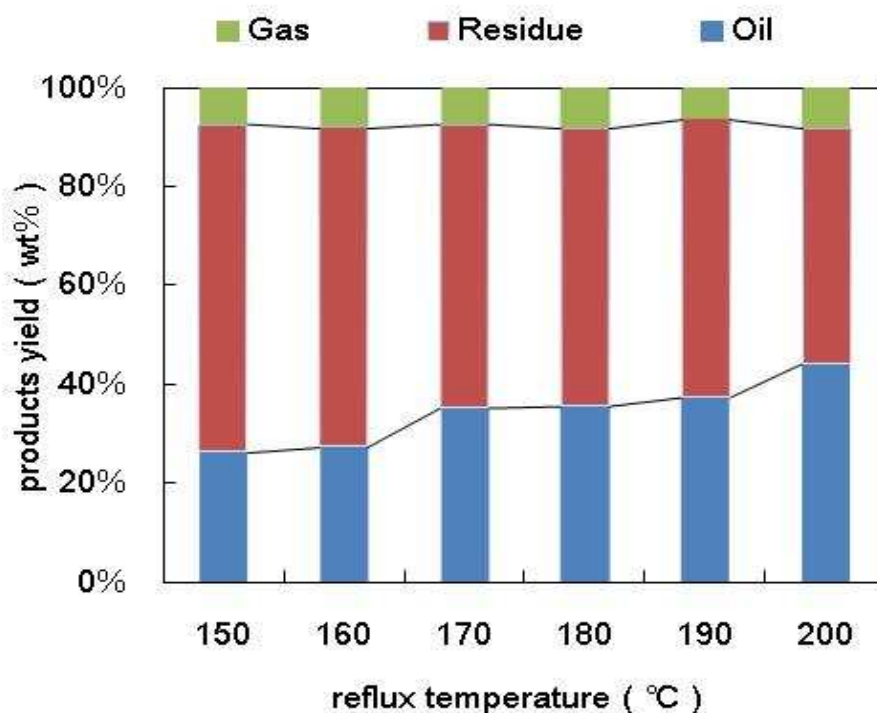

Fig.2 products yield distribution by various reflux temperature via pyrolysis

The GC/MS analysis of the product oil by the reflux temperature (150 ℃, 170℃, 200 ℃) shows figure 3. In the case of 150 ℃ of reflux temperature, the carbon number was found C_5 to C_{13} and the molecular weight components also smaller than others (reflux

temperature 170ºC, 200 ºC).If the reflux temperature of 170ºC and 200 ºC , the carbon

number was $C_5 \sim C_{13}$ and $C_5 \sim C_{21}$. It considered that if the reflux temperature is high, the

higher molecular weight components from escaping through the reflux condenser. From

Figure 3, we saw all hydrocarbon compounds are straight chain hydrocarbon

compounds and some are branch chain hydrocarbon compounds are as well. From the

fuel we found alkane group and alkene group compound. Long chain hydrocarbon

compound showing at retention time 26.38 minutes and compound is Heneicosane

$(C_{21}H_{44})$ and molecular weight is 296. In the fuel all hydrocarbon compounds contains

heavy hydrocarbon and their derivatives as well as hydrocarbon range is C_5-C_{21}.In the

detail analysis prospects maximum compounds are mention from the analysis result

index. Such as in detail analysis according to the retention 1.88 and trace mass 42,

compound is Pentane (C_5H_{10}), retention time 2.53 and trace mass 41, compound is

Cyclopropane,1-ethyl-2-methyl-,cis-(C_6H_{12}), retention time 2.69 and trace mass,

compound is Hexane (C_6H_{12}), retention time 3.28 and trace mass 41,compound is

1-Heptene (C_7H_{14}), retention time 3.35 and trace mass 41, compound is Heptane

(C_7H_{16}),retention time 5.81 and trace mass 41, compound is 1-Octene (C_8H_{16}), retention

time 6.08 and trace mass 43, compound is Octane (C_8H_{18}), retention time 6.92 and trace

mass 41,compound is 1-Nonene (C_9H_{18}), retention time 7.07 and trace mass

43,compound is Nonane (C_9H_{20}), retention time 8.75 and trace mass 41,compound is

1-Decene ($C_{10}H_{20}$),retention time 8.85 and trace mass 43, compound is compound is

Decane ($C_{10}H_{22}$), retention time 11.10 and trace mass 43, compound is 1-Undecene

($C_{11}H_{22}$), retention time 11.29 and trace mass 43, compound is Undecane

($C_{11}H_{24}$) ,retention time 13.18 and trace mass 41, compound is 1-Decene ($C_{10}H_{24}$),

retention time 14.71 and trace mass 43, compound is Dodecane ($C_{12}H_{26}$), retention time

16.23 and trace mass 41, compound is 1-Tridecane ($C_{13}H_{28}$), retention time 16.36 and

trace mass 43, compound is Tridecane ($C_{13}H_{28}$), retention time 17.64 and trace mass 41,

compound is 1-Tetradecene ($C_{14}H_{28}$) , retention time 17.76 and trace mass 43,

compound is Tetradecane ($C_{14}H_{30}$), retention time 17.92 and trace mass 41, compound

is 1-Pentadecene ($C_{15}H_{30}$), retention time 18.35 and trace mass 43, compound is

Pentadecane ($C_{15}H_{32}$), retention time 19.06 and trace mass 41, compound is

1-Hexadecene ($C_{16}H_{32}$), retention time 19.22 and trace mass 57, compound is

Hexadecane ($C_{16}H_{34}$), retention time 20.18 and trace mass 41, compound is

E-14-hexadecenal, ($C_{16}H_{30}O$), retention time 20.29 and trace mass 57, compound is

Heptadecane ($C_{17}H_{36}$), retention time 21.35 and trace mass 41, compound is

1-Nonadecene ($C_{19}H_{38}$), retention time 21.45 and trace mass 57, compound is

Nonadecane ($C_{19}H_{40}$), retention time 22.45 and trace mass 85, compound is Eicosane

($C_{20}H_{42}$), retention time 22.55 and trace mass 57 , compound is Heneicosane ($C_{20}H_{42}$)

etc. In the ultimate phase of the analysis index at retention time 23.54 and trace mass 43,

compound is Heneicosane ($C_{20}H_{42}$), retention time 24.42 and trace mass 85, and

compound is Heneicosane ($C_{20}H_{42}$) as well, retention time 26.38 and trace mass 71,

compound is Heneicosane ($C_{21}H_{44}$), retention time 28.08 and trace mass 57, compound

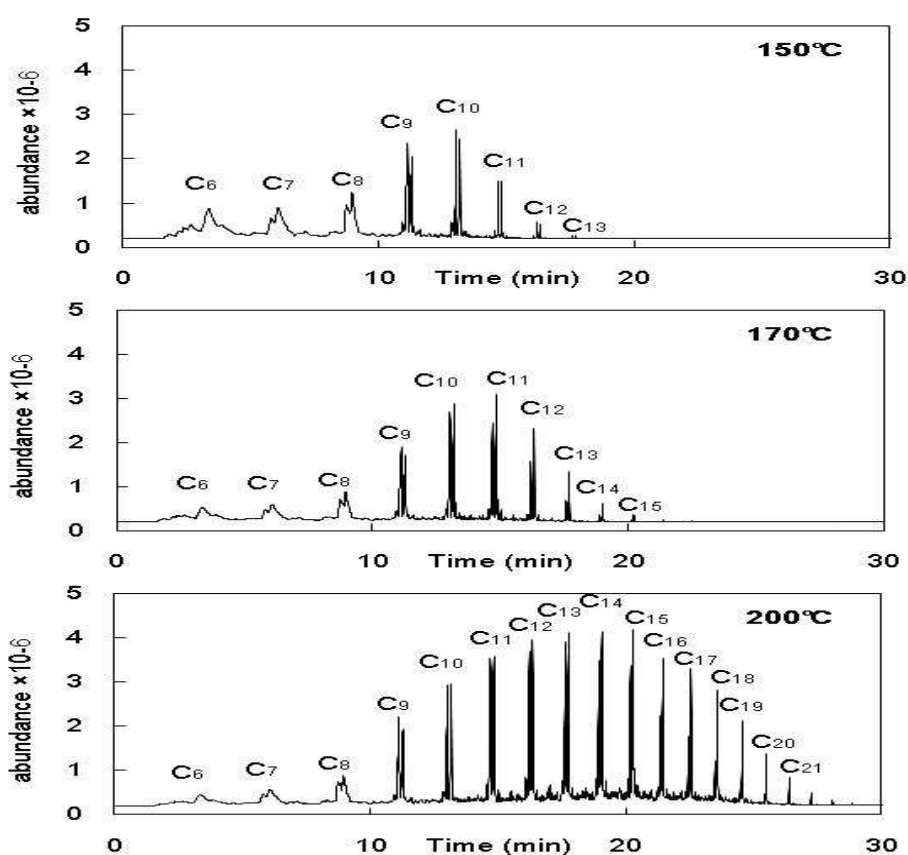is Heneicosane ($C_{21}H_{44}$) respectively.

Fig.3.GC/MS analysis of the product oil by the reflux temperature (150 ºC, 170ºC, 200

ºC)

6. 4. Conclusion

  High density polyethylene was pyrolyzed by using a reflux-condenser apparatus at

450ºC and the product oil was analyzed by using GC/MS. If the reflux temperature is

low, the oil yield has decreased and, but it can be residual wax to the residue. By using a

oil produced from the results GC/MS.

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Chapter 7

General Conclusions

The most common used of electrical and electronic equipments of resin   Br-ABS   and the most general waste plastics of polyethylene (PE) resigns were pyrolyzed by using a reflux-condenser apparatus at 450ºC and the product oil was analyzed by using GC/MS. The brominated acrylonitrile -butadiene -styrene "Br-ABS" was pyrolyzed to reduce the content of bromine compounds in prrolysis oil and the polyethylene was pyrolyzed to remove wases in pyrolysis oil using a reflux condenser apparatus.

In chapter 2, the acrylonitrile butadiene styrene (ABS) containing brominated flame retardants (Br-ABS) was pyrolyzed at 450◦C to obtain the oil with low halogen content to use as fuel. Experiments were carried out using sodium hydroxide (NaOH) as additive and pine charcoal as capture for reducing bromine content in product oil. The contents of bromine in oil obtained at 450 °C was 3.2 wt % without both additive and capture, and those by using capture and additive decreased to 1.74 wt% and 1.25 wt%, respectively. By using both NaOH and capture, the content of bromine in oil mostly decreased to 0.6 wt %. The pyrolysis oil was tested by combustion test to measure the colorific value and corrosion for use as fuel. It was found that the pyrolysis oil with the

content of bromine in pyrolysis oil less than 2000 mg/L can be utilized as fuel without

corrosion.

In chapter 3, the acrylonitrile butadiene styrene "ABS" resin is used in a variety of

exterior and chassis electrical products, it have been contained brominated flame

retardants to prevent fire accidents. If the resin (ABS) was thermally decomposed, the

bromine compound was mixed in the pyrolysis oil. In this work, the fraction of

acrylonitrile butadiene styrene "ABS" containing brominated flame retardants was

pyrolyzed by using a reflux-condenser apparatus installation at 450°C.And we used

additives of sodium hydroxide "NaOH", calcium hydroxide "Ca(OH)2" and scallop

shell. The bromine compound in product oil could be reduced until to 27 mg/L by

NaOH.

In chapter 4, ABS resin containing brominated flame retardant was pyrolyzed at 450°C

using a reflux condenser to produce oil with low content of bromine compounds. The

oil obtained via pyrolysis in all experiments consisted primarily of isopropyl alcohol,

toluene, ethylbenzene, styrene, cumene, propylbenzene, α-methylstyrene, and

butylbenzene, which are similar to the content of heavy oil. The bromine compounds in

the oil were 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol. With increasing

reflux condenser temperature, the yield of oil decreased, yield of residue increased, and

the yield of bromine compounds decreased. Hence, the bromine content in oil obtained

via pyrolysis with the reflux condenser was lower than that obtained without the reflux

condenser.

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In chapter 5, the resign of Br-ABS are pyrolyzed with or without sodium hydroxide by

using a reflux-condenser at 450ºC. It is demonstrated that using a reflux-condenser in

combination with sodium hydroxide is expected for reducing to trace amounts of

bromine compound in product oil. The main objective of this study is to elucidate the

influence of a reflux condenser and additive on the debromination of pyrolysis oil. The

total bromine compounds could be reduced from 296 mg/L to 46 mg/L

respectively.These results indicate that the oil containing low bromine compounds can

be obtained via pyrolysis with NaOH and using a reflux condenser. The halogen was

found a lot at residue.

In chapter 6, polyethylene is heated in an inert atmosphere and the volatile products are

condensed, the molecular weight distribution (MWD) of the product obtained is very

wide. In addition, this product is very waxy, has poor low properties, and is unusable as

a liquid fuel. To improve the product quality, various catalysts are usually used in the recycling process. However, these catalysts are costly. On the other hand, if the higher boiling fractions of the volatiles evolved due to degradation are not allowed to escape, then the MWD of the final product can be improved. This paper we have studied pyrolysis of High Density Polyethylene (HDPE) by using a reflux-condenser apparatus at 450 ℃ for removing of waxes in the pyrolysis oil. The product oil was analyzed by using GC/MS. The analysis result indicates that HDPE waste plastic to produced heavy fuel hydrocarbon chain range C_5 to C_{21} and light gas are also present and hydrocarbon range is C_1-C_4.

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Renewable Energy 2010 The 4th International Solar Energy Society Conference,Asia Pacific Region.

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Removal of waxes from the pyrolysis oil, 18th Symposium on Power and Energy

System.2013, Pg; 47-48.

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Compounds in Oil Produced from Brominated Flame Retardant Plastics via Pyrolysis

Using a Reflux Condenser, Journal Conference on Environmental Science and

Development. 2014, Vol.5,No.2, Pg;207-211.

List of Publications

[1] Z.Z. Hlaing, T. Wajima, S. Uchiyama and H. Nakagome, International Journal of Environmental Science and Development. Vol.5, No.2, April2014,
Pg; 207-211

"Reduction of Bromine Compounds in Oil Produced from Brominated Flame Retardant

Plastics via Pyrolysis Using a Reflux Condenser"

http://www.ijesd.org/list-50-1.html

[2] Z.Z. Hlaing, T. Wajima, S. Uchiyama and H. Nakagome, submitted to Journal Conference on Environmental Science and Development. (in press)

"Reduction of bromine compounds in the pyrolysis oil of computer casing plastics using

Shell, $Ca(OH)_2$ and NaOH "

Achievements

[1] Z.Z. Hlaing, M. Adachi, S. Uchiyama and H. Nakagome, submitted to 18th Symposium on Power and Energy System. Pg; 47-48

"Thermal pyrolysis of High Density Polyethylene (HDPE) plastic by using a reflux-condenser apparatus; Removal of waxes from the pyrolysis oil"

Best presentation awarded at 2013 18th Symposium on Power and Energy System, June 20-21, 2013, Chiba University, Japan.

[2] Z.Z. Hlaing, T. Wajima, S. Uchiyama and H. Nakagome, submitted to Journal Conference on Environmental Science and Development. Vol.5,No.2,April2014, Pg;207-211

"Reduction of Bromine Compounds in Oil Produced from Brominated Flame Retardant

Plastics via Pyrolysis Using a Reflux Condenser"

Best presentation awarded at 2013 4th Journal Conference on Environmental Science and Development (JCESD 2013 4th), October 26-27, 2013, Hong Kong.

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