# 마이크로웨이브 열분해를 이용한 폴리스티렌으로부터의 고분자 원료 물질의 회수에 관한 연구

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# Study on the Recovery of Polymeric Raw-materials from Waste Polystyrene by the Microwave Thermal Decomposition

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**Abstract**

A novel microwave-induced pyrolysis of polystyrene in motor oil was performed using a quartz tube reactor with silicon carbide as the microwave absorbent. Different pyrolysis conditions were investigated, such as time range from 30 minutes to 1 hour and power range from 180 to 250 watt. The distillate components were analyzed with GC-MS, and styrene, 1-methyl styrene, toluene, ethyl benzene were the four main products. Among these, styrene took over 70 percentages. Temperature of the complete pyrolysis using microwave was much lower than that of conventional thermal pyrolysis method.

Key words: pyrolysis, microwave-induced pyrolysis, polystyrene

## 1. Introduction

With the consumption of plastics in the whole world, waste plastics have become an environmental problem because of recycling limitations and their resistance to natural decomposition. A great deal of research has been done over the last two decades into recycling methods to deal with this amount of waste in an economical and ecological way.

Pyrolysis, which has been proposed as a method for recovering the chemical value of waste plastics, is a method where heat is applied to waste plastics in an inert environment to break the polymers into smaller molecules. The smaller molecules may then be blended into refinery streams for the production of fuels. In addition, these smaller molecules could be separated and refined into more specialized chemical feedstock[1].

On the pyrolysis of plastics, there were some related literature works. Guffey et al. (1991)[2] used polystyrene and other polymers to model the pyrolysis of tar sand bitumen in the presence of a heavy oil. Their results showed that polystyrene in the presence of a heavy oil would decompose at temperatures near 400℃. Inomata et al. (1974)[3] investigated the pyrolysis of polystyrene and heavy oil in a screw

type reactor. The temperature used in their research was 470-600℃. John A. Marsh et al.(1993)[4] investigated the thermal degradation(pyrolysis) of waste polystyrene in heavy oil as the recycling method, and distillate products from the reaction were characterized by gas chromatography/mass spectroscopy.

Microwave, as a kind of electromagnetic wave in the wavelength range of one millimeter to one meter, since the mid-1980s, has been used for chemical applications. Microwave heating has many advantages over conventional heating including more even distribution of heat and better control over the heating process.

Microwave-induced pyrolysis proposed in this study is a new approach, which involves plastics, motor oil, and a highly microwave-absorbent material, namely, silicon carbide. Microwave can penetrate deep inside and break bonding structures of the molecules. Application of this characteristic will lead to high recovery of chemical feedstock from polymeric materials as plastics, and also reduce the thermal energy needed for pyrolysis.

In this research motor oil was used. When the polystyrene dissolved in the oil, the molecules would have greater freedom of motion leading to easier decomposition. Also the motor oil would serve to reduce coke and gas production, increase distillate yield, and decrease process energy requirements.

This study presented a lab-scale microwave-induced pyrolysis apparatus. The distillates were detected by GC-MS.

## 2. Experiments

### 2.1. Apparatus

The experimental apparatus developed and used for this investigation is shown in Figure 1. The microwave thermal decomposition system consists of microwave generator, remote head, circulator, three stub tuners, waveguide, quartz reactor, and dummy load. Microwave generator (ASTEX applied science and technology inc, USA) used in this study has the 2450MHz frequency and can produce the power ranging from 250 to 2500w. The size of quartz reactor had the dimension of 2cm diameter and 120cm length. A nitrogen sweeping gas was used to carry vapor from the reactor to the collection flasks.

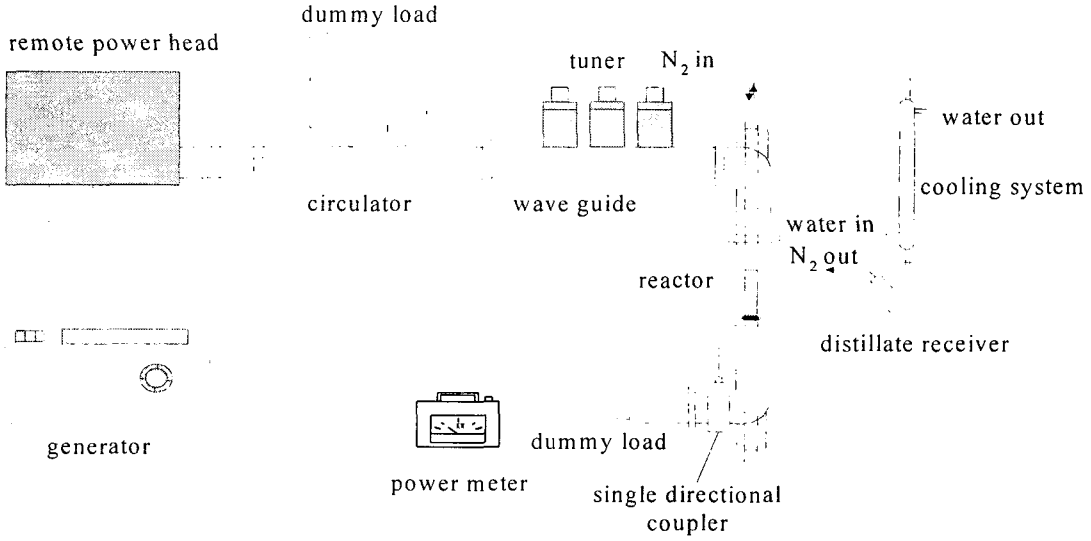


Figure 1. Schematic drawing of the microwave-induced pyrolysis apparatus

Forward power meter (Cober Electronics, USA) was installed at the end of the waveguide to get the

microwave power absorbed by dummy load, with this and the forward power and reflected power on the microwave generator, the effective power for the pyrolysis could be obtained as:
Effective power = Forward power — reflected power — absorbed power

### 2.2. Materials and Procedures

Polystyrene was selected as a model polymer because of its wide use, and because its pyrolysis products are easily distinguishable from those of the oil. Polystyrene packaging beads were used as a source for the waste polystyrene. The beads were heated at 150℃ for five minutes to densify them[4]. A 30 weight motor oil (SK Corporation, Korea) was pretreated by heating it with a power around 100 watts higher than the reaction power to insure that any light ends in the oil would not show up in the products and be mistaken for decomposition products.

25 gram of silicon carbide, 2 gram of pretreated polystyrene and 15 gram of pretreated motor oil were put into the reactor accordingly, then, the reactor was installed in the waveguide. As long as the cooling system and dummy load were set ready, the power could be turned on, the microwave generated by the generator could go along the waveguide through the reactor until the dummy load. Silicon carbide heated by microwave energy would transfer its thermal energy to the polystyrene and motor oil by conduction, then, pyrolysis began its first step. With cooling system, the distillate was collected for future GC-MS and data analysis.

### 2.3. Product Analysis

Gas chromatography/Mass spectroscopy (GC/MS) was used to find the chemical composition of the distillate products. The analysis was done on a 6890N GC/ 5973 MSD system (Agilent Technologies). The separation was performed on a 15m fused silica capillary column HP-5MS. The carrier gas was helium. The temperature was ramped from 30 to 200℃ at 3℃/min.

## 3. Results and Discussion

### 3.1. Silicon carbide and motor oil amount

Microwave-induced pyrolysis is different from traditional thermal decomposition as the name indicates. Since the oil and polystyrene could not absorb microwave energy, silicon carbide was taken as the microwave absorbent, and in this research, 25 gram of silicon carbide addition was decided for all the experiments. Table 1 shows the power absorbed by silicon carbide with respect to microwave input power.

Table 1. Silicon carbide performance as microwave absorbent

| Group | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Forward power (w) | 275 | 300 | 325 | 350 | 375 | 400 |
| Effective power (w) | 158 | 172 | 187 | 201 | 215 | 230 |

In pyrolysis of polystyrene process, motor oil played an important role in preventing the decomposed bonds recombine [4]. In this research, a new 30 weight oil was used to simulate the used motor oil. As for the amount of motor oil, John A. Marsh [4] gave a weight percentage of polystyrene to motor oil of 1:10 as the appropriate one, while in our research, 1:7.5 was chosen as the normal weight percentage of polystyrene to oil.

### 3.2. Microwave power and time effect on distillate amount

Compared with the importance of temperature in traditional pyrolysis, power played a key role in microwave-induced pyrolysis.

As what a commonsense could be, the distillate amount should increase with the increase of power and reaction time. In order to verify whether this rule would apply to our research, 15 experiments were made according to different effective power as: 180w, 200w, 220w, 240w and 250w, and different pyrolysis time as: 30 minutes, 45 minutes and 60 minutes. Both based on these experiments, Figure 2 and Figure 3, are aimed to give a comprehensive show for the results.

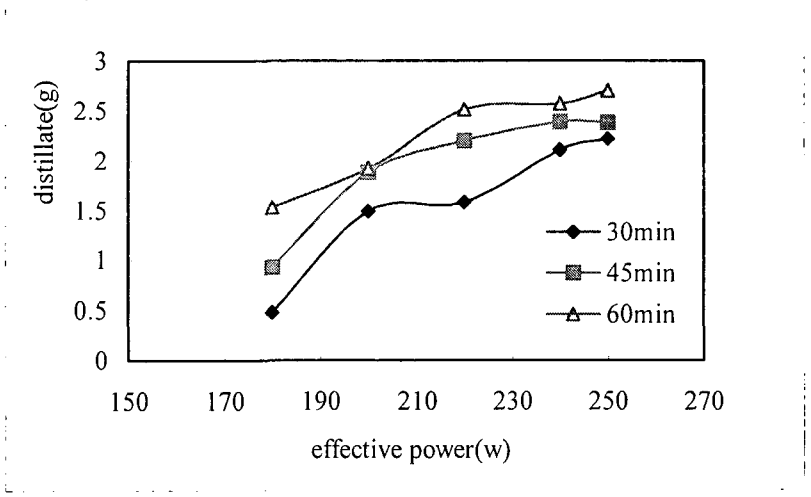


Figure 2. Power effect on distillate for different reaction time

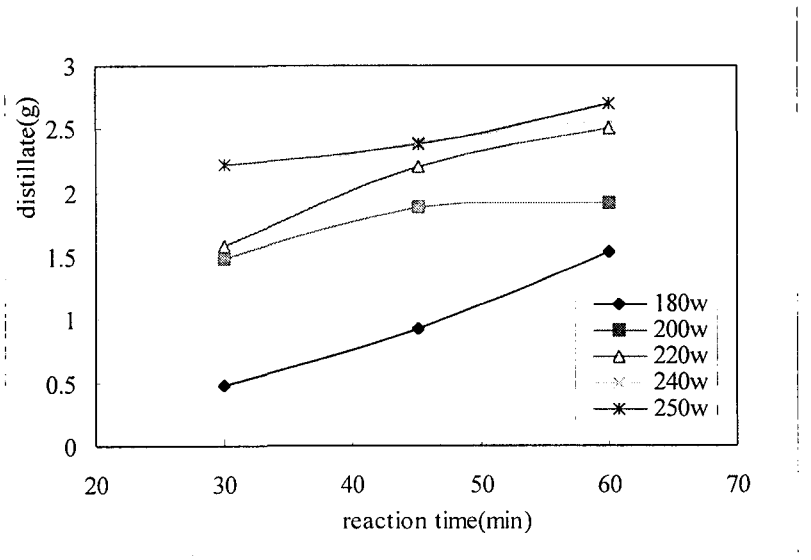


Figure 3. Time effect on distillate for different power

From the two graphs, the preceding commonsense was definitely reasonable and it was possible to

completely convert polystyrene to valuable distillate products when a polystyrene/oil mixture was pyrolized at the conditions of microwave power greater than 220W. At those conditions bed temperature of the reactor was around 300℃. Compared with the temperature requirement higher than 400℃[2][3][4] for a complete conventional pyrolysis of polystyrene, microwave-induced method made the complete pyrolysis at much lower temperature. This may result from the special performance of microwave, which could penetrate deep into the molecules and break the bonding structures.

### 3.3. GC-MS product analysis

Gas chromatography/mass spectroscopy was used to find the chemical composition of the distillate. In John A. Marsh's conventional polystyrene pyrolysis research, styrene, methyl-styrene, toluene, ethyl benzene and cumene were the main components. Among those, styrene took 25 weight percent of the total distillate and 50 weight percent of compounds produced from the pyrolysis of polystyrene. Ours gave a more promising result. The components generated from polystyrene were identified as styrene, 1-methyl-styrenen, toluene, and ethyl-benzene. Styrene was the primary product (over 30 weight percent of the total distillate). When the distillate products were considered by themselves, styrene accounted for approximately over 70 weight percent of the compounds produced from the pyrolysis of polystyrene. Table 2 shows one GC/MS analysis result among the 15 and Figure 4 displays the styrene recovery results under different time and power.

Table 2. Distillate composition as determined by GC/MS from the pyrolysis of polystyrene in motor oil at 220w for 1 hour

| Component | Overall weight percent (%) | Weight percent based on polystyrene products (%) |
|---|---|---|
| Styrene | 36.80 | 73.94 |
| 1-Methyl-styrene | 6.84 | 13.74 |
| Toluene | 5.01 | 10.07 |
| Ethyl benzene | 1.12 | 2.25 |
| Components from heavy oil | 50.23 | - |

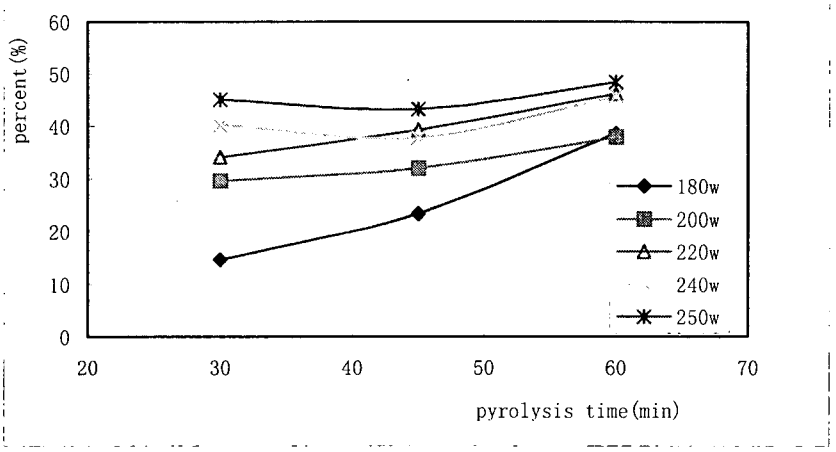


Figure 4. Styrene recovery at various process variables

Styrene, as the main distillate product, gave an objective comparison on pyrolysis under different conditions, such as microwave power and reaction time. The higher the microwave power, the longer the pyrolysis time, the greater the styrene weight percentage.

## 4. Conclusions

This research investigated the microwave-induced pyrolysis of polystyrene in the presence of a motor oil. The following conclusions can be drawn from the results of this study:

(1) Microwave-induced pyrolysis showed favorable performance on the thermal decomposition of poystyrene in improving the recovery of valuable products from polystyrene and lowering the pyrolysis temperature, compared with previous works.

(2) Waste polystyrene could completely decompose to distillate products at 220w (around 300℃) in the presence of a motor oil.

(3) The distillate products from the pyrolysis of waste polystyrene include on the average styrene (71.60 weight %), 1-methyl-styrene (15.42 weight %), toluene (7.84 weight %) and ethyl-benzene (5.14 weight %). Pyrolysis products from the heavy oil accounted for 71.56% of the total distillates.

**Acknowledgement**

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