

PYROLYSIS AND OXIDATIVE PYROLYSIS EXPERIMENTS WITH ORGANIC ION EXCHANGE RESIN

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ABSTRACT

Pyrolysis may be an important pretreatment step before vitrification in a cold crucible melter (CCM). During vitrification of organic resin the carbon or other remaining residues may harm the performance of the cold crucible melter or the eventual stability of the final glass product. Hence, it is important to reduce or prevent such harmful waste from entry into the cold crucible melter. Pretreatment with pyrolysis will generally provide volume reduction resulting in less amount of solid waste that needs to be handled by the CCM; in addition, the pyrolytic processes may breakdown much of the complex organics causing release through volatilization resulting in less carbon and other harmful substances. Hence, KEPRI has undertaken studies on the pyrolysis and oxidative pyrolysis of organic ion exchange resin.

Pyrolysis and oxidative pyrolysis were examined with TGA and a tube furnace. TGA results for pyrolysis with the flow of nitrogen indicate that even after pyrolyzing from room temperature to about 900 °C, a significant mass fraction of the original cationic resin remains, approximately 46%. The anionic resin when pyrolytically heated in a flow of nitrogen only, from room temperature to about 900 °C, produced a final residue mass fraction of about 8 percent. Oxidation at a ratio of air to nitrogen, 1:2, reduced the cationic resin to 5.3% when heated at 5 C/min. Oxidation of anionic resin at the same ratio and same heating rate left almost no solid residue. Pyrolysis (e.g. nitrogen-only environment) in the tube furnace of larger samples relative to the TGA produced very similar results to the TGA. The differences may be attributed to the scale effects such as surface area exposure to the gas stream, temperature distributions throughout the resin, etc.

INTRODUCTION

Pyrolysis may be an important pretreatment step before vitrification in a cold crucible melter (CCM). Waste characteristics play an important role for the vitrification considerations. During vitrification of organic resin the carbon or other remaining residues may harm the performance of the cold crucible melter or the eventual stability of the final glass product. Hence, it is important to reduce or prevent such harmful waste

from entry into the cold crucible melter. Pretreatment with pyrolysis will generally provide volume reduction resulting in less amount of solid waste that needs to be handled by the CCM; in addition, the pyrolytic processes may breakdown much of the complex organics causing release through volatilization resulting in less carbon and other harmful substances. Pyrolysis may be utilized with oxidation processes to further reduce the quantity of residue.

The pyrolysis workscope covers experimental design and construction, attainment of appropriate operating conditions, testing of various wastes including raw cationic and anionic resin for off-gas release, volume reduction, ash quality including morphology; and oxidation of residue left from pyrolysis. The testing of raw resin will eventually be followed by the doping of resin with various metals such as cesium, cobalt, iron, etc.

Past Work on the Pyrolysis of Organic Resin. Understanding the waste characteristics is essential for any pretreatment. The resin used in the experimentations at KEPRI are the resin used in Korean nuclear power plants: Amberlite IRN77 (cationic) and Amberlite IRN78 (anionic). Neely (1981) of Rohm and Haas, the supplier of IRN77 and IRN78, has characterized similar polymer carbons derived from porous sulfonated polystyrene. Others have examined anionic ion exchange resins and noted that after pyrolysis, the residue from these resins is generally very small (e.g. less than 5%).

The thermal decomposition of polystyrene has been shown to proceed by a combination of depolymerization (unzipping) and chain scission reactions (Cameron et. al, 1967). The first observable weight loss occurs at 260 C in air and 350 C in nitrogen with complete volatilization by 440 C. Crosslinked polystyrenes convert readily to carbonaceous residues between 300 and 500 C indicating condensation processes competing with chain scission (Winslow et. al, 1956). The yield of carbonaceous solid increases (Hirano et. al, 1973) with 50% divinylbenzene giving a residue equivalent to 6% of the original skeleton (Winslow et. al, 1955) and 100% trivinylbenzene giving about a 55% weight yield (Winslow et. al, 1956). The weight yield of 100% DVB is increased from 8% to about 80% by carbonization at high pressure (Hirano et. al, 1973). The composition of volatile products changes with temperature and cross-linker level. Below 50% DVB, the first volatile product is mainly styrene but methane, ethylene, benzene, toluene and hydrogen are produced at higher temperatures. Reaction of polystyrene with oxidants has been shown to increase the yield of carbonaceous product and change the character of the resulting solid.

Neely (1981) found when examining the highly acidic cationic resins with a sulfonic group that microporosity is created during heat treatment and as the temperature rises the volume of micropores increases and the effective size of the micropores decreases. The micropore volume increases linearly as the skeletal volume decreases with half the volume lost by the skeleton creating new micropores and the other half appearing as shrinkage of the bead. When examining the sulfur volatiles when the resin was heated from room temperature to 300 C, he concluded that the primary form of volatile sulfur was SO₂ with the general absence of SO₃ and H₂S.

Peterson and Kemmler. There has been some experience on resin pyrolysis. Peterson and Kemmler (1984) carried out the pyrolysis of powder resins in a pilot system with a capacity of about 30 kg/hr. The resin was first pre-treated by drying such that 50% of its weight was reduced. The resins were heated around 300-350 C and the weight reduction was about 90% based on 65% water content of the starting material. The residues or ash

was found to mainly consist of carbon. Due to the low temperature of the pyrolysis process, the radioactive components remained in the residue.

Matsuda et. al. They concluded that pyrolysis of spent ion exchange resin is one of the most effective methods for reducing radioactive waste volume and for making the final waste form more stable. Fundamental experiments were performed to clarify the pyrolysis characteristics of anion and cation exchange resins. Residual elemental analyses and off-gas analyses showed that the decomposition ratio of cation resins was only 50 wt % at 600 C, while that of anion resins was 90 wt% at 400 C. Infrared spectroscopy for cation resins attributed its low decomposition ratio to formation of a highly heat-resistant polymer (sulfur bridged) during pyrolysis. Measurements of residual hygroscopicity and cement package strength indicated that the optimum pyrolysis temperatures for preventing resin swelling and package expansion were between 300 and 500 C.

EXPERIMENTAL SET-UP

In addition to various TGA runs, a tube furnace was utilized for the pyrolysis of larger quantities of resin. The tube furnace experimentation allows us to examine some of the basic characteristics of waste at a small scale to help better design and understand what would happen in large scale experiments. In addition, even though the tube experiment processes are relatively small-scale in comparison to real scale, they allow observations of processes on a larger scale than the TGA. In addition, the bench-scale experiments also allow modifications in the experimental set-up that may not be allowed with the TGA.

General Set-Up. Nitrogen is fed in from one end of the tube furnace and exhausted out the other end. The samples to be pyrolyzed or oxidatively pyrolyzed were situated midway in the tube.

Tube furnace. The tube furnace is a quartz tube furnace that is electrically heated along its walls. It is surrounded by alumina insulation. The tube diameter is about 7cm while the length of the tube is roughly 90 cm. Temperature control is allowed at three axial positions of the tube furnace: one midway along the length of the tube and the other two equidistant (12 cm) from the midway controller. Two thermocouple probes are located midway along the length of the furnace. One probe is centered on the axis while the other probe is placed into the resin material. Typical temperature profiles are shown below.

Wastes. Amberlite-77, divinylbenzene-SO₃H, and Amberlite-78, divinylbenzene-N(CH₃)₃OH, are the cation and anion resins, respectively. The size for resin balls vary between 0.3 mm and 1.2 mm. The average is roughly 0.55 mm. The polymer is styrene and divinyl benzene polymerized together. For cation, the active group is Poly-SO₃-H. For anion the active group is Poly-N(CH₃)₃-OH. The density for cation is nominally 1.2 g/ ml. For anion, the density is 1.06 g/ml. The water content is nominally 58 to 60% for IRN78(anion) and for IRN77(cation), the water content is nominally 51 to 53%. The water in the bead is held in an equilibrium within the hydraion zone of the charged exchange sites. Melting and points are generally not relevant since polymer decomposition will result before melting or boiling occurs. The fundamental decomposition products for anion resins include the following: trimethyl amine and subsequent decomposition products of trimethyl amine, various organic acids and alcohols.

From cation resins, they are sulfuric acid, phenol sulfonic acid, sulfobenzoic acid, phenol sulfonic acid, and various organic acids.

OPERATIONAL CONDITIONS.

Batches of resin were dried in a muffle furnace for 24 hr. at 100 C. The water content of about 51% correlates very well with that of prior known data. The resin was weighed using a mass balance. The oven temperature profile for a particular run is shown in Fig. 1. This reflects the temperature of the quartz tube temperature at the various locations. The cylindrical quartz tube was cleaned after every experiment.

The sample of resin, around 1.5 or 3 g, was placed at the center of the quartz tube in a boat shaped ceramic crucible. Nitrogen was continually fed into the furnace usually at 2 l/min. The temperatures were changed by varying the oven control conditions after the oxygen detection limits were near 0. Temperatures were recorded for the oven wall temperatures, centerline, and resin.

IMR recordings were also made. The IMR 3000P was used to examine the oxygen content level in the tube furnace. After about 3 minutes, the level of oxygen reached about 1 to 2%. Eventually after a few more minutes, the level of oxygen could be brought below the detection limits of the IMR. The IMR was used to scan the levels of O₂, CO, CO₂, SO₂, NO, NO₂, H₂S etc. The incoming air was slightly above room temperature.

After each experiment, the quartz tube was cleaned with a solution of acetone. The acetone was generally effective in cleaning the tube. Heptane was also available for cleaning.

EXPERIMENTAL ANALYSIS

The following equipment were used for the experimental analysis: SEM, TGA, Mass Balance, and thermocouples.

RESULTS OF THE EXPERIMENTS.

Many of the results/conclusions of the experiments with cations and anions of IRN-77 and IRN-78, respectively, can be substantiated by past research. Although the brand of organic ion exchange resin was not exactly the same as those used by past researchers, the functional groups and their characteristics are similar.

Several experiments were performed to understand the characteristics of cationic and anionic exchange resin. The data provide much information on the evolution of resin during various pyrolytic conditions.

Rohm and Haas noted that during the decomposition of the cationic resins (IRN-77), oily residues, carbon substances, sticky sulfur based substances, etc. arise. For these cationic resins, the decomposition products likely include sulfuric acid, polystyrene sulfonic acid, sulfobenzoic acid, phenol sulfonic acid, and various organic acids. For anion resins, the decomposition products include trimethyl amine with subsequent decomposition products of trimethyl amine, various organic acids and alcohols. Many of these by-products for cations and anions were condensed or adsorbed on the wall of the quartz cylindrical tube .

TGA Results. A TGA provides analyses into the mass loss behavior of resins as a function of temperature for various ambient conditions. Heating of material can occur under pure pyrolytic conditions (e.g. pure nitrogen environment) or under oxidative conditions (e.g. with oxygen present). It is noteworthy to note that the TGA analyzes only a very small sample (e.g. approx. 10 mg) while typical pilot-scale waste pre-treatment units would pyrolyze relatively very large samples (e.g. in the several kilograms) at a time. Even though the TGA results may not deal with the other effects (e.g. turbulence, mixing, surface area exposure to gas stream, etc.) that would exist with larger scale pyrolysis units, it should provide some fundamental understanding in the behavior of the resin that would be true in the larger scales.

As shown in Fig. 2, TGA results for pyrolysis with the flow of nitrogen indicate that even after pyrolyzing from room temperature to about 900 °C, still a significant mass fraction of the original cationic resin remains, approximately 46%. This is consistent with the results of Neely (1981). This is most likely due to the formation of a highly heat resistant polymer (sulfur bridged) during pyrolysis. Matsuda et al. (1987) reported that a part of the functional sulfonic acid group would form sulfonyl bridges (-SO₂-) between the base polymers at about 300 °C. In the KEPRI TGA analysis, about 400 °C was observed in contrast to 300 °C. The difference is under investigation. This difference may partly be attributed to the use of slightly different resins and hence, the difference in, perhaps, impurities.

A sample of the cation resin was oxidatively pyrolyzed. The flow rate through the pyrolysis chamber was comprised of 25 cc/min. of air with 50 cc/min of nitrogen. The fraction of original resin still left was approximately a significant 5.3% as shown in Fig. 3. There appear to be further oxidation at 400 °C for further significant release of volatiles at 400 °C and then, also at around 800 °C. Kinoshita et al. (1990), however, show in their TGA analysis of similar cations, almost no residue when heated to about 900 °C. They state that the final decomposition entails combustion of the remaining base polymers. However, Kinoshita et al. do not report what were the conditions of the TGA environment (e.g. nitrogen, oxygen concentrations) and they note that the complete decomposition time was much longer than that for the anion resins.

TGA analyses were performed on an 8.2 mg sample of anion. The specimen when pyrolytically heated in a flow of nitrogen only from room temperature to about 900 °C produced a final residue mass fraction of about 8 percent. Fig. 4 shows a dramatic release of volatiles that start at about 200 °C and 400 °C. This agrees well with the data of Matsuda et. al (1986). Their results showed that anion resin, too, was composed of a copolymer of styrene and divinylbenzene, and a functional group of quaternary ammonium. It is likely that the behavior of the volatilization of the sample can be explained from their observations as well. At 200 °C, it is likely that methylamine gas was generated. They had noticed a decrease in the nitrogen content in the residue. This would indicate that the functional group would decompose at this temperature. Later, hydrocarbon gases would be generated since they had noticed that the carbon content in the residue decreased above 400 °C, corresponding to the base polymer pyrolysis. For the oxidative pyrolysis trial where nitrogen was fed in at 50 cc/min and air at 25 cc/min, the resulting mass loss curve as shown in Fig. 5, shows a continual mass decrease until almost no residue is left. These trials are in stark contrast to the cation trials where significant amount of residue still remained.

Tube Furnace Gravimetric Results. The tube furnace pyrolysis results (e.g. pure nitrogen environment) provide volume reduction data for larger resin samples. Fig. 6 and Fig. 7 show the results from the experiments for mass reduction as a function of temperature for anionic resin and cationic resin, respectively. The results are very similar to the TGA pyrolysis results. Differences may partially be attributed to the differences in scale effects. For example, the larger sample, will have effects of surface area exposure to gas stream, less uniform temperature distribution, etc. compared to the smaller sample. The tube furnace experiments will be expanded to examine the effects of mixed resin, excess air, and others.

CONCLUSION

Pyrolysis and oxidative pyrolysis were examined with TGA and a tube furnace. TGA results for pyrolysis with the flow of nitrogen indicate that even after pyrolyzing from room temperature to about 900 °C, still a significant mass fraction of the original cationic resin remains, approximately 46%. The anionic resin when pyrolytically heated in a flow of nitrogen only, from room temperature to about 900 °C, produced a final residue mass fraction of about 8 percent. Oxidation at a ratio of air to nitrogen, 1:2, reduced the cationic resin to 5.3% when heated at 5 C/min. Oxidation of anionic resin at the same ratio and same heating rate left almost no solid residue. Pyrolysis (e.g. nitrogen-only environment) in the tube furnace of larger samples relative to the TGA produced very similar results to the TGA. The differences may be attributed to the scale effects such as surface area exposure to the gas stream, temperature distributions throughout the resin, etc. Many more tests are still required to examine the effects of mixed resin, excess air, heating rates, etc.

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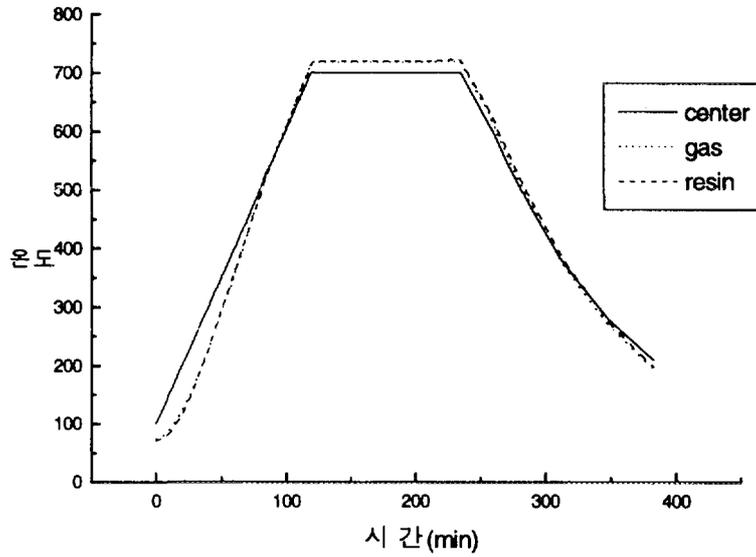


Fig. 1 Temperature profiles at the midway point of the length of the tube along the axis as shown by *gas*, resin temperature as shown by *resin*, and temperature at the bottom of the quartz tube as measured for the temperature controller as shown by *center*.

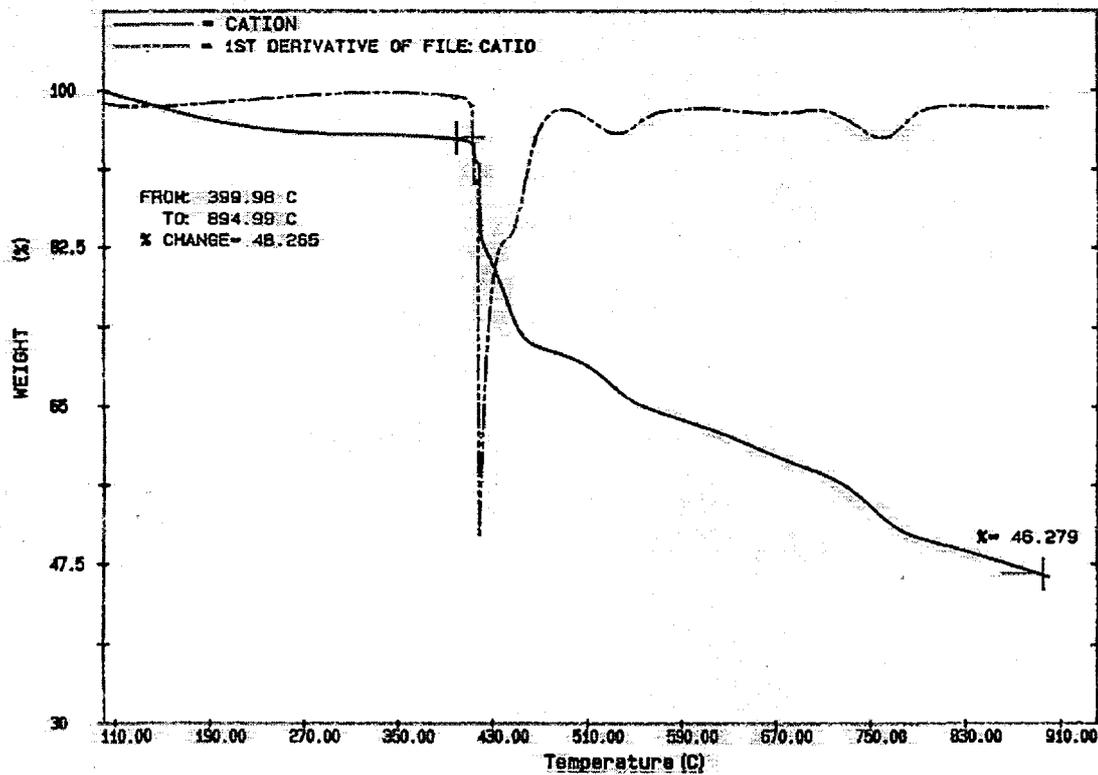


Fig. 2. Pyrolysis of cationic exchange resin in a flow rate of 75 cc/min of nitrogen. The heating rate is 5 C/min.

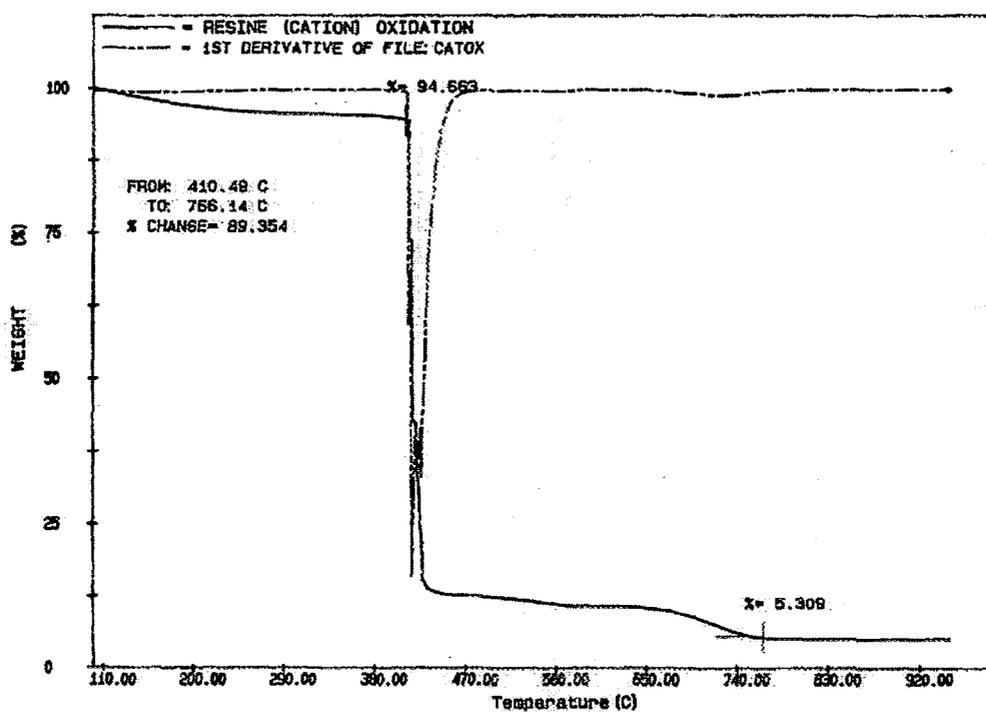


Fig. 3. Oxidative pyrolysis of cationic resin at 25 cc/min of air and 50 cc/min of nitrogen. The heating rate is 5 C/min.

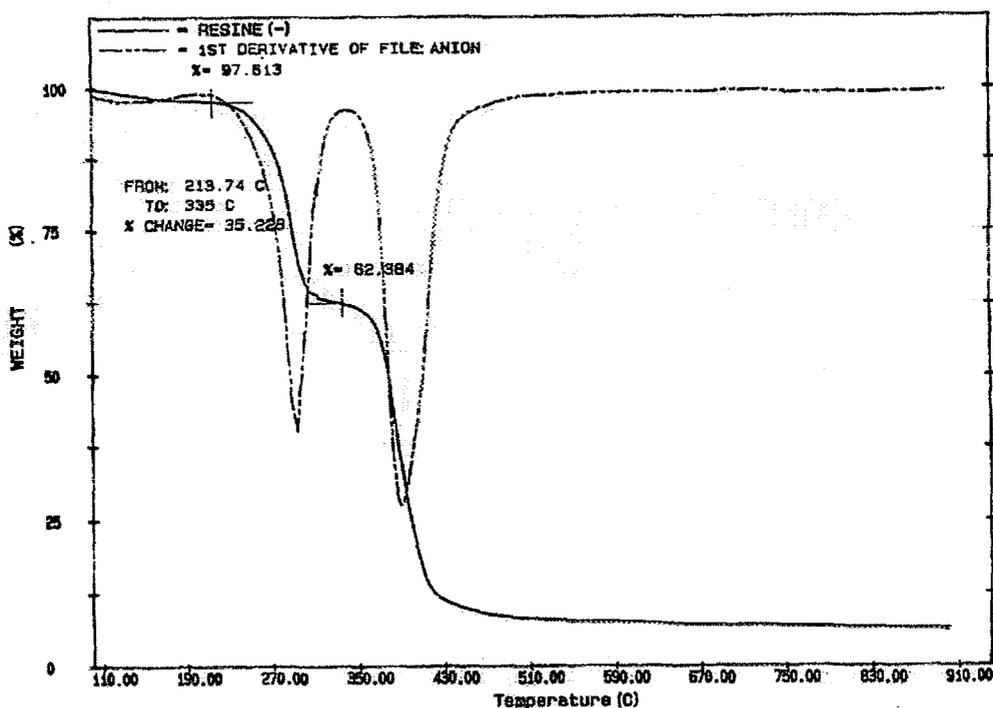


Fig. 4. Pyrolysis of anionic exchange resin in a flow rate of 75 cc/min of nitrogen. The heating rate is 5 C/min.

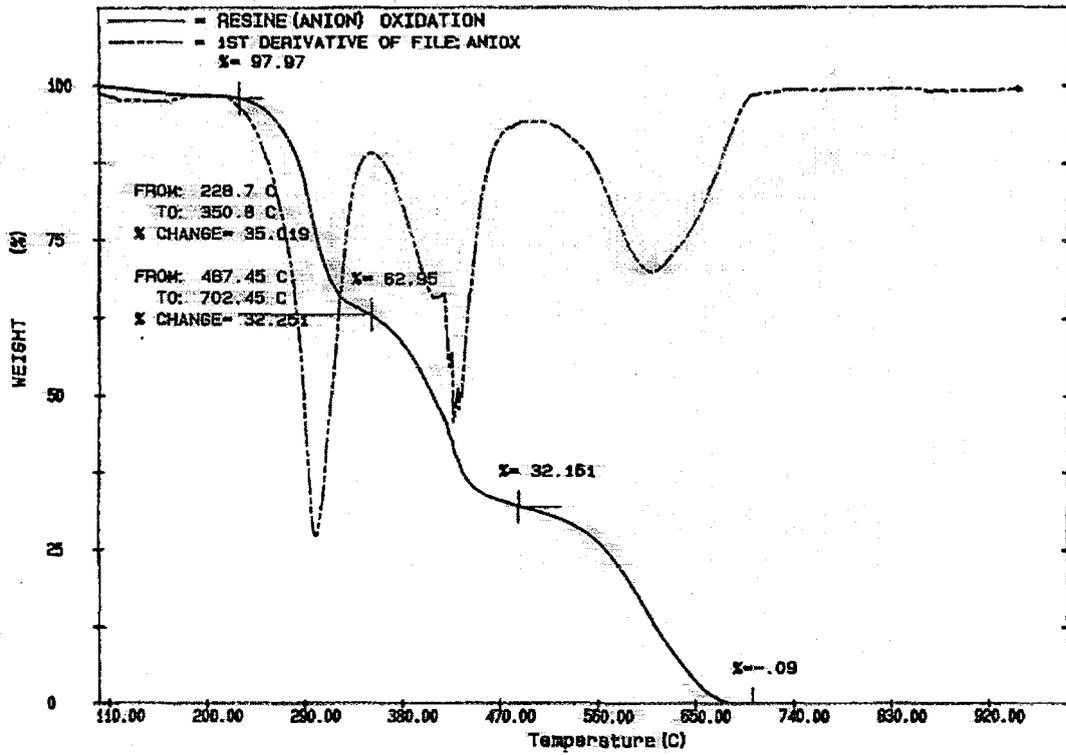


Figure 5. Oxidative pyrolysis of anionic resin at 25 cc/min of air and 50 cc/min of nitrogen. The heating rate is 5 C/min.

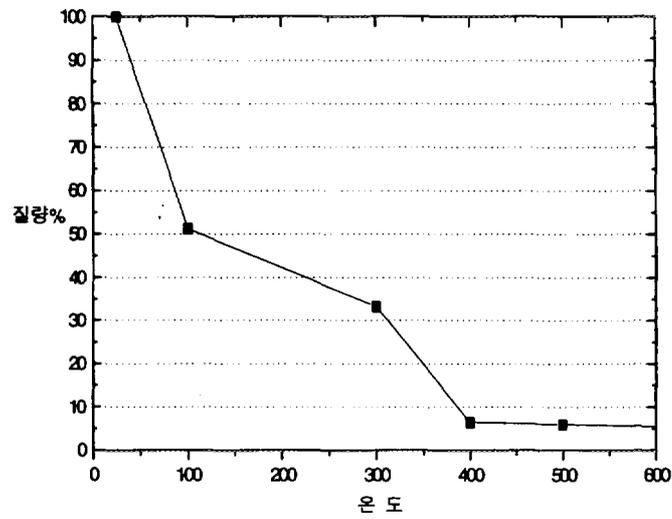


Figure 6. Gravimetric results for anionic resin with tube furnace.

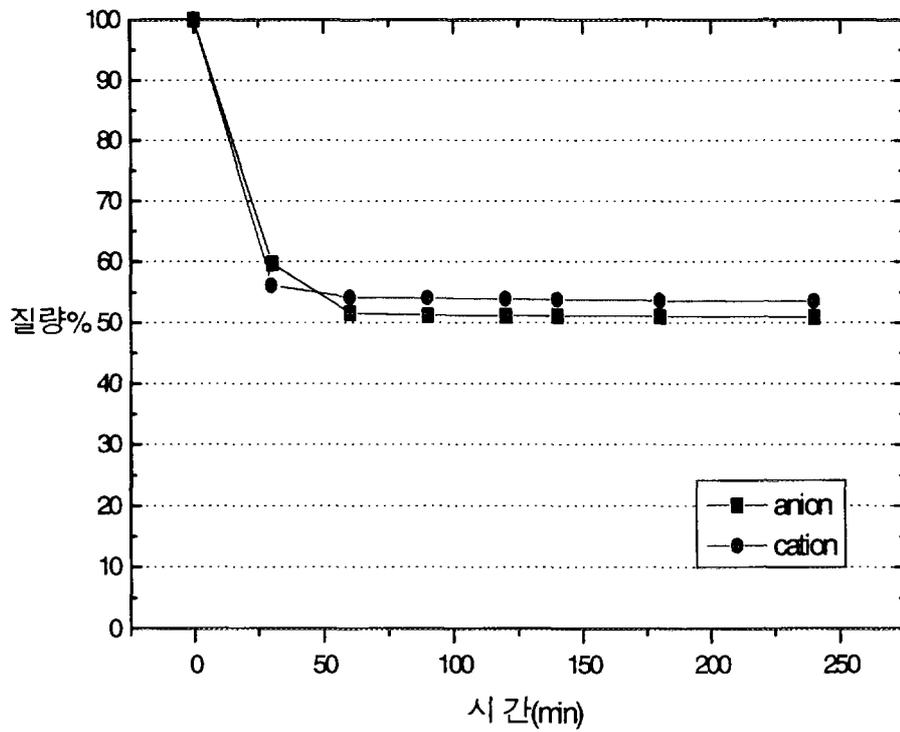


Fig. 7. Gravimetric results for cationic resin with tube furnace.