

Experimental studies of the influence of temperature on the process of polystyrene processing in a supercritical water environment

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Abstract. This paper discusses a hydrothermal method for processing polystyrene in a supercritical water environment. This depolymerization process is carried out in a closed reactor where water serves as a solvent, catalyst and reactant. When approaching the critical point, water changes its properties. These significant changes allow supercritical water to cause rapid, selective reactions to convert polystyrene into low molecular weight hydrocarbons. In this work, experimental studies were carried out on the processing of polystyrene in supercritical water at temperatures $T = 375 - 425$ °C, a volume of water equal to $V = 200$ ml, for a time $\tau = 10 - 120$ minutes. Hydrothermal processing of polystyrene in supercritical water leads to the formation of a liquid phase, which was analyzed with a Crystal 9000 gas chromatography-mass spectrometer. The analysis results indicate the content of styrene, ethylbenzene, benzene, toluene, and naphthalene in the liquid phase. It was found that at temperature $T=375$ °C and time $\tau=10-15$ minutes, a significant amount of styrene is formed. This work also examined the mechanism of depolymerization of polystyrene in supercritical water.

1 Introduction

Nowadays polymers are used to produce various products. The most common polymer is polystyrene. Polystyrene is a synthetic material that is obtained by refining oil. Today, polystyrene is used to make: disposable tableware, food packaging, thermal insulation of houses, ceiling panels, and plumbing products. Polystyrene products do not decompose in the natural environment. One of the methods for processing polystyrene is pyrolysis.

However, in recent years there has been interest in an alternative method for recycling polystyrene waste in a supercritical water environment. Waste plastic is chemically treated to extract low molecular weight monomers or other useful compounds. One of the promising methods for depolymerization of polymers is hydrothermal synthesis in supercritical water.

Supercritical water is used as an inexpensive, non-toxic and non-polar solvent for the chemical recycling of polymer waste. It has the properties of both liquid and gas phases, has a density close to that of a liquid, and therefore is capable of dissolving many components. While its high diffusivity and low viscosity allow it to behave similarly to a gas [1-5].

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Polymers obtained by polymerization are easily decomposed to monomers by hydrolysis in supercritical water. Polymer processing in supercritical water was carried out under the following parameters: $T = 350\text{-}450\text{ }^{\circ}\text{C}$, and reaction time $\tau = 10\text{-}180\text{ min}$ [3-7].

Mojca Skerget [8] conducted a study on the processing of polyethylene in supercritical water. Experimental studies were carried out in the temperature range $T=425\text{-}450\text{ }^{\circ}\text{C}$, and reaction time $\tau=15\text{-}240\text{ min}$. As a result of the experimental study, gas and liquid phases were obtained. Gas phase samples were analyzed by gas chromatography/mass spectrometry (GC/MS). The liquid phase was examined using a total organic carbon (TOC) analyzer. It was found that the oil phase was mainly composed of hydrocarbons, while the gas phase contained various gases such as CO_2 , and light hydrocarbons $\text{C}_1\text{-C}_6$.

Wan-Ting Chen [9] conducted a study on the processing of polypropylene in supercritical water. Experimental studies were carried out at temperature $T=380\text{-}500\text{ }^{\circ}\text{C}$, and reaction time $\tau=30\text{-}300\text{ min}$. As a result of the experimental study, olefins, paraffins, cyclic and aromatic compounds were obtained.

Gyou-Cheol Hwang [10] carried out the degradation of polystyrene in supercritical n-hexane. Experimental studies were carried out at temperature $T=330\text{-}390\text{ }^{\circ}\text{C}$, and reaction time $\tau=30\text{-}90\text{ minutes}$. The main product of polystyrene degradation was styrene.

H. Kwak [11] studied the kinetics of polystyrene degradation in supercritical water. Experimental studies were carried out at temperature $T=370\text{-}420\text{ }^{\circ}\text{C}$ and reaction time $\tau=5\text{-}60\text{ minutes}$. As a result of the experimental study, monomers, dimers and trimers of styrene, toluene, ethylbenzene, isopropylbenzene, and triphenylbenzene were obtained. The activation energy for degradation in supercritical water was determined to be 159 kJ/mol .

This work examined the processing of polystyrene in a supercritical water environment. Experimental studies of polystyrene processing were carried out in supercritical water at temperatures $T = 375 - 425\text{ }^{\circ}\text{C}$, water volume equal to $V = 200\text{ ml}$, for a time $\tau = 10 - 120\text{ minutes}$. The mechanism of polystyrene depolymerization in supercritical water is presented.

2 Materials and methods

The diagram of the experimental installation for processing polystyrene in a supercritical water environment is shown in Figure 1.

A description of the experimental setup is presented in [12].

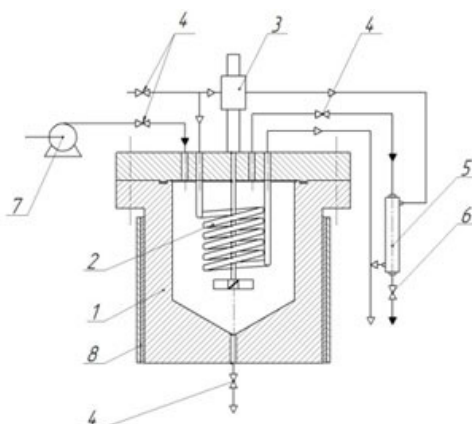


Fig. 1. Diagram of the experimental setup: 1 - reactor, 2 - cooling coil, 3 - magnetic stirrer, 4 - valve, 5 - heat exchanger for cooling, 6 - back pressure regulator, 7 - pump, 8 - electric heating jacket.

Polystyrene weighing $m=20$ g is loaded into a reactor (1), into which deionized water with a volume of $V=200$ ml is pre-filled. The reactor (1) is sealed, then the temperature is increased to $T=375-425$ °C using an electric heating jacket (8). When the set temperature is reached, the time starts counting in the range $\tau=10-120$ min. The final pressure depends on the amount of water added and the reaction temperature. Cooling of the reactor occurs after the end of the experiment by supplying water from the cold-water supply network to the coil (2). After cooling, the reactor is depressurized and liquid reaction products are removed.

Then the liquid reaction products are analyzed on a Crystal 9000 gas chromatography-mass spectrometer.

In this work, general purpose polystyrene (GPSON) is used as a processed polymer - grade 0107 TU 20.16.20. 110-002-02365817-20018 CHEMICS, Russia.

To fill the reactor, deionized water is used, corresponding to GOST 6709-72.

3 Results and discussion

The results of the gas chromatography-mass spectrometer of liquid products are presented in Figure 2.

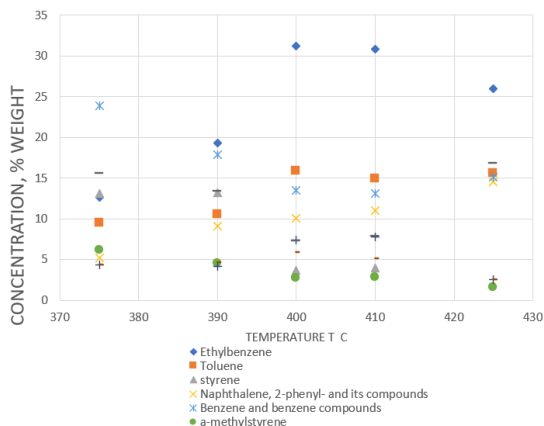


Fig. 2. Results of chromatography-mass spectrometer of liquid polystyrene products in supercritical water in the temperature range $T=375-425$ °C and reaction time $\tau=120$ min.

Also, experimental studies were carried out at temperature $T=375$ °C, water volume $V=200$ ml, and reaction time $\tau=10-15$ minutes. Liquid gas chromatography-mass spectrometer results are presented in Table 1–2.

Table 1. Results of chromatography-mass spectrometer of liquid products after destruction of polystyrene in supercritical water at temperature $T= 375$ °C, and reaction time $\tau=10$ min.

Names of the substance	Concentration, % wt.
Styrene	54.81
Toluene	18.28
Ethyl ether	8.66
Benzene and benzene compounds	8.27
Other connections	3.01
α-Methylstyrene	2.26
Ethylbenzene	2.05

Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	1.65
1,2-Diphenylcyclopropane	1.01

Table 2. Results of chromatography-mass spectrometer of liquid products after destruction of polystyrene in supercritical water at $T=375\text{ }^{\circ}\text{C}$, and reaction time $\tau=15\text{ min}$.

Names of the substance	Concentration, % wt.
Styrene	46.62
Toluene	20.23
Benzene and benzene compounds	9.56
Ethyl ether	7.64
Other connections	4.07
Ethylbenzene	3.44
α -Methylstyrene	3.16
Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	1.85
Cyclopenten-1-carboxylic acid, 4-[2-(diphenylmethyl)-2propen-1-yl]-, methyl ester	1.31
1,2-Diphenylcyclopropane	1.11
1,1':3',1''-Terphenyl, 5'-phenyl-	1.01

The results of phase analysis at temperature $T=375\text{ }^{\circ}\text{C}$ and reaction time $\tau=120\text{ min}$ are presented in Table 3.

Table 3. Results of phase analysis of liquid products after destruction of polystyrene in supercritical water at $T= 375\text{ }^{\circ}\text{C}$, and reaction time $\tau=120\text{ min}$.

Names of the substance	Concentration, % wt.
Styrene	13.15
Ethylbenzene	12.63
Toluene	9.5
Benzene and benzene compounds	23.9
α -methylstyrene	6.18
Naphthalene, 2-phenyl-	5.22
1,1':3',1''-terphenyl, 5'-phenyl-	4.35
1,1':2',1''-terphenyl, 4'-phenyl-	4.3
1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	1.39
1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	0.78
1,2-diphenylcyclopropane	3.01
Other connections	15.59

As time increases ($T=375\text{ }^{\circ}\text{C}$, $\tau=120\text{ min}$), the formation of styrene decreases, the formation of toluene, benzene, and ethylbenzene increases.

4 Reaction mechanism

The depolymerization reaction of polystyrene in supercritical water occurs by two mechanisms [13]. The first mechanism of polystyrene depolymerization in supercritical water is presented in Figure 3.

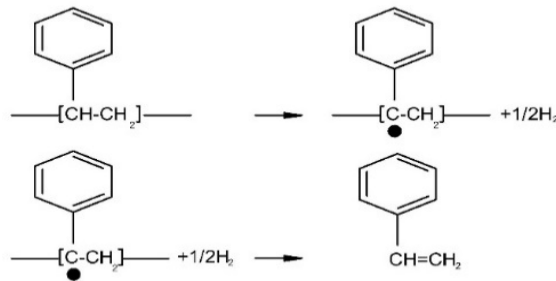


Fig. 3. Mechanism of pyrolysis of polystyrene in supercritical water.

In Figure 3, polystyrene is broken at the C-H bond, then at the C-C bond to form styrene. The second mechanism of polystyrene depolymerization is presented in Figures 4-8.

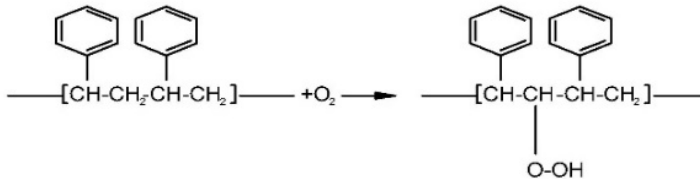


Fig. 4. Mechanism of polystyrene depolymerization in the presence of oxygen.

When polystyrene depolymerizes in the presence of oxygen, peroxide is formed. The peroxide decomposes into an activated polystyrene molecule (R), followed by the formation of styrene as shown in Figure 5.

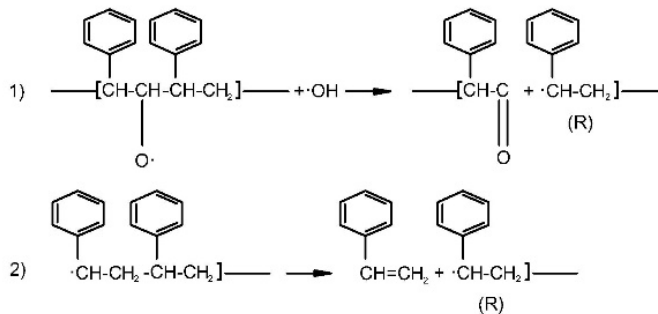


Fig. 5. Mechanism of depolymerization of polystyrene to form styrene (1-2).

Further destruction of the radical structure of polystyrene leads to the formation of toluene and benzene according to the scheme in Figure 6.

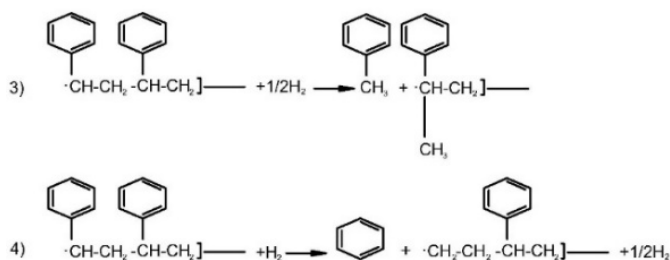


Fig. 6. Mechanism of polystyrene depolymerization with the formation of: 3) toluene, 4) benzene.

The mechanism of polystyrene depolymerization to form phenol is shown in Figure 7.

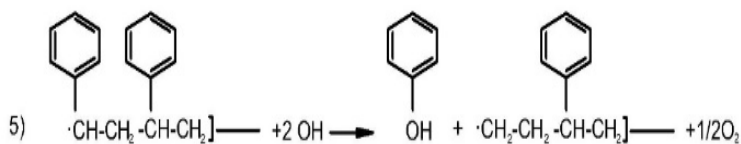


Fig. 7. Mechanism of polystyrene depolymerization with the formation of phenol.

Also, when the radical structure of polystyrene is destroyed, an active molecule of styrene (R) and ethane are formed. This reaction is shown in Figure 8.

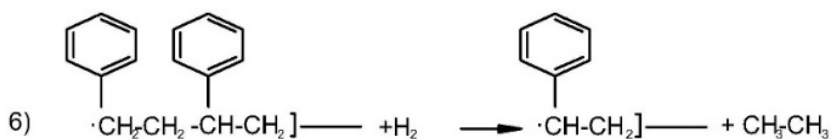


Fig. 8. Mechanism of polystyrene depolymerization to form styrene and ethane.

Figures 3-8 show the mechanism of depolymerization of polystyrene in supercritical water with the formation of: styrene, toluene, benzene, phenol, ethane.

5 Conclusion

In this work, an experimental study of the depolymerization process of polystyrene in supercritical water was carried out. As a result, the following were obtained: styrene, ethylbenzene, benzene, toluene and naphthalene. It was found that at a temperature $T = 375$ °C and time $\tau = 10-15$ minutes, a significant amount of styrene is formed. As the reaction time increases to $\tau = 120$ min, at a temperature $T = 375$ °C, the amount of styrene decreases, and the amount of toluene, benzene, ethylbenzene increases. The formation of naphthalene as a result of aquathermolysis of polystyrene is questionable.

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