

# WASTE EXPANDED POLYSTYRENE RECYCLING BY CYMENE USING LIQUID OR SUPERCRITICAL CO<sub>2</sub> FOR SOLVENT RECOVERY.

M<sup>a</sup> Teresa García González\*, Juan Francisco Rodríguez Romero, Antonio de Lucas, Ignacio Gracia Fernández, Gema Duque Gutiérrez.  
Departamento de Ingeniería Química. Universidad de Castilla-La Mancha.  
Facultad de Ciencias Químicas. Avda. Camilo José Cela, 10. 13004 C. Real. España.

[teresa.garcia@uclm.es](mailto:teresa.garcia@uclm.es)

## Abstract

The amount of waste of Polystyrene (PS) foams is increasing in last years due to their use in isolation, protecting, and storing many different food products. Continuous accumulation of waste plastics leads to serious problems all over the world. For that reason their recycling is steadily gaining importance. Conventional methods of recycling such as crushing and shrinking by heated air or frictional heat have the disadvantages of molecular degradation, resulting in a reduction of the quality of the recycled polymer.

Solvent extraction is one of the cheapest and more efficient processes for polystyrene recycling but in the solvent recovery process thermal molecular degradation it is produced. In this way, CO<sub>2</sub> supercritical technology appears like an interesting alternative process for the elimination of solvents.

This work proposes a global process to polystyrene recycling in two steps: a polystyrene dissolution with suitable solvents followed by solvent elimination by supercritical fluids. It was determined that, to develop an environmental friendly technology, it would be more appropriate the use of natural solvents like cymene.

## 1. Introduction

Expanded polystyrene (XPS) is widely used in packaging in food industry, electronics, etc, because of its good shock absorptive properties, low thermal conductivity and cost effectiveness. The management of these residues involves serious difficulties due to its low density. The transport of these big volume residues and their low biodegradability make almost unfeasible their landfill disposal. Up to now the incineration with heat recovery seems to be the best technological solution [1]. For that reason their recycling is steadily gaining importance. Conventional methods of recycling such as crushing and shrinking by heated air or frictional heat have the disadvantages of molecular degradation caused by oxidation and contamination by other materials, resulting in a reduction of the quality of the recycled polymer [2, 3]. Other method as organic solvent extraction has several disadvantages related to the use of organic solvents (toxic, residue generation, low selectivity) and to the low velocity of penetration of the solvent into XPS due to the viscosity [4].

Solvent extraction is one of the cheapest and more efficient processes for XPS recycling. If it is done in house of waste producers the separation between plastics would be effective and the transport costs of would be eliminated. Nevertheless, during

the solvent elimination step the polymer chain degradation can be produced due to the high temperatures that are reached in this process. To solve this problem, CO<sub>2</sub> supercritical technology appears as an interesting alternative process for the solvent elimination.

This work proposes a global process to recycle polystyrene in two steps: a polystyrene dissolution with suitable solvents followed by solvent elimination by liquid or supercritical fluids. It was determined that, to develop an environmental friendly technology, it would be more appropriate the use of natural solvents like cymene.

## 2. Experimental

### 2.1. Materials

P-cymene was supplied by Aldrich.

Liquid CO<sub>2</sub> (purity 99.5%) was supplied by Carbueros Metalicos S.A. (Madrid, Spain)

Extruded polystyrene waste composition is shown in Table 1.

**Table 1. Extruded Polystyrene Waste**

COMPOSITION	% w/w
XPS	90-93
Flame retardant (HBCD)	2-3
Nucleating agent (Talc)	0-1
Ethanol	2
Pigments	0.2-0.3
Polydispersity	1.7
Decomposition Temperature (°C)	421

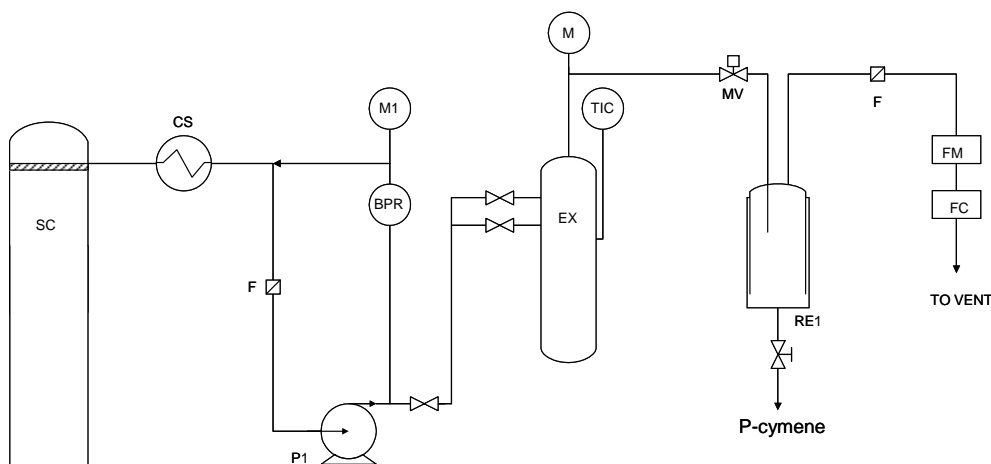
### 2.2. Solubility determination

The solubility of PS foams in the solvents has been determined gravimetrically as the minimum solvent weight necessary to completely dissolve a sample of PS foam. The solubility was expressed as the mass of PS and the solvent volume ratio expressed in mL.

### 2.3. Apparatus and solvent elimination procedure

The experiments were carried out in a batch-type apparatus, as shown in Figure 1. Liquid CO<sub>2</sub> from a stainless-steel cylinder (SC) was cooled (CS), filtered (F), and compressed by a positive-displacement pump (P). The pressure was regulated by a back-pressure regulator (BPR) and checked by a manometer (M). The compressed fluid was passed through a 75 mL stainless-steel cylinder (EX). To keep the extractor

temperature at the desired value, a digital controller (TIC) was employed to regulate the electric current through the resistor surrounding the extraction cylinder. The p-cymene-laden gas from the extractor was passed through a heated metering valve (MV) where the supercritical CO<sub>2</sub> was depressurized, and the p-cymene was collected in receiver (RE). The gas flow through the extractor was measured by a turbine flow meter (FM) and totalled by a digital flow computer (FC).



**Figure 1. Schematic diagram of the experimental system**

### 2.3. Polydispersity index

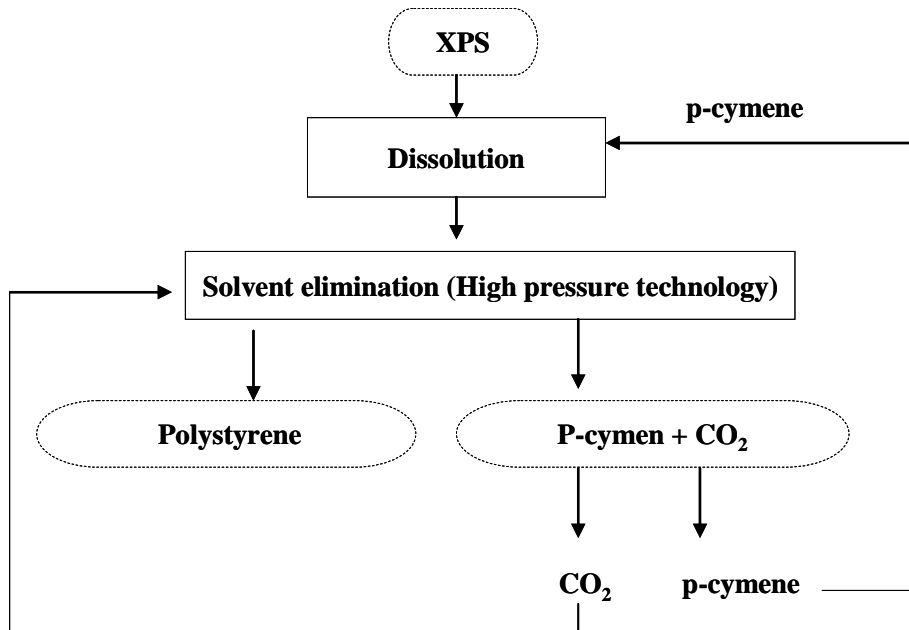
Analysis was performed on a Waters Associates Liquid Chromatography system (Waters 717, Rydalmere) equipped with a differential refractometer and two  $\mu$ -Styragel columns (HR1 and HR4). The mobile phase was tetrahydrofuran (THF) at a flow rate of 1 ml/min. Polymer was dissolved in THF and filtered through 0.45  $\mu$ m filter before analysis. The system was calibrated with narrow disperse polystyrene standards and molecular weights are reported as polystyrene equivalents.

### 2.4. Decomposition temperature

The decomposition temperature was determined by thermogravimetric analysis (TA-DSC Q 100), where the weight loss due to the volatilization of the degradation products is monitored as a function of temperature. The sample weight varies from 10 to 15 mg. Samples are heated from the room temperature to 500 °C at a heating rate of 15 °C/min.

## 3. Results and discussion

This work proposes a two stage process for the polystyrene recycling process: polystyrene dissolution with suitable solvents followed by solvent elimination by liquid or supercritical fluids. The proposed process scheme is shown in Figure 2.



**Figure 2. Global process to polystyrene recycling**

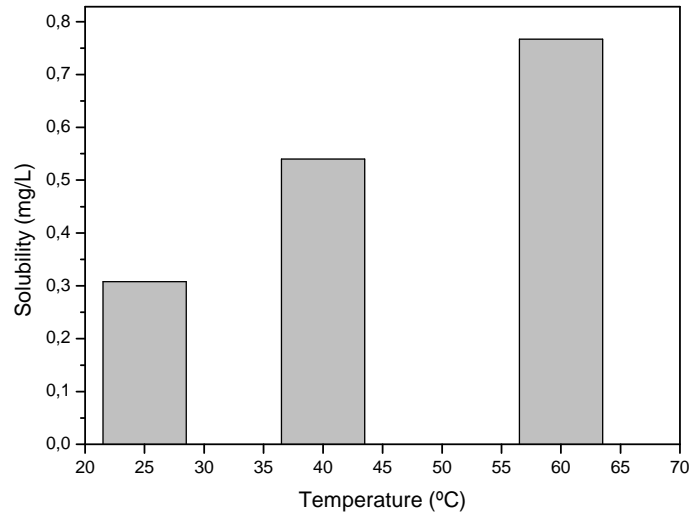
### 3.1. Step 1: Solubility determination

It is well known that some aromatic compounds are good solvents of PS foams [5]. Certain foods items have been shown to be incompatible with the expanded polystyrene used for the manufacture of food containers, since, the dissolution of polystyrene by certain essential oils are produced [6]. The treatment of PS with d-limonene has been reported as an attractive alternative for PS solubilisation [7].

In this work, in order to develop an environmental friendly technology, it would be more appropriate the use of natural solvents like cymene.

The first group of experiments was carried out in order to determine the temperature, T, at which dissolution should be performed since it is well known that this variable affects to the solubility in organic solvents of polystyrene. The temperature was varied from 25 to 60°C. Higher temperatures were not tested to prevent polymer degradation. Results obtained are shown in Figure 3. It can be observed that the solubility increase with increasing temperatures.

Polymer chain degradation generally involves changes into the molecular weight distribution of the polymer and in the decomposition temperature. These changes can give an idea of the degradation level that the treatment with the solvent generates into the initial characteristics of the polymer. Table 2 shows the polydispersity and decomposition temperature of XPS. It can be observed that, although the decomposition temperature practically does not vary the polydispersity slightly increase with increasing temperatures probably due to the beginning of degradation chains.



**Figure 3. Effect of temperature on solubility**

**Table 2. Effect of temperature on Polydispersity and Decomposition temperature**

	25 °C	40°C	60°C
Polydispersity	1,80	1,90	1,95
Decomposition temperature (°C)	415	416	417

Considering these results it may be stated that temperatures higher than atmospheric are not interesting for the polystyrene recycling process because, although solubility is higher at higher temperature, it do not compensate for incipient polymer thermal degradation and higher energy costs associated to increasing temperatures. Then, according to these experiments, the temperature of 25°C was selected for subsequent experiments.

### 3.1. Step 2: Solvent elimination

The solvent elimination will be carried out by means of liquid or supercritical technology. The cymene is selectively removed to the CO<sub>2</sub> phase, in a process that combines the distillation and extraction process by means of specific interactions between cymene and CO<sub>2</sub>.

The experiment was conducted at 40°C and 75 bar. In these conditions the cymene is completely separated from polystyrene. Tables 3 shows the results of polydispersity and decomposition temperature of polystyrene recovered.

It can be observed that the polydispersity and decomposition temperature remain unchanged. Therefore, considering the results obtained, it is possible to affirm that polymer degradation does not occur during the solvent elimination process.

**Table 3. Polydispersity and Decomposition temperature of Polystyrene recovered**

	polystyrene
Polydispersity	1.74
Decomposition temperature (°C)	417

#### 4. Conclusions

This work presents a global process to polystyrene recycling in two steps. In the first stage a polystyrene dissolution with p-cymene solvents is done, while in the second stage solvent elimination by supercritical fluids occurs. The polymer degradation was not produced in any of the stages.

#### 5. Reference

- [1] Garforth, A. A., Ali, S., Hernández-Martínez, J., Akah, A. *Current Opinion in Solid State and Materials Science*. 8 (6): 419-425 (2004).
- [2] British Plastic Federation. Plastic waste management: <<http://www.bpf.co.uk/bpfissues/Waste/Management.cfm>>
- [3] Brandrup, J., *Recycling and recovery of plastics*, In: G. Menges, Munich, 1996, pp. 393–412.
- [4] Lee, M., *Recycling polymer waste*, 7: 515–516 (1995).
- [5] Karaduman A, Simsek EH, Cicek B, Bilgesu AY. Thermal degradation of polystyrene wastes in various solvents. *Journal of Analytical and Applied Pyrolysis* 2002; 62: 273-280.
- [6] Monte WC, Landau-West D. Solubility of polystyrene in certain vegetable oils, essential oils and their constituents. *Journal of food science* 1982; 47 (6): 1832-1835.
- [7] Nocuchi T, Miyashita M, Inagaki Y, Watanabe H. A new recycling system for expanded polystyrene using a natural solvent. Part 1. A new recycling technique. *Packaging Technology and Science* 1998; 11: 19-27.