Sustainable Transformation of Polystyrene Waste through Pyrolysis

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Abstract

The escalating issue of single-use plastic waste accumulation demands innovative solutions that can transform environmental liabilities into economic assets. Pyrolysis of polystyrene waste offers a promising route to address this challenge by converting discarded plastics into valuable products. The objective is to develop a sustainable and economically viable PS pyrolysis process. By doing so, a circular approach to managing plastic waste is obtained, thereby reducing the environmental burden and dependency on virgin plastic production. A model for the combination pyrolysis reactor-separation of liquids is proposed, and the net present value considering a time span of 10 years is calculated as 4.85 MMU$S resulting in a potentially feasible process at this stage.

**Keywords**: Pyrolysis, Polystyrene, Depolymerization, Circular Economy.

* 1. Introduction

Urban solid waste (USW) is a mixture of various solid wastes generated by human activities. The components of USW include food waste, paper, biomass, glass, metals, plastics, rubber, and textiles (Lu *et al.*, 2020). Currently it is possible to manage this waste through landfills, composting and incineration. The annual global USW production rate is currently over two billion tons and will increase to four billion tons before the next century. Sustainable Development Goal number 11 "Sustainable cities and communities" establishes that for a sustainable development of modern societies, the components of USW are a significant raw material to obtain new products. Sustainable processes must manage to transform waste and value it, promoting the idea of obtaining new added-value products. Within the framework of the "Circular Economy" (Ismail and Dincer, 2023), plastic waste, like any other waste, constitutes a great opportunity for the development of new technologies. In the sustainable future, new economic models will maximize the value of raw materials by encouraging practices such as reuse and remanufacturing. The recycling of polystyrene, a widely used plastic polymer known for its versatility and lightweight properties, has gained increasing attention due to the environmental concerns associated with plastic waste. PS is used in packaging, disposable products, and various industries. However, the inherent difficulties in recycling PS (Thakur *et al.*, 2018) have contributed to its significant presence in landfills and the environment. While research aims to make efforts towards finding effective methods to manage plastic waste, pyrolysis has emerged as a promising approach, offering the potential to transform discarded PS materials by depolymerization.

Pyrolysis, a thermal decomposition process conducted in the absence of oxygen, allows for converting waste and residues into valuable products such as liquid fuels, platform chemicals, and feedstocks. In recent years, research efforts have focused on optimizing the pyrolysis process parameters, understanding the kinetics of PS decomposition, and evaluating the quality and potential applications of the pyrolytic products. Pyrolysis takes place at high temperatures, between 400-800 ºC and energy is required to raise the feedstock temperature to the temperature of the endothermic parallel reactions.

The pyrolysis process allows for the thermal degradation of the waste, and products obtained have a wide range of liquid and gaseous hydrocarbons that can be recovered, guaranteeing the reduction of the volume of waste and the generation of new products with added-value (Xue, Johnston and Bai, 2017). Products are a liquid fraction or pyrolytic oil, a solid fraction or carbon, and a fraction of non-condensable combustible gases. Pyrolytic oil is usually composed of a complex mixture of hydrocarbons ranging from light alkanes to heavy oils, naphtha, aromatics, and paraffins (Al-Salem *et al.*, 2017). Plastic waste, such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), are suitable materials to produce fuels or chemical raw materials with high added-value, through a catalytic pyrolysis process. The use of catalysts could selectively convert plastic waste into aromatic compounds such as benzene, toluene, ethylbenzene, xylene, and naphthalene. These chemical compounds are widely used as raw materials, solvents, and additives in the chemical, pharmaceutical, cosmetic, transportation, and various other industries (Mangesh *et al.*, 2020). It was experimentally determined that the β cleavage of the final PS chain is the main mechanism for the formation of styrene monomers (Park *et al.*, 2020), which could be used again in the formulation of new plastic materials, aligning the process with the circular economy.

The objective of this work is to obtain a mathematical model for the PS pyrolysis-separation process, which would allow to perform a preliminary economic analysis to decide about the feasibility of this method for the depolymerization of polystyrene.

* 1. Experimental
		1. Materials and methods

Experimental work was needed for model parameters estimation. A pyrolysis reactor on a laboratory scale was created and assembled, comprising a heating module and a condensation module. The reactor has an entry point for plastic and N2 gas at one end, while the other end features a reduction zone for placing the catalyst. This design allows the gases produced during the thermal degradation of plastic to pass through both the catalyst and the condensation module. To enhance pyrolysis efficiency, the following experiments were conducted:

* + - 1. Pyrolysis of polystyrene (PS) without catalyst:

The reaction occurred at temperatures of 400, 450, and 500 ºC, establishing a temperature-dependent model for control purposes. The sample was introduced into the reactor, heated at a rate of 100 ºC/min (fast pyrolysis) until reaching the reaction temperature. After reaching the desired temperature, the sample underwent a 4-minute reaction at a constant temperature. Cooling down was uncontrolled, and the resulting pyrolysis gases were condensed to obtain the liquor.

* + - 1. Pyrolysis of PS with various catalysts:

Different catalysts were tested for the catalytic pyrolysis of PS. The catalysts included CeO2 synthesized through the combustion method and commercial Al2O3. Additionally, modified Co/CeO2 and Co/γAl2O3 supports were obtained through the wet impregnation method.

The catalysts underwent characterization using XRD and BET area measurements. Reaction conditions were optimized, and the resulting liquids were analyzed using a Gas Chromatograph coupled to a Perkin Elmer GC/MS mass spectrometer, specifically the Clarus 500 MS TurboMass software with the NIST 14 spectral library.

* 1. Pyrolysis model

The kinetics of the pyrolysis of polystyrene (PS) is a critical aspect that governs the thermal degradation process and the formation of pyrolytic products. Understanding the kinetics is essential for optimizing the pyrolysis process, designing efficient reactors, and predicting the yield and composition of the resulting products. Several models have been proposed to describe the kinetics of PS pyrolysis, with varying degrees of complexity and accuracy. One such model is the Distributed Activation Energy Model (DAEM), which has been widely used to characterize the pyrolysis kinetics of polymers, including PS, and considers that the pyrolysis reaction involves a distribution of activation energies, accounting for the different types of chemical bonds present in the polymer matrix. This model assumes that the rate of reaction is determined by the distribution of activation energies across the polymer structure. The DAEM equation can be expressed as follows:

|  |  |
| --- | --- |
|  | (1) |

Where *α* is the extent of reaction , *t* is time, *A* is the pre-exponential factor, *n* is the number of reaction pathways, *gi(α)* is the distribution function of the extent of reaction, *fi(T)* is the distribution function of the temperature, *Ei* is the activation energy for each pathway, *R* is the gas constant, *T* is the temperature

The DAEM provides a more realistic representation of the complex pyrolysis process by accounting for the different activation energies associated with the various bonds present in the molecule of polystyrene. This allows for a better prediction of the reaction rate and product distribution across different temperature ranges.

To determine the parameters of the DAEM, experimental data from thermogravimetric analysis (TGA) or other pyrolysis experiments are typically used. These data are fitted to the model using parameter estimation techniques to obtain the values of pre-exponential factors, activation energies, and distribution functions. By incorporating the resulting kinetic parameters into the simulation software, it is possible to predict the behavior of the pyrolysis process under different conditions.

In recent years, research efforts have been directed towards improving the accuracy of kinetic models for PS pyrolysis by considering more sophisticated mechanisms and reaction pathways. For example, particle size of the polystyrene has influence on the speed of the pyrolysis process and so in the DAEM model (Jiang *et al.*, 2020). Additionally, the coupling of experimental data with advanced computational techniques, such as molecular dynamics simulations, has provided deeper insights into the pyrolysis process and its kinetics (Potnuri *et al.*, 2022).

* 1. Results
		1. Experimental results

From the experiences conducted, it was found that commercial Al2O3 was the catalyst of choice, as it gave the highest yield of styrene. Chromatographic profile for this experience is shown in Figure 1, showing the styrene peak in the second position of the profile. This was used as the case of study for the modeling and simulation of the process.



Figure 1: Chromatographic profile for pyrolysis using Al2O3 as catalyst

* + 1. Pyrolysis simulation results

Using the results of the experiences conducted, a model as shown in Section 3 was obtained for the extent of the main reactions for the catalyst Al2O3. It was used as a base for estimating the volume of the pyrolysis reactor at a larger scale, assuming that the conditions are such that the reactions take place as in the experimental setup. The model obtained is proprietary and cannot be disclosed. The pyrolysis liquid composition resulting from the simulation is used for the separation step and shown in Table 1.

* + 1. Separation results

For the separation of the pyrolysis liquid, distillation is the process of choice. The thermodynamic behavior of the mixture was predicted using data from ASPEN® databank, with binary parameters derived from APV10 VLE-RK. Additionally, binary interaction parameters involving styrene with α-methylstyrene and toluene were sourced from (Dahal *et al.*, 2023). The significance of the binary interaction parameter between styrene and toluene lies in ensuring simulation results align with experimental values.

For the simulation it was considered a feed comprising the main components present in the pyrolysis liquid. A distillation column with side extraction was simulated to yield styrene with a purity of approximately 97% w/w. Heavy components were represented as a single pseudo component for simulation purposes. The primary objective was to obtain pure styrene, contributing to the circular economy by serving as feedstock to produce new polystyrene (PS). Detailed data and simulation results are presented in Tables 1, 2, and 3.

Styrene is withdrawn from a side stream, while lighter components are collected in the distillate stream, and heavier components in the bottom stream. To estimate the cost of obtaining pure styrene through distillation in $/t, a feed rate of 1 t/h with the composition outlined in Table 1 was utilized as the basis. This composition results from the simulation of PS pyrolysis at 450 °C using Al2O3 as the catalyst, with DAEM model including all the reactions to obtain the products present in the chromatography results. The net present value of the whole process for this basis was computed using data from Aspen Economics, it is shown in Table 3. It indicates that the current stage renders the process economically feasible. The IRR is 43% and the investment was calculated using a conservative approach while the price of styrene was reduced 25% with respect to global price.

Table 1: Feed composition (F) – Pyrolysis simulation.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Component | Mass % |  | Component | Mass % |
| Acetone | 0,05 |  | α-ethylstyrene | 0,05 |
| Benzene | 0,04 |  | 2-methylindene | 0,04 |
| Toluene | 1,69 |  | Naphthalene | 0,04 |
| Ethylbenzene | 0,27 |  | Diphenylmethane | 0,05 |
| Styrene | 83,04 |  | (E)-stilbene | 0,1 |
| Cyclopropylbenzene | 0,2 |  | s-diphenylethane | 0,77 |
| α-methylstyrene | 1,98 |  | 1,2 diphenylpropane  | 0,32 |
| Benzene derivative | 0,27 |  | 1,3 diphenylpropane | 0,47 |
| Indene | 0,21 |  | (E)-1-Phenyl-1-butene | 8,41 |
|  |  |  | Heavier -Pseudo component | 2,00 |

Table 2: Column simulation data and NRTL parameters for the pairs Toluene/Styrene and Styrene/ α-methylstyrene, to be used for the equations
 ; as shown in Dahal et. al, (2023b).

|  |  |
| --- | --- |
| Number of stages (top-bottom) | 20 |
| Feed flow rate F [kg/h] | 1000 |
| Feed location | 14 |
| Distillate flow rate (D) [kg/h] | 6 |
| Sidestream flow rate (S) [kg/h] | 830 |
| Sidestream (S) location | 8 |
| Reflux ratio [mass] | 200 |
| Condenser pressure [barabs] | 0.05 |
| Interstage pressure drop [bar] | 0.0001 |
| **NRTL model parameters**  |  |
| Toluene/Styrene bij/K | -227.0 |
| Toluene/Styrene bji/K | 275.9 |
| Toluene/Styrene cij/K | 0.2 |
| Styrene/ α-methylstyrene Bij/K | 606.5 |
| Styrene/ α-methylstyrene Bji/K | -469.7 |
| Styrene/ α-methylstyrene cij/K | 0.2 |

Table 3: Simulation results (only main components are shown, but all components shown in table 1 were used for the simulation)

|  |  |  |  |
| --- | --- | --- | --- |
| Main Components mass fraction | Distillate | Sidestream | Bottom |
| Toluene  | 0.7513 | 0.0017 | 0.0000 |
| Styrene  | 0.0336 | 0.9950 | 0.0034 |
| α-methylstyrene | 0.0179 | 0.0000 | 0.1456 |
| Acetone | 0.0381 | 0.0000 | 0.0000 |
| Benzene | 0.1758 | 0.0000 | 0.0000 |
| Ethylbenzene | 0.0010 | 0.0031 | 0.0000 |
| Cyclopropylbenzene (Phenylcyclopropane) | 0.0000 | 0.0000 | 0.0150 |
| Total flow rate [kg/h] | 20.00 | 830.00 | 150.00 |
| Styrene recovery | 0% | 99.9% | >0.1% |
| **NPV** MM$ 4.85 |  |  |  |

* 1. Conclusions

The amount of liquid obtained at the experimental step depends strongly on the condensation setup. Future work will be directed towards improving this stage. To do so, online gas chromatography is used to analyze online the composition of the pyrolysis gas to find if the recovered amount of styrene could be higher by using an improved condensation stage. This would improve the parameter estimation in the pyrolysis model. However, the pyrolysis model represents appropriately the experimental results.

Distillation was found as a suitable method for conducting the separations although a high reflux ratio is required. As an alternative, the distillation process can be coupled with a pervaporation membrane or with an adsorption process to further improve the separation and/or reduce the column size. This will be subject of further investigation, as well as the optimization of the process. This product has a benefit, since it can be used as a platform molecule or in the manufacture of new plastic materials, managing to add value to a polluting residue difficult to dispose of. In this way, the process is aligned with the principles of sustainable development. The process is potentially feasible as the Net Present Value for a time horizon of 10 years is 4.85 MMU$S.

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