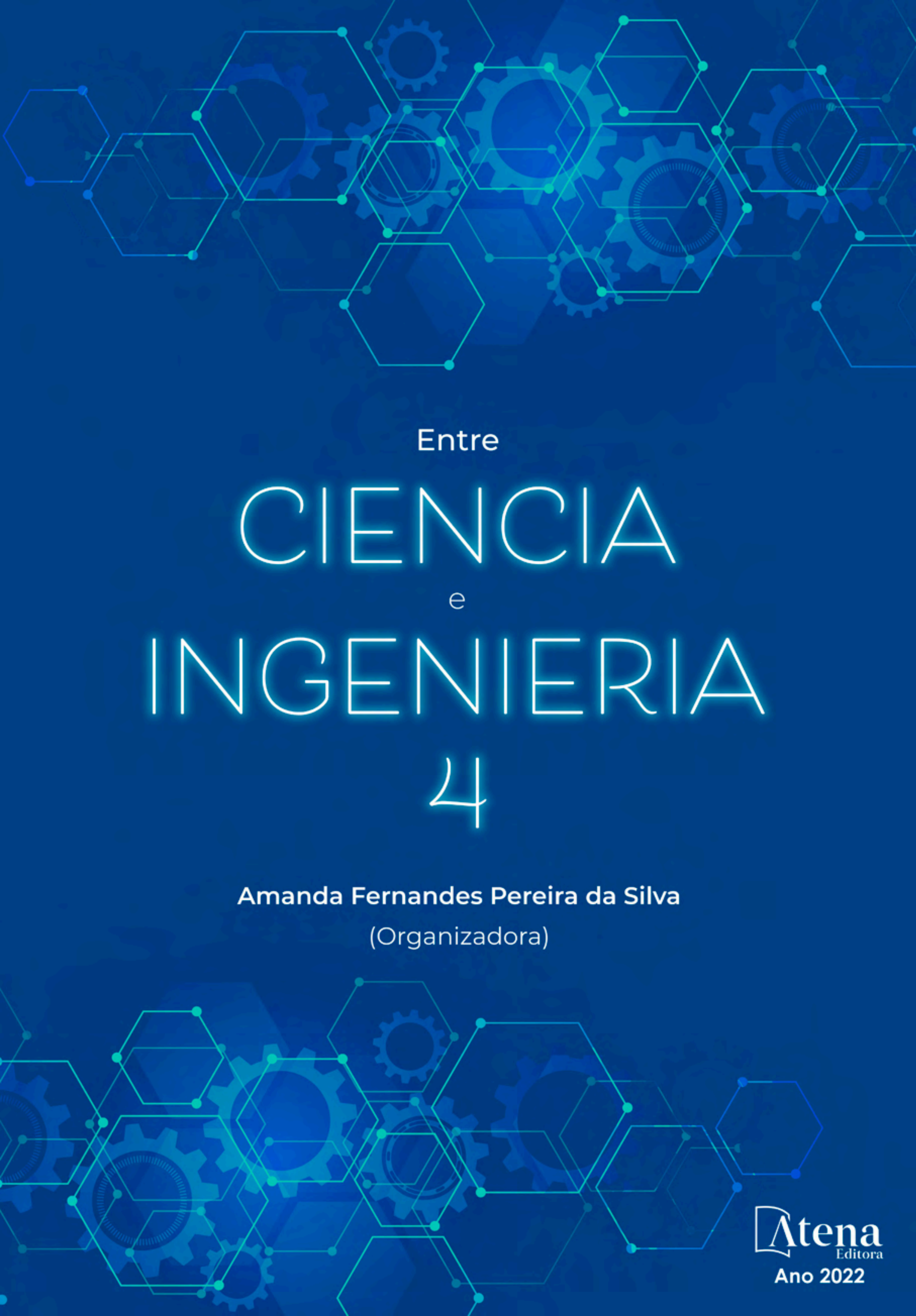

Entre

CIENCIA

e

INGENIERIA

4

Amanda Fernandes Pereira da Silva

(Organizadora)

Atena
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Ano 2022

Entre CIENCIA e INGENIERIA 4

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CIÊNCIAS EXATAS E DA TERRA E ENGENHARIAS

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A coleção “Entre Ciencia e Ingenieria 4” é uma obra que compreende os processos sob os quais se desenvolve, aplica e divulga a ciência, tecnologia e a inovação. Seu objetivo consiste em difundir trabalhos científicos que abrange diversos campos da Ciência e Engenharia que compõem os capítulos.

O volume abordará de forma categorizada e clara pesquisas e publicações com o objetivo central de analisar processos que possam ser utilizáveis em projetos e/ou trabalhos futuros. Além disso, apresenta uma análise ao desenvolvimento de temáticas que envolvem a saúde pública e coletiva, área das engenharias e ciência.

Desta forma, esse material se torna bem interessante por constituir temas, conhecimentos acadêmicos desenvolvidos e discutidos por diversas instituições de ensino e pesquisa do país e fora do país. Por isso, para necessária compreensão comum e explicitar trabalhos de forma altamente eficaz, a Atena Editora é capaz de oferecer e difundir a transferência de conhecimento com os mais debates centrados da liderança da ciência e engenharia com esta mais nova coleção.

Amanda Fernandes Pereira da Silva

SUMÁRIO

SUMÁRIO

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CAPÍTULO 2

CATALYTIC PYROLYSIS OF WASTE EXPANDED POLYSTYRENE TO OBTAIN STYRENE

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ABSTRACT: In this research project, a catalytic pyrolysis process was studied that allows the transformation of waste expanded polystyrene (WEPS) to its styrene monomer, in order to be reused in the polystyrene industry for the manufacture of new products and, in this way, carry out its recycling. Polystyrene, unlike other polymers, has great potential to produce its monomer through a pyrolysis process and it is possible to increase its yield by using a suitable catalyst. Due to the low density of WEPS, it is necessary to reduce its volume by dissolving it in an appropriate solvent. The criteria for selecting the solvent were: good solubility, not being classified as toxic (carcinogenic), having low cost and availability in the market. Tests were carried out with different basic catalysts to determine which one provides the best styrene yield. MgO was selected as the best catalyst due to its stability and cost. This catalyst was characterized by N_2 physisorption (BET area), XRD and SEM-EDS. The kinetics of the WEPS pyrolysis reaction was determined.

RESUMEN: En este proyecto de investigación se estudió un proceso de pirolisis catalítica que permite transformar los residuos de poliestireno expandido (WEPS) a su monómero de estireno, con la finalidad de ser reutilizado en la industria del poliestireno para la fabricación de nuevos productos y, de esta manera, efectuar su reciclaje. El poliestireno, a diferencia de otros polímeros, tiene un gran potencial para producir su monómero a través de un proceso de pirolisis y es posible aumentar su rendimiento utilizando un catalizador adecuado. Debido a la baja densidad de los WEPS es necesario reducir su volumen, disolviéndolo en un solvente apropiado. Los criterios para seleccionar el solvente fueron: buena solubilidad, no estar clasificado como tóxico (cancerígeno), tener bajo costo y disponibilidad en el mercado. Se realizaron pruebas con diferentes catalizadores básicos para determinar cuál es el que proporciona el mejor rendimiento de estireno. El MgO fue seleccionado como el mejor catalizador por su estabilidad y costo. Este catalizador se caracterizó mediante fisisorción de N_2 (área BET), XRD y SEM-EDS. Se determinó la cinética de la reacción de pirolisis de los WEPS.

KEYWORDS: Catalytic pyrolysis, expanded polystyrene waste, styrene, recycling.

1 | INTRODUCTION

In the 2020 Solid Waste Inventory prepared by the Ministry of the Environment (SEDEMA) of the Government of Mexico City, it is reported that during that year 12,306 daily tons of urban solid waste were generated, an amount that is not only attributed to its resident population, but also to the floating population that daily enters the entity to carry out its activities. On the other hand, in the Basic Diagnosis for the Integral Management of Solid Waste 2020 published by the Ministry of Environment and Natural Resources (SEMARNAT) of the Mexican Federal Government specifies that the average weight percentage of WEPS is 1.55% of the total solid waste generated in Mexico, therefore, it is estimated that in 2020, around 190.74 tons of WEPS were generated in Mexico City per day, of which only 0.09 tons/day were recycled, as reported in the 2020 Solid Waste Inventory, mentioned above.

Polystyrene is abundant in the waste that floats in the oceans. Like most synthetic polymers, polystyrene degrades very slowly, mainly due to the effect of UV radiation from the sun, producing smaller and smaller particles, down to micro or nano-sized polymer fragments, which can be easily ingested by marine wildlife such as mussels, fish, seabirds and whales. Ingestion of microscopic plastic particles can harm animals via the release of plastic monomers and toxic chemical additives, such as phthalates. The presence of microscopic plastic particles in fish and marine wildlife is massive and well documented.

2 | METHODOLOGY

First, a WEPS collection of used disposable cups and plates, as well as discarded packaging material, was carried out. Subsequently, a size reduction of the WEPS gathered was carried out to obtain small fragments of between 0.5 and 2 cm.

2.1 WEPS solubility experiments

WEPS solubility experiments were carried out in toluene, orange essential oil and a mixture of 50% toluene-50% orange oil, in 100 mL of solvent the WEPS, previously weighed, was added until it no longer dissolved WEPS and by difference of the remaining weight of the WEPS the dissolved weight was determined. The criteria to select the best solvent were: that the WEPS had good solubility in the solvent, that it was not toxic (or carcinogenic), and that it had low cost and availability in the market.

By dissolving WEPS in a solvent, while reducing its volume, also the air trapped inside the WEPS is eliminated, which is necessary for the pyrolysis process, since it must be carried out in complete absence of oxygen.

2.2 Determination of the WEPS average molecular weight

In order to carry out the characterization of WEPS, their average molecular weight was estimated by measuring the viscosity of WEPS solutions in toluene at different concentrations at 25°C, with the help of a Brookfield viscometer. As is known, (Gowariker et al., 2005) viscosity data can be used to calculate the average molecular weight of WEPS, using the Mark-Houwink equation:

$$[\eta] = KM^{\alpha} \tag{1}$$

Where: $[\eta]$ = intrinsic viscosity, M = average molecular weight, K and α are constants for a particular polymer-solvent system. According to Gowariker et al. (2005), the constants K and α for the polystyrene-toluene system have the following values: $K = 11\times10^{-3}$ mL/g y $\alpha = 0.725$. Intrinsic viscosity is given by the equation:

$$[\eta] = (\ln \eta r/C)_{C\rightarrow 0} \tag{2}$$

Where C is the concentration g/mL and ηr is the relative viscosity that is given by the equation:

$$\eta r = \mu/\mu_0 \tag{3}$$

Where μ is the viscosity of the solutions of WEPS in toluene, determined above and μ_0 is the viscosity of the pure solvent. If the ln (ηr)/C is plotted against concentration C (in g/mL), the intrinsic viscosity [η] shall be given by the ordinate at the origin of this graph.

2.3 Catalytic pyrolysis experiments

WEPS pyrolysis experiments were performed without catalyst and with MgO and calcined dolomite as catalysts. These variables remained constant: external temperature at 400°C, internal temperature at 250°C (Park et al., 2003), WEPS:catalyst ratio 10:1 in weight (Zhang et al., 1995) and N_2 flow at 0.1 L/min as a carrier gas. In all experiments, 25 g of WEPS dissolved in 100 mL of toluene were used, at atmospheric pressure, using the experimental equipment shown in Figure 1. The number 1 corresponded to the entry of N_2 as a carrier gas, flow was measured with the rotameter marked with the number 2 (Cole Parmer, from 0.1 to 0.5 L/min). The number 3 corresponded to the glass reactor with 1 L of capacity. The reactor was heated with an electrical resistance (number 4). The number 5 corresponded to the reactor lid, which had four mouths. A neoprene and Teflon gasket was placed between the reactor and the lid to prevent leakage. In one of the mouths of the lid was placed a pressure gauge (Metron), with scale from 0 to 2 kg/cm^2. Another of the mouths of the lid corresponded to the carrier gas entrance to the reactor (red). In another of the mouths of the lid a thermowell was placed to indicate the temperature inside the reactor. The last mouth allowed the exit of the gaseous products from the reaction.

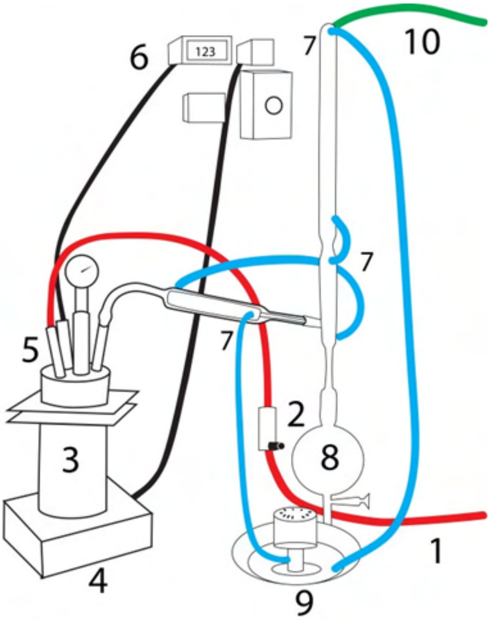


Figure 1. Glass reactor diagram and its components.

To keep the heating temperature at the set value, a thermocouple was connected from the electrical resistance to the temperature controls (number 6), which consisted of a rheostat, a digital electronic pyrometer and a relay that constituted an automatic system.

The pyrolysis vapors were condensed with three glass refrigerants (numbers 7). The liquid products were recovered in the glass accumulator-separator (separation funnel, number 8), where it was possible to take fractions of liquid products at a certain time by means of a valve at the bottom.

The cooling system (number 9) consisted of a vessel containing a mixture of water and methanol (50%), to which dry ice was added and, in this way, the temperature of the cooling fluid was reduced to -5°C. A submersible pump was installed to recirculate the coolant fluid.

The incondensable gases left the system along with the carrier gas by means of a hose into the atmosphere (number 10, green).

The liquid product of WEPS pyrolysis, using MgO as a catalyst, was analyzed with an infrared spectrometer (Perkin Elmer, Frontier model). The composition of the liquid products in each experiment was determined using a Varian CP-3380 gas chromatograph, a flame ionization detector and a 30 m x 0.25 mm ID x 0.25 µm of polyethylene glycol as stationary phase capillary column. These are the analysis conditions recommended by the standard ASTM D5135-16 method.

An experiment was conducted at a temperature of 400°C with the catalyst that provided the highest styrene yield.

2.4 Catalytic pyrolysis kinetics

The kinetics of the WEPS pyrolysis reaction were determined by the following procedure:

1. In the facility shown in Figure 1, experiments were carried out evaluating the weight of liquid products as a function of time.

2. The solvent was removed by heating it to 117°C (the toluene boiling point is 111°C), which was clearly observed not to be part of the reaction products. Pyrolysis began at approximately 200°C, when this temperature was reached it was considered t = 0 min, for the purposes of determining kinetics.

3. Once most of the solvent was exhausted, which was visually possible, the toluene was extracted from the condensate collector No. 8 and the reaction time itself began and the vapors due to thermal or catalytic pyrolysis began to form and condense in the gas-liquid accumulator-separator No. 8.

4. Sampling was carried out every 10 min by taking the accumulated liquid product at each time in the separation funnel No. 8.

5. Each sample was weighed on an analytical balance and analyzed by gas chromatography.

The determination of the kinetics of WEPS catalytic pyrolysis was performed based on weight, to express the kinetic equation as reported in the literature. The kinetic equation for a heterogeneous system can be proposed as (Imani Moqadam et al., 2015):

$$-\frac{dm}{dt} = \mathrm{k}\, m^{n} \tag{4}$$

Where: m = WEPS mass (g) in a reaction time, t = reaction time (min), k = specific reaction constant and n = reaction order. In various studies of WEPS pyrolysis (Camiti et al., 1991; Aguado et al., 2003; Encinar y González, 2008; Mo et al., 2013; Imani Moqadam et al., 2015; Artetxe et al., 2015; Nisar et al., 2019), it has already been reported that the kinetics of WEPS pyrolysis is of first order, if n = 1 equation (4) can be integrated as follows:

$$-\int_{m0}^{m} \frac{dm}{m} = \mathrm{k} \int_{0}^{t} dt \tag{5}$$

Solving the integral leads to equation (6), which was the kinetic equation used with the data thrown in the experiments carried out:

$$\ln \frac{m0}{m} = \mathrm{k\ t} \tag{6}$$

2.5 Catalyst Characterization

2.5.1 N_2 Physisorption (BET Area)

The N_2 adsorption-desorption isotherm of the MgO catalyst was determined with a NOVA Quantachrome Instruments version 11.0 equipment, using the N_2 physiosorption at 77.35°K. Before adsorption, the sample received a degassing pretreatment at 300°C for 5 h under a vacuum of $1x10^{-4}$ torr. The weight of the sample was 0.2482 g and the volume of the sample of 0.06708 cm^3. With this analysis, the BET specific area, the pore volume and the distribution of the pore diameter were determined by applying the standard BET model (Brunauer et al., 1938). To quantify the pore volume (Vp) of the samples, the T-plot method was used (Lippens y Boer, 1965). The distribution of the pore diameter was obtained from the BJH model (Barrett et al., 1951), using isothermal desorption and assuming pore geometry as cylindrical.

2.5.2 X-Ray Diffraction

The XRD diffractograms of the MgO catalyst, before and after the pyrolysis reaction, were obtained with a Rigaku diffractometer (Phillips Xpert) equipped with a Cu tube anode (Phillips Xpert) (30 kV, 20 mA), which uses CuKα radiation. The scan was performed in the range of $2\theta \sim 10\text{-}100°$, with a 2°/min rate.

2.5.3 Scanning Electronic Microscopy (SEM) y EDS

Images of the MgO catalyst microstructure were taken by scanning electronic microscopy (SEM), before and after the pyrolysis reaction, with field emission and high resolution in a Joel microscope (model JFM-6701-F, Japan) using secondary electrons.

3 I RESULTS AND DISCUSSION

3.1 WEPS solubility experiments

WEPS solubility experiments on toluene, orange oil and a mixture of 50% orange oil-50% toluene were 0.6018, 0.4163 y 0.5633 g/ml of solvent, respectively. The result of the WEPS solubility in toluene was similar to that obtained by García et al. (2009).

Toluene was found to be the most suitable solvent for dissolving WEPS, because it offered the highest solubility among the solvents analyzed, the toluene safety sheet mentions that there is no evidence that it is carcinogenic and that toluene has a relatively low cost and good availability in the market.

3.2 Determination of the WEPS average molecular weight

It is observed that the viscosity increases exponentially with the WEPS concentration in toluene. As can be seen in Figure 2, the curve fits well to the equation: $y = 0.0069e^{0.2892x}$.

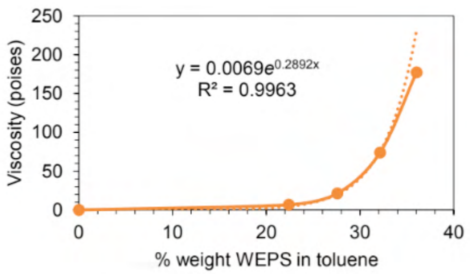


Figure 2. Viscosity against WEPS concentration dissolved in toluene at 25°C.

With the viscosity data of the WEPS solutions in toluene at different concentrations, the graph in Figure 3 is obtained, ln(**ηr**)/C against the WEPS concentration in toluene in g/mL. The intrinsic viscosity is the ordered to the origin, so [η] = 39.285 mL/g.

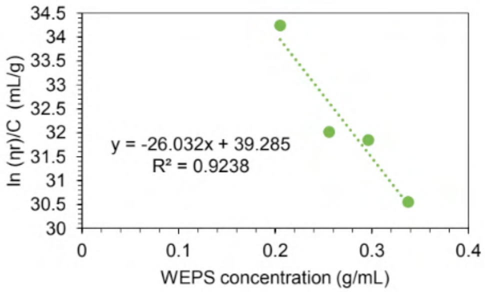


Figure 3. ln(**ηr**)/C against WEPS concentration in toluene

Applying the Mark-Houwink equation (1) and using the constants reported by Gowariker et al. (2005): K = 11x10^{-3} mL/g and **α** = 0.725, results in a WEPS average molecular weight of M = 79,517.15 g/mol.

3.3 Catalytic pyrolysis experiments

The infrared (IR) spectrum obtained from the liquid products of WEPS pyrolysis, using MgO as a catalyst, is shown in Figure 4. The interpretation of this spectrum is as follows:

a) The bands between 3030-3080 cm^{-1} and 910-990 cm^{-1} represent the vinyl group, characteristic of styrene.

b) The band in 1631 cm^{-1} suggests the presence of C=C.

c) The bands between 730-770 cm^{-1} and the small peaks between 1700 y 1900 cm^{-1} indicate the presence of monosubstituted benzene.

d) The bands between 1450-1500 cm^{-1} indicate the presence of aromatic groups.

e) The bands between 2930-2980 cm^{-1} characterize C-H groups.

d) The band in 1580 cm^{-1} corresponds to substitution in the benzene ring.

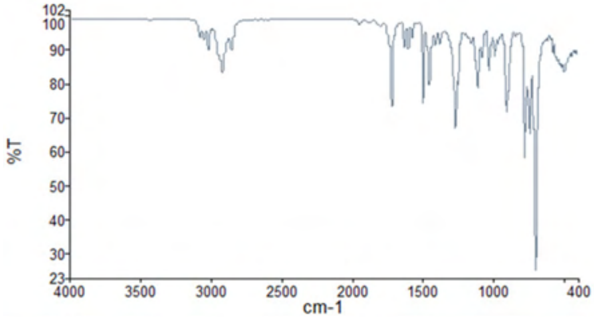


Figure 4. IR spectrum of WEPS pyrolysis products obtained, using MgO as catalyst

The styrene yield obtained without catalyst and with MgO and calcined dolomite as catalysts, at 250°C, are detailed in Table 1, are compared with the results reported by Zhang et al. (1995).

Catalyst	Temperature (°C)	Styrene yield (wt. %)	Styrene yield Zhang et al. (1995) (wt. %)	Residue (wt. %)
Without catalyst	250	23.27	56.07	5.43
MgO	250	56.29	62.9	6.13
Calcined dolomite	250	50.69	This catalyst has not been used before	7.37

Table 1. Yields obtained from WEPS pyrolysis

According to Zhang et al. (1995) using BaO as a catalyst resulted in a higher yield, obtaining 71.4% by weight of styrene at 350°C. However, BaO has about five times a higher cost than MgO. Therefore, it was decided that MgO is the most appropriate catalyst for industrial purposes. Once MgO was selected as the most industrially suitable, an experiment was conducted at a temperature of 400°C, in which a styrene yield of 66.42% by weight was achieved.

3.4 Catalytic pyrolysis kinetics

The weight loss of WEPS over time of the experiment without catalyst is shown in Figure 5a, if $\ln(m_0/m)$ is plotted against time t, according to equation (6), Figure 5b results, where it is observed that it is very close to a straight line. Fitting to a straight line using the least squares method resulted a slope of $k = 0.0146\ min^{-1}$, with a correlation coefficient of $R^2 = 0.9965$.

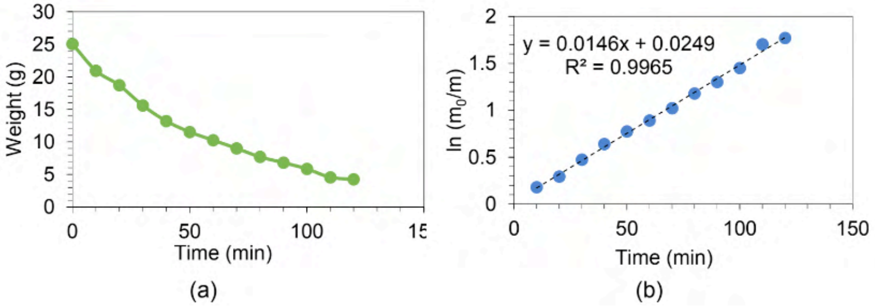


Figure 5. Experimental test data without catalyst. (a) WEPS weight loss with time t, (b) ln(m_0/m) against time t.

In the WEPS catalytic pyrolysis experiment in which MgO was used as a catalyst (Figure 6a), a similar decrease was observed as a function of time to the case of reaction without catalyst. When applying equation (6), a straight line was obtained (Figure 6b) using the least squares method, the slope gave k = 0.0156 min^{-1}, with a correlation coefficient of R^2 = 0.9927, therefore, it is corroborated that the WEPS pyrolysis reaction follows a first order kinetics, using toluene as a solvent.

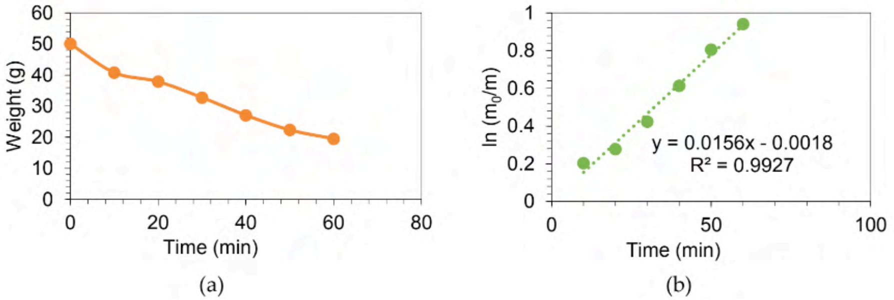


Figure 6. Experimental test data using MgO as catalyst. (a) WEPS weight loss with time t, (b) ln(m_0/m) against time t.

3.5 Catalyst Characterization

3.5.1 N_2 Physisorption (BET Area)

Using the Cumulative Desorption Method DH a surface of 45.63 m²/g was obtained. With the Cumulative Desorption Method BJH resulted a pore volume of 0.1016 cm^3/g. With the DH Method by desorption (Dv(d) mode) an average pore diameter of 3.645 nm was obtained. Figure 7 shows the N_2 adsorption and desorption isotherm of the MgO catalyst at a temperature of 77.35°K, where it is observed that the isotherm is type IV according to the IUPA classification (Contreras et al., 2015), therefore, the MgO catalyst is mesoporous.

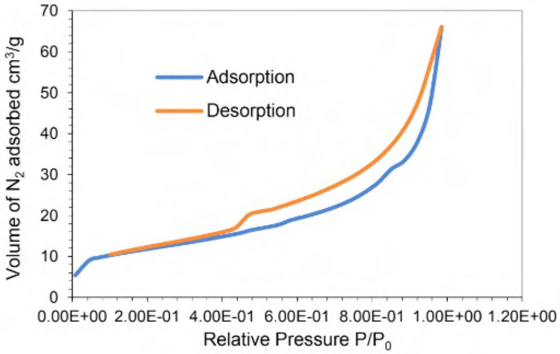
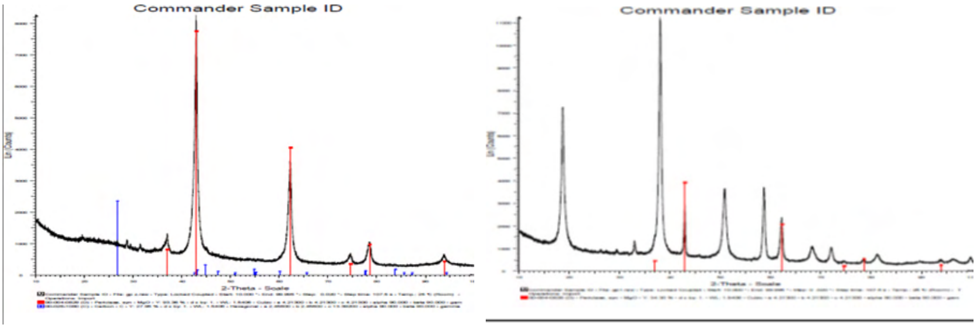


Figure 7. MgO catalyst adsorption and desorption isotherm

3.5.2 X-Ray Diffraction

The diffractogram of the MgO catalyst before pyrolysis (Figure 8a) shows a great coincidence with the periclase diffractogram (93.36%). Figure 8b presents the diffractogram of the catalyst after pyrolysis, in which a probable coke phase is observed. However, this analysis shows that the MgO catalyst is not modified after pyrolysis, as periclase diffractions remain.



(a)
(b)

Figure 8. MgO X-ray diffractogram, (a) before pyrolysis, (b) after pyrolysis

3.5.3 Scanning Electronic Microscopy (SEM) y EDS

Figure 9a shows the image obtained by scanning electronic microscopy of the MgO catalyst before pyrolysis, Figure 9b corresponds to the Mg mapping by EDS of the catalyst, Figure 9c corresponds to the mapping of Si by EDS, Figure 9d corresponds to the mapping of Ca by EDS, Figure 9e corresponds to the mapping of O by EDS and its chemical composition is detailed in Table 2.

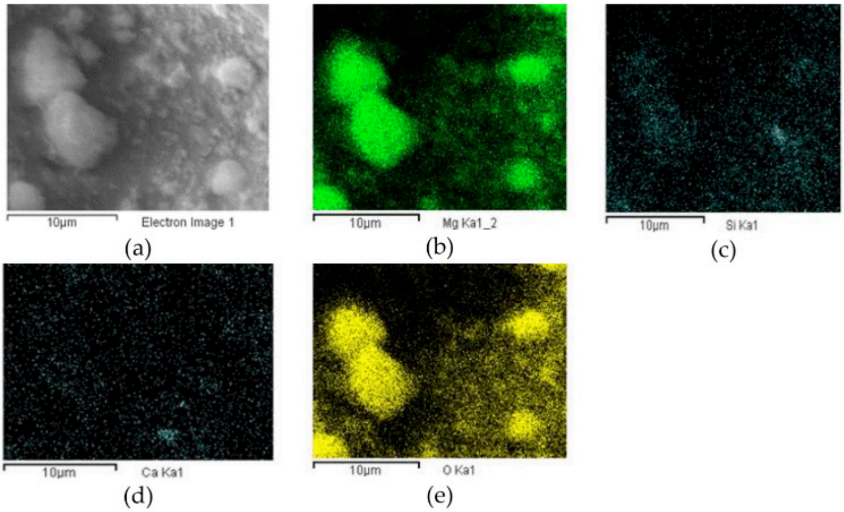


Figure 9. Scanning electronic microscopy and mapping of MgO catalyst elements prior to MgO pyrolysis. (a) SEM image, (b) Mg mapping by EDS, (c) Si mapping by EDS, (d) Ca mapping by EDS and (e) O mapping by EDS.

Element	Weight %	
	Before pyrolysis	After pyrolysis
O	79.94	34.82
C	---	48.95
Mg	19.3	12.95
Si	0.38	2.33
Ca	0.38	0.71
S	---	0.24

Table 2. MgO catalyst chemical composition before and after pyrolysis

Figure 10 shows the images of the MgO catalyst after pyrolysis, obtained with the scanning electronic microscope and Table 2 reports its chemical composition. This analysis performed with scanning electronic microscopy and EDS shows that, after the pyrolysis reaction, carbon is formed on the MgO catalyst and the presence of sulfur traces that did not exist before the WEPS pyrolysis was found.

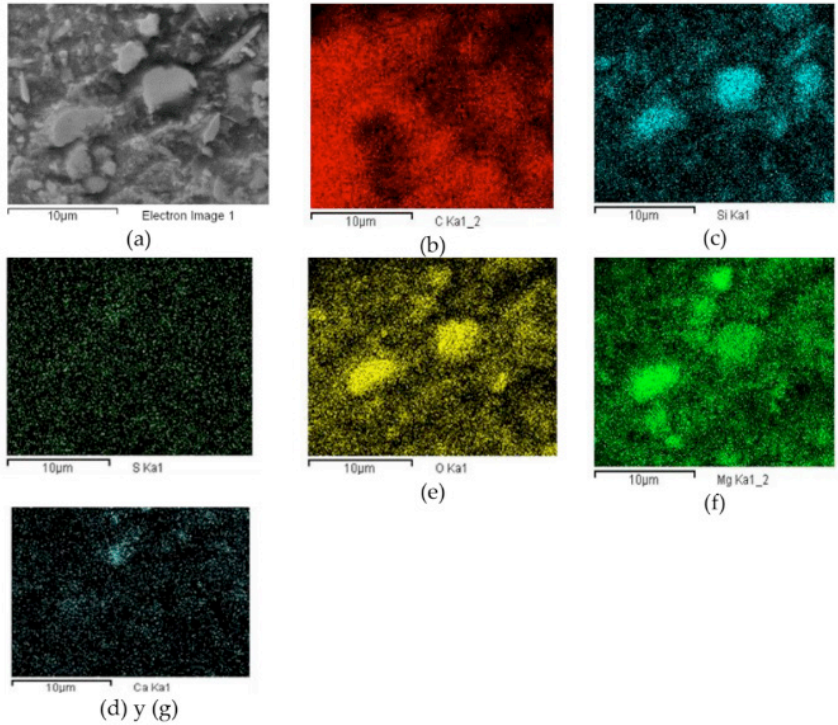


Figure 12. Scanning electronic microscopy and mapping of MgO catalyst elements after pyrolysis. (a) SEM image, (b) C mapping by EDS, (c) Si mapping by EDS, (d) S mapping by EDS, (e) O mapping by EDS, (f) Mg mapping by EDS and (g) Ca mapping by EDS.

4 | CONCLUSIONS

The most appropriate solvent to dissolve WPS is toluene, because it dissolves WEPS very well, because there is no evidence that it is carcinogenic, has a relatively low cost and availability in the market. MgO catalyst is the most suitable for WEPS pyrolysis for industrial purposes, due to its stability, low cost and availability in the market. The highest styrene yield obtained was 66.42% by weight with MgO as catalyst, at a temperature of 400°C. The pyrolysis of polystyrene follows a kinetics of first order. MgO catalyst is mesoporous and does not undergo any modification after pyrolysis.

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