



A new Valorization Route of Petrochemical Wastewater: Recovery of Phenolic Derivatives and their Subsequent Application in a PP Matrix for the Improvement of their Durability in Multiple Applications

Joaquín Hernández-Fernández^{1,2,3} · Karen Marulanda⁴ · Esneyder Puello-Polo⁵

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Abstract

Wastewater from industrial processes contains different compounds that can be of great use to improve its circularity. The potential of wastewater can be exploited by applying extraction techniques to obtain compounds of interest and recirculate them in the process. In this study, the residual water generated during the polypropylene deodorization process was evaluated. The residues of the additives used during the synthesis of the resin are extracted from these waters. With this recovery, contamination of water bodies is avoided and the circularity of the polymer production process is increased. Solid phase extraction and HPLC were used to recover the phenolic compound, obtaining a recovery of more than 95%. FTIR and DSC were applied to evaluate the purity of the extracted compound. Finally, the effectiveness of the phenolic compound was evaluated by applying it to the resin and evaluating its thermal stability by TGA, obtaining as a result, that the recovered additive improves the thermal properties of the material.

Keywords Recovery · Phenolic compounds · Irganox 1010 · Extraction · Circularity

Introduction

A petrochemical process plant's unit operations generate a large amount of pollutants that are disposed of in wastewater, which contains hydrocarbons, oils, organic compounds, and other contaminants [1–3]. These waters are characterized by high contaminant load values and a wide range of concentrations of the different parameters that determine the quality of the water, which is why it is sometimes not possible to treat all these contaminants through conventional processes [2–4]. Petrochemical wastewater is characterized by having a high chemical oxygen demand (COD) and, in turn, a high biological oxygen demand (BOD) due to certain substances present in its effluents, such as volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), phenols, and dissolved minerals, among others [5], [6]. Many of these pollutants, since they cannot be purified by means of conventional wastewater treatments, are finally disposed of in different bodies of water where they enter the aquatic environment and become emerging pollutants (EP), which represent a high risk to human health and the ecosystem [7–9]. These substances, despite being present in low concentrations, are usually toxic and many of them have a

✉ Joaquín Hernández-Fernández
jhernandezf@unicartagena.edu.co

Esneyder Puello-Polo
esneyderpuello@mail.uniatlantico.edu.co

¹ Chemistry Program, Department of Natural and Exact Sciences, San Pablo Campus, University of Cartagena, 130015 Cartagena, Bolívar, Colombia

² Chemical Engineering Program, School of Engineering, Universidad Tecnológica de Bolívar, Parque Industrial y Tecnológico Carlos Vélez Pombo, Km 1 Vía Turbaco, 130001 Turbaco, Colombia

³ Department of Natural and Exact Science, Universidad de la Costa, 30300 Barranquilla, Colombia

⁴ Centro de investigación e invención en ciencias e ingenierías, CECOPAT&A. Cartagena, 130015 Bolívar, Colombia

⁵ Grupo de Investigación en Oxi/Hidrotratamiento Catalítico Y Nuevos Materiales, Programa de Química- Ciencias Básicas, Universidad del Atlántico, 081001 Puerto, Colombia

high solubility in water. Within these substances and due to their great use in the petrochemical industry, phenols and substituted phenols stand out. The elimination of phenols in waste is fundamental for the protection of the environment. Among the most used technologies for its elimination are biodegradation, thermal decomposition and adsorption. [10–13]. However, these techniques are not highly effective in the elimination of phenols substances. These phenolic compounds, in addition to representing highly toxic pollutants, constituted compounds of great added value and of great importance in various industrial sectors, which is why their recovery is important [13].

Phenolic antioxidants are used as additives in the polymer processing industry. These compounds are capable of retarding or inhibiting oxidation, improving their mechanical properties [14], [15]. Oxidative degradation processes in polymers are generated as a result of the exposure of the polymer to factors such as heat, light, or mechanical stress, which generates the formation of free radicals, the loss of some of the properties of the material and a health risk [16]. There are different types of antioxidants, which are classified according to their oxidation mechanism and substrate. In the case of polyolefins, oxidation is a very recurrent phenomenon that takes place during their processing [17–19].

Polypropylene (PP) is a widely used polymer of petrochemical origin thanks to its very low density, a property that makes it very useful in various industries because it can be heated, cooled, and heated again without degrading its composition. PP has high thermal stability, chemical resistance, mechanical strength, and low production cost [7], [8], [20–22]. In addition, it is a product of great economic interest with high demand, which encourages the increase in its production, a situation that raises possible concerns regarding the environmental problems associated with its production and disposal. In polypropylene, phenolic antioxidants are mainly responsible for generating greater resistance to oxidation [23]. We can commonly find Irganox 1010, which is a phenolic antioxidant and a non-discoloring stabilizer that is very effective on substrates such as polyolefins and is recommended for use in polymer processing.

Unfortunately, during the PP production process, a large number of pollutants with potential effects on health and the environment are generated. Among these contaminants are volatile organic compounds and phenols of synthetic origin, which are used as additives to improve the properties of PP [24]. The presence of these substances in industrial waste argues the need to evaluate its efficiency in processing and motivates the development of a more efficient and environmentally friendly PP production process. One of the processes during the synthesis of PP is deodorization, where compounds that were not absorbed and that generate odors in the polymer are removed. If these compounds are

recovered, they can be revalued in the PP matrix and used in the PP extrusion process.

In this article, it is proposed to recover the Irganox 1010 additive and incorporate it into the process of obtaining PP as a way to make its production process more efficient and reduce losses in its synthesis. The recovered additive was added to the polypropylene matrix to evaluate its effectiveness in improving the thermal properties of the material.

Materials and Methods

Additive Recovery

Sampling Location

The collection of the samples was obtained from a polypropylene production plant that uses 4 stages (Fig. 1) for the production of this material: (1) receipt and purification; (2) polymerization; (3) additive and pelletizing; and (4) desorption. The samples are basically obtained from the condensates of the extrusion and deodorization stages [25]. The polymer extrusion process is carried out at a high temperature, so it requires the use of water to reduce its temperature and produce a more uniform grain. About 30 tons of PP can be processed in 50 min, so due to the high processing volume and process speed, samples were taken every 12 min, obtaining 5 samples. Samples were taken from the desorption unit in triplicate every hour, knowing that its operation process (desorption time) is 4 h. The effect of the time in which the samples are taken with respect to the migration of phenols in the condensates is studied, as well as the way in which they are present in the condensates of these two units.

Extraction of Solid Phases (SPE)

Before carrying out the extraction, the sample was filtered through a polytetrafluoroethylene filter (PTFE). For the SPE, 15 ml of the sample was placed in Strata X-33 tubes (500 mg, 6 ml) at a flow rate of 1 ml/min. The filtrate was previously conditioned with 5 ml of methanol and 5 ml of distilled water. The filtrate was washed with MeOH: H₂O 80:20. The retentate was eluted with 10 ml of acetonitrile (ACN) and stripped with nitrogen at 5 psi. The extracted solution was dissolved with ACN to make 1 ml [7] to later be analyzed by HPLC. The preconcentration process was repeated until a concentrate volume of 500 mL was obtained. These 500 mL were pre-concentrated and dried with a stream of N₂. The resulting solid is subsequently analyzed by FTIR, DSC, TGA and HPLC-MS. The recovered solid (Irganox 1010) is stored in a cabin with temperature

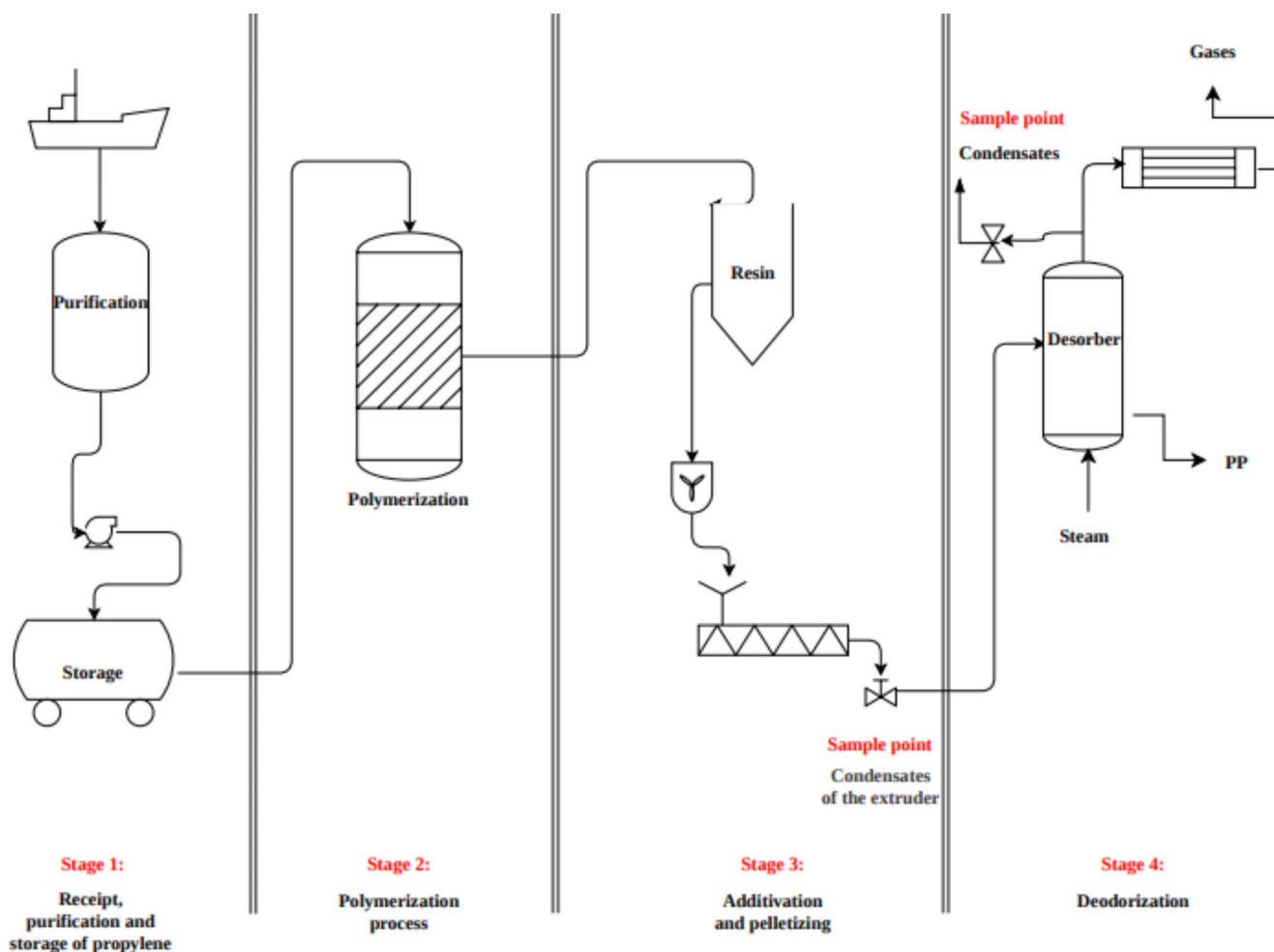


Fig. 1 Polypropylene production stages

and relative humidity control, to later be added to the virgin PP resin.

High-performance Liquid Chromatography with Diode Array Detector and mass-mass Spectrometry (HPLC-DAD/MS/MS)

For this analysis, an Agilent 1100 HPCL and coupled to a Micromass Quattro II triple quadrupole mass spectrometer. MS and MS/MS acquisition of spectra is possible. system was used, consisting of: degasser (G1322A), quaternary pump (G1311A), automatic sampling system (G1313A), column carrier (G1316A), DAD detector (G1315B) with chemstation, column Lichrosorb RP-18(4.6×200mm×5microns), 5 and 10 syringes, and a precision balance and a separate dual pump system and autosampler for automatic injection in the MS with or without use of the HPLC-column. The chromatography conditions were established with the prepared solution of Irganox 1010 in ACN. The separation was done with the solvent mixture ACN and H₂O,

where these were mixed in different proportions, as follows: 84% and 16% (1 min, 15 ml/min); 92% and 8% (2 min, 2, 0 ml/min); 96% and 4% (3.5 min, 3.5 ml/min); 100% and 0% (8 min, 3.5 ml/min). The column was set to 50 °C, 20 L of irrigation volume, and a wavelength of 200 nm [7], [26], [27]. fragment ion mass information derived from MS and MS/MS is used for the identification of additive.

Addition of the Recovered Additive to the PP Matrix

Preparation of the PP Samples

The PP resin used was prepared using a virgin resin without additives. The resin was mixed with the recovered Irganox 1010, PP–Recovered Irganox 1010 blend samples were premixed by adding 0.1 wt% of recovered Irganox 1010 additive to PP powder using a Prodex Henschel 115JSS standard mixer at 800 rpm for 7 min at room temperature. Subsequently, samples were blended by melt-extrusion by means of a Welex-200 24.1 extruder being the operating

Table 1 Recovery of Irganox 1010

Generated wastewater flow (Kg/h)	Average concentration of Irganox 1010 recovered ^a (mg/kg)	Theoric value ^b (mg/kg)	Recovery Irganox 1010 ^c (%w/w)	Irganox 1010 rat recovery ^c (Kg/h)
1000	16,430 ± 226	16,731	98.1 ± 1.35	16.43 ± 0.23

^a = average of 10 measurements, ^b = expected theoretical concentration, ^c = % of Irganox 1010 recovered = (measured value/theoretical value) x 100.

temperatures measured inside the extruder paths 190, 195, 200, 210, and 220 °C. The blends were further processed into films (300 mm diameter films of ≈ 100 μm in thickness) by compression molding in a hot press CARVER 3895. The PP solid was pelletized and granules with a concentration of 1000 mg/kg for recovered Irganox 1010 were obtained. For the preparation of the standard, Irganox 1010 was diluted in ACN to obtain a solution with a concentration of 500 mg/L, and 2.5 ml of this solution were dissolved up to a volume of 50 ml to obtain a solution of 25 mg/L.

Evaluation of the PP Additive

Fourier Transformed Infrared Analysis (FTIR)

The FTIR analysis was performed using a Nicolet 6700 infrared spectrometer, with measurements between 4000–600 cm⁻¹ and a resolution of 2 cm⁻¹ (reflection). To carry out this study, the sample was previously subjected to a temperature of 400 °C in order to induce thermal degradation and to be able to study the changes in the polymeric matrix [20], [28].

Differential Scanning Calorimetry Analysis (DSC)

For the calorimetric analysis, a DSC Q2000 V24.11 Build 124 apparatus was used, with which the oxidation induction time (OIT) was determined. Results were obtained under nitrogen and oxygen atmospheric conditions using a 6.1 mg sample. The variation in the atmosphere of the experiment is made to study the effects of oxidation on the material and its volatility. Nitrogen, on the other hand, guarantees us a controlled inert atmosphere through which it is possible to study the effects of decomposition on the sample. This process was done under different conditions, first isothermally at 60 °C for 5 min, then the temperature was increased from 60 to 200 °C for 20 min under a nitrogen atmosphere of 50 ml/min. Afterwards, the ambient conditions for the analysis were changed, and it was exposed to an air flow of 50 ml/min, oxidation condition, at a temperature of 200 °C for 30 min. With the oxidation flow, a change in the slope from the exothermic heat was evidenced. This transformation allows obtaining the OIT value that corresponds to the time at which the change in slope occurs [25].

Thermogravimetric Analysis (TGA)

This analysis was carried out in a temperature range of 30–700 °C on a Perkin Elmer TGA7 thermobalance under a nitrogen atmosphere of 50 ml/min. The initial degradation temperature was determined in the TGA as the temperature at which 5% mass loss occurs, and the maximum degradation temperature was established from the DTG curve [20], [29], [30].

Results

Additive Recovery

In the work by Hernandez et al. (2019) [7], the use of ACN (mobile phase) was determined as a solvent to carry out the extraction, given its high selectivity towards the analyte, and an rat recovery of Irganox 1010 of 16.73 Kg/h was established, with the 10 reproductions of the method obtaining a recovery of more than 98% as shown in Table 1.

HPLC-DAD/MS/MS Additive Evaluation

In the mass spectrometry result, important and common fragmentations are exhibited for both pure and recovered irganox 1010 (See Figs. 2 and 3). these were: Molecular ion MH⁺ was absent a small peak has been observed as a m/z ratio of 1176. A fragment with an m/z of 899 was observed and that corresponds to the loss of one of the 4 rings of Di-ter-butylphenol-CH₂-CH₂COO ion. Each Di-tert-butylphenol-CH₂-CH₂COO ring has an M/Z of 277. In the spectrum, 278 is observed, which should refer to the 13 isotope of carbon. Each Di-tert-butylphenol-CH₂ ring has an M/Z of 219, Each Di-tert-butylphenol-CH-CH-CO ring has an M/Z of 259, Each Tert-butylphenol-CH₂ ring has an M/Z of 162 o M/Z 163. Each of these fragments is observed in the spectrum. The chemical nature of this fragmentation is related to the formation of an oxonium ion species, which is chemically stable and structurally contains a neighboring carbonyl oxygen in a six-membered ring. It is important to highlight mass losses of 57 Da. These sequential losses correspond to the structures of the Ter-butyl groups that are present in the molecular structure of Irganox 1010 (See Fig. 4). These 8 tert-butyl branches with molecular units of

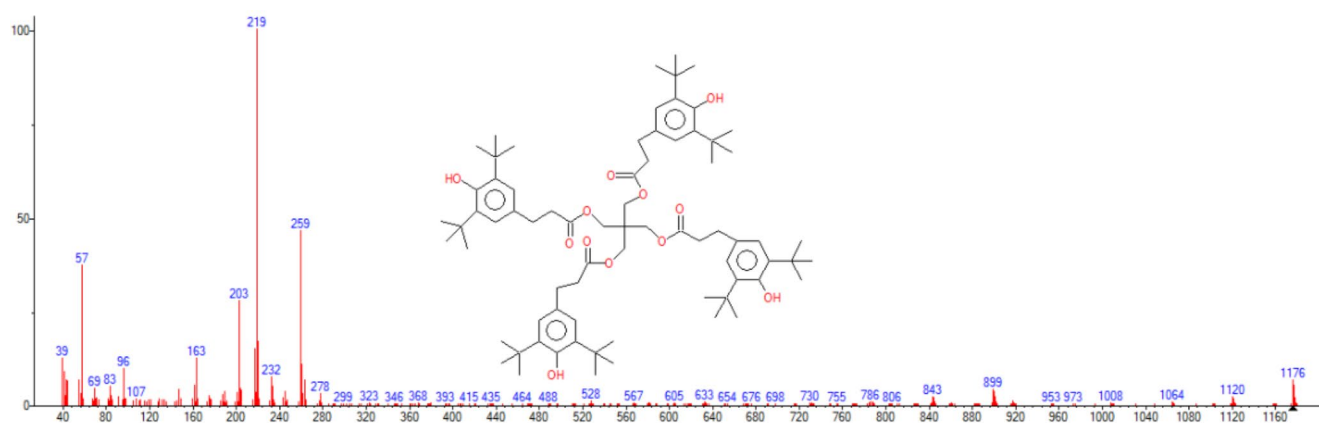


Fig. 2 MS spectra of pure Irganox 1010

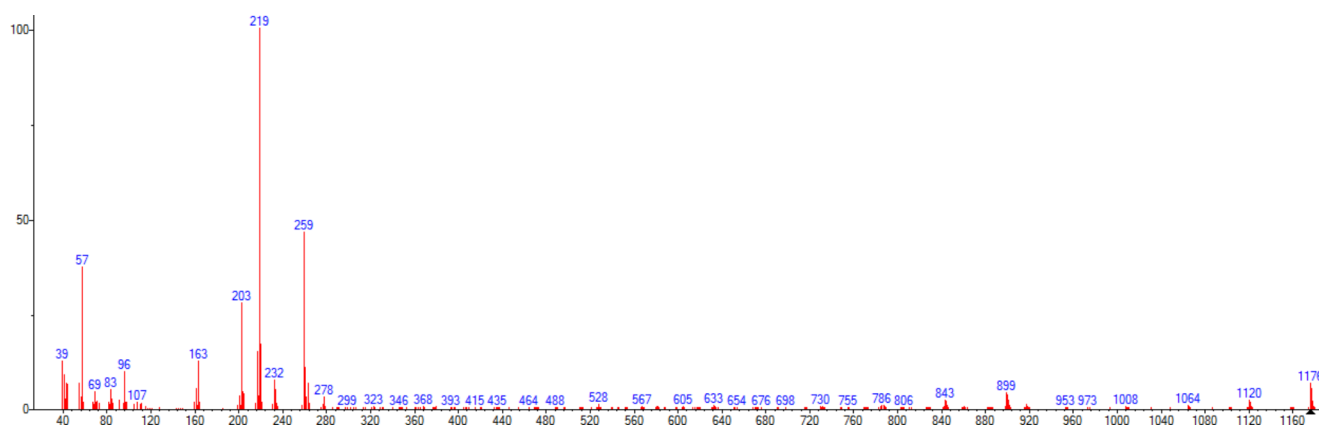


Fig. 3 MS spectra of recovery Irganox 1010

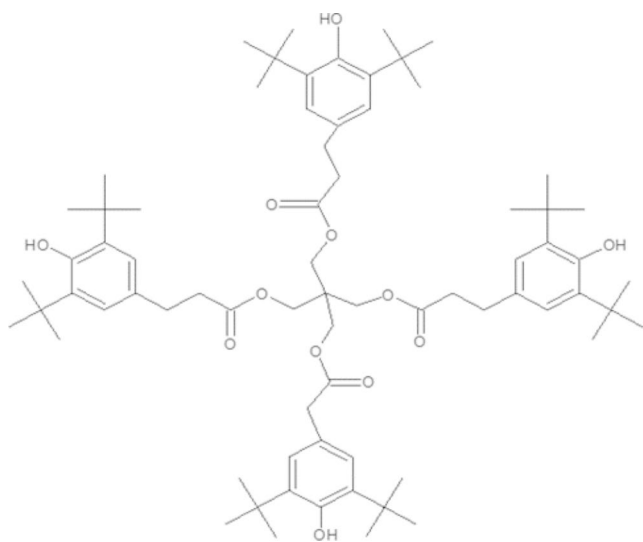


Fig. 4 Structural formulas of the Irganox 1010

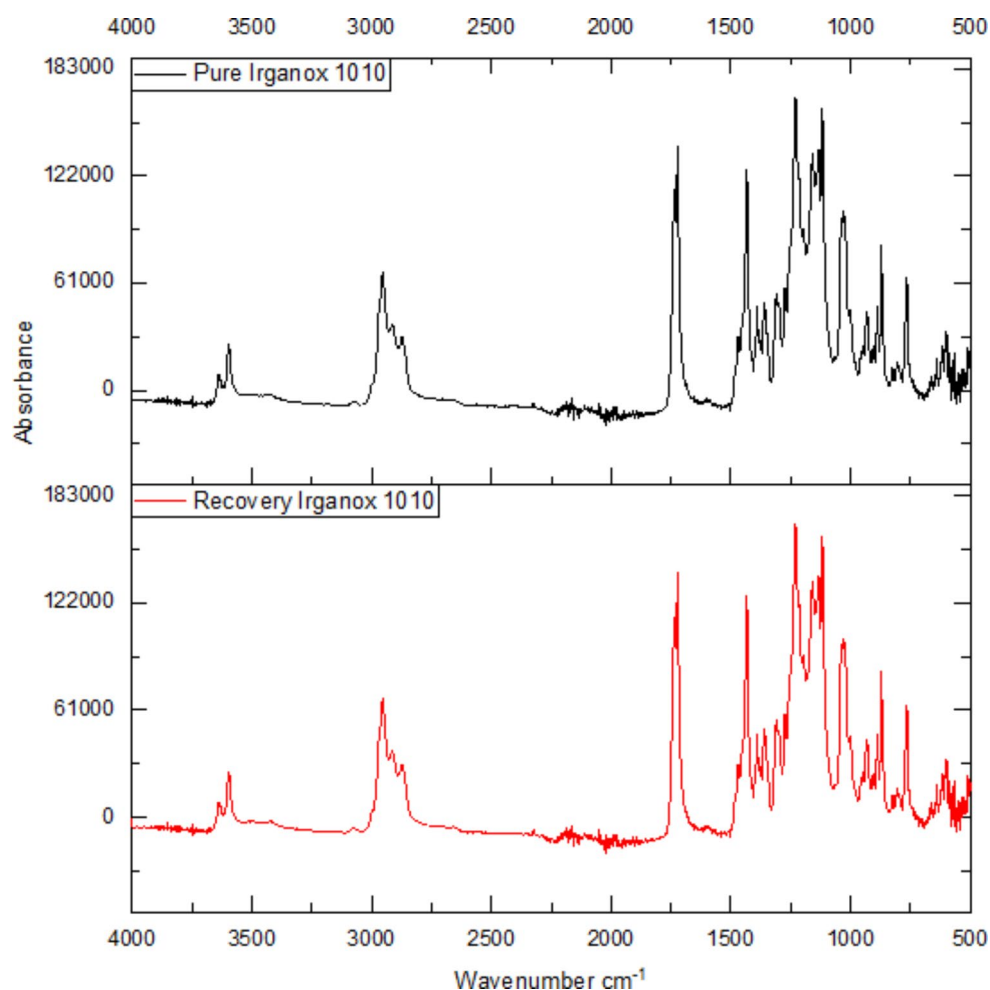
isobutene are responsible for the production of a series of abundant ions that are characterized by mass differences of 57 Da. For example M/Z of 1120, 1064, 1008, 953, 899, 843, etc. The comparison of the fragmentation patterns of

the recovered Irganox 1010 and the pure Irganox 1010 have a high similarity, revealing the high purity of the recovered Irganox.

FTIR Additive Evaluation

The recovered Irganox 1010 and pure Irganox 1010 were subjected to Fourier transform infrared spectroscopy (FTIR) before and after its reintegration into the PP, in order to differentiate the spectra of the recovered substance, and after its addition to the PP, in order to study the compatibility of the components in the composite matrix [31]. From the preliminary results of the FTIR before being coupled to the PP, it was found that the spectrum obtained from recovery Irganox 1010 (Fig. 5) is quite similar to the spectrum of the pure additive obtained from the literature [32]. The fingerprint of the spectrum is shown in a similar way in both spectra, as well as the most pronounced peaks. Slight differences are shown in the spectra given the noise in the signals obtained for this test and the low concentrations of the analyte that are reflected in lower values of absorbance in the region of 2250–1900 cm^{-1} .

Fig. 5 IR spectra of recovered Irganox 1010 and pure Irganox 1010



From the spectrum obtained (Fig. 5), it can be seen that the peak obtained around 1735 cm^{-1} is characteristic of the ester group ($\text{O}=\text{C}$) present in the Irganox structure and between 1300–1050 cm^{-1} there are two bands that correspond to the symmetric and asymmetric stretching of the ester group of irganox. One stretch is of greater intensity than the other. On the other hand, the peak at 3670 cm^{-1} demonstrates the presence of the group derived from phenols in the structure of Irganox 1010. In the region between 2950 and 2970 cm^{-1} the typical band of the CH_3 groups is observed. These groups can also be seen in the chemical structure of Irganox. The existence of aromatic groups in the spectrum is also evidenced by a slightly intense absorption in the region of 1450–1500 cm^{-1} , characteristic spectrum of aromatic compounds [33], [34]. The analysis of the peak in the Irganox spectrum allows us to corroborate the presence of the recovered analyte as well as its efficiency, a fact that is not estimated for this study through spectrophotometry, because through this it is more desirable to measure the coupling and the difference between the peaks when the Irganox enters to couple in the PP matrix. Figure 4 shows the molecular structure of Irganox 1010.

Analysis of Irganox 1010 in the PP

FTIR

FTIR was used to evaluate the incorporation of the recovered Irganox 1010 and the pure Irganox 1010 into the virgin PP resin. Figure 6 shows that the IR spectrum of virgin PP does not present the characteristic peak of the carbonyl functional group in 1735 cm^{-1} . This functional group is typical of Irganox 1010, as shown in Fig. 4 and Fig. 5. This carbonyl peak is clearly seen in the IR spectrum of virgin PP+Irganox 1010 pure and in virgin PP+Irganox 1010 recovered.

DSC

This analysis was done previously on the recovered Irganox to characterize it and later to see its influence on the PP matrix.

Under the established conditions and a flow of 10 $^{\circ}\text{C}/\text{min}$, the heat flow data in mW as a function of temperature were obtained (Fig. 7), where the endothermic fusion of the

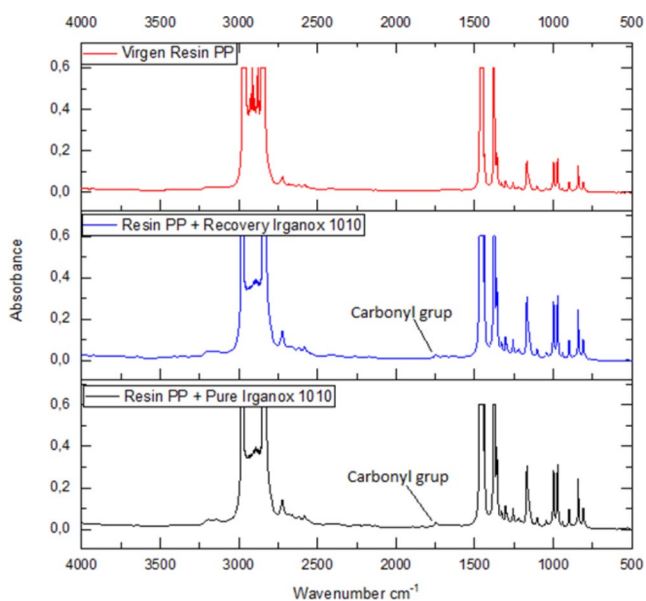


Fig. 6 IR spectra for virgin resin PP, virgin resin PP + recovery Irganox 1010 and virgin resin PP + pure Irganox 1010

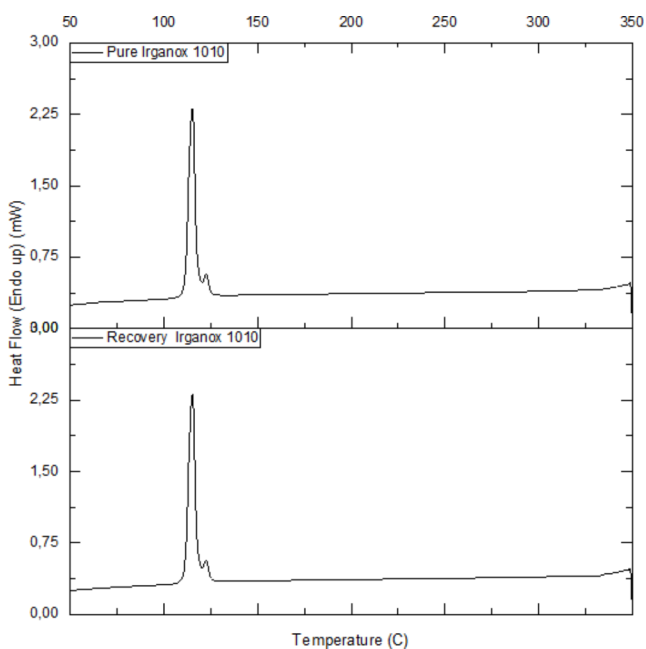


Fig. 7 DSC of recovered Irganox 1010 and pure Irganox 1010

recovered analyte and pure (Irganox) is shown, with a peak obtained between 100 and 125 °C, the highest value peak at 115.14 and 2.31 mW, indicating the melting temperature for the sample and a distinctive structure of the sample that can vary depending on the heat of fusion and analyte exposure [35–40]. At close to 340 °C, the degradation of the analyte is evident. The equality between Fig. 7 evidence the high purity of the recovered Irganox 1010.

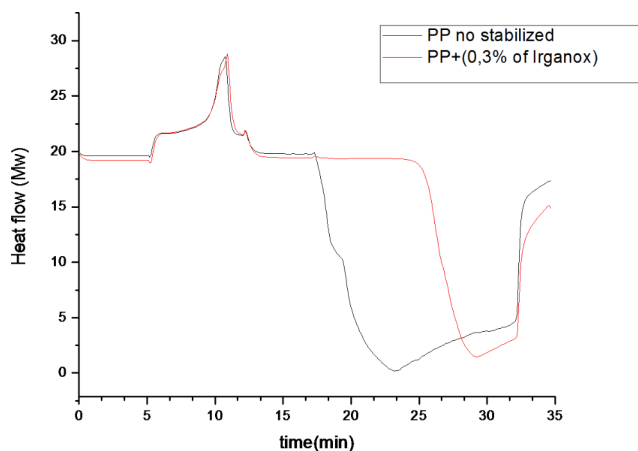


Fig. 8 DCS, OIT of PP and PP stabilized with Irganox 1010

Additivated Resin DSC

For the determination of the oxidation time, the changes in the slope of the curve generated by the DSC with respect to the estimated time and the heat flux are considered. As can be seen in Fig. 8, Firstly, it was observed a peak coming from an endothermic process, but after time and with the change of the atmosphere, a change in the slope of the curves is obtained and a new exothermic phenomenon is observed that corresponds to oxidation. The oxidation time corresponds to the time at which the change in this slope occurs, and for unstabilized PP it can be seen that a much lower value of induced oxidation time (OIT) is presented than when the PP has a certain amount of additive. The OIT value for the unstabilized PP is 0.7 min, taking as reference the change in slope at 17.3 min, and the OIT for the PP with the additive added is 8 min, which shows that the presence of the additive slows down the oxidation processes of PP and improves its thermal stability due to its coupling in the polymeric matrix and thanks to the fact that the additive reduces thermo-oxidation due to the presence of OH in its rings, which favors the elimination of free radicals.

TGA

A TGA was performed in order to study the thermal stability that the recovered Irganox gives to the PP. Figure 9 shows the results obtained from the change in mass as a function of temperature. From these results, the thermal degradation of the material is studied, and the main parameters of this analysis are determined [40–48].

For the pure and recovered Irganox 1010, a very similar weight loss trend is observed in the TGA. The degradation process in both Irganox is observed from 290 °C. The great similarity of the thermal performance of the recovered irganox 1010 and the pure one is directly related to

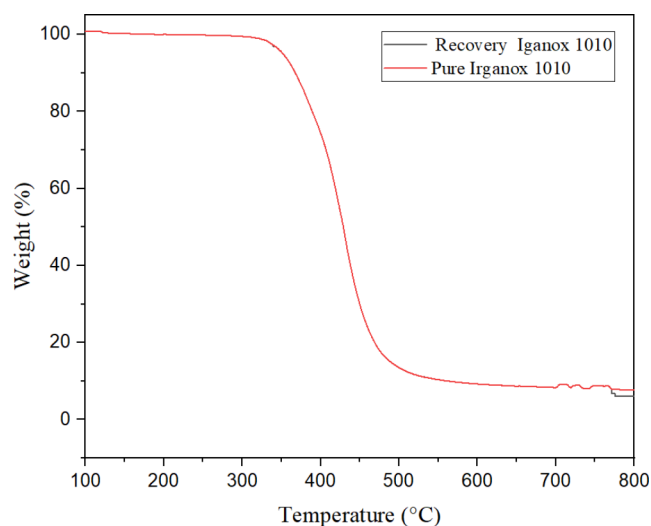


Fig. 9 TGA for Pure and recovery Irganox 1010. TGA and DTG for stabilized and unstabilized PP.

Table 2 Onset degradation temperatures (T5%) and the maximum degradation temperatures (Tmax)

Sample	T 5% [°C]	T 5% [°C]	% loss at 350 °C	% loss at 400° C
Virgin PP	373	460	2.5	14.0
Virgin PP+ Recovery Irganox 1010	377	460	1.9	12.3
Virgin PP+ pure Irganox 1010	376	460	1.8	12.5

the purity higher than 98% that was obtained in this recovered irganox. From the results obtained for the TGA, a very similar weight loss trend is observed between the PP and the PP with the added Irganox. The degradation process in both samples is observed after 290 °C, being slightly higher for the PP with Irganox 1010. Then, two temperature ranges were taken into consideration for further TGA study, from 250 to 350 °C and from 250 to 400 °C (Table 2). The PP loaded with caffeic acid resulted in a lesser weight loss, indicating a minor degradation effect than the studied antioxidants derived from petrochemical source. In addition, the weight loss in the material decreases with the addition of the additive, which shows that the recovered Irganox is capable of slowing down the degradation process in the PP sample even at low concentrations. The recovered additive has been adjusted to the PP matrix and has shown an improvement in the thermal stability of the material produced by the OH present in the phenols (additive) that stabilize the free radicals of the PP carbon.

Kinetic Parameters

The determination of the kinetic parameters to estimate the lifetime and the degree of degradation of the prepared thermoplastics were obtained using the Coats–Redfern and

Table 3 Ea values calculated by Coats and Horowitz models

Sample	Coats (Ea)	Horowitz (Ea)
Virgin PP	126	177
Virgin PP+ Recovery Irganox 1010	143	194
Virgin PP+ pure Irganox 1010	145	196

the Horowitz-Metzger methods [20]. The Coats–Redfern method was used for the determination of the pre-exponential factor (A) and the apparent activation energy (Ea, kJ mol⁻¹). The study of the kinetic parameters by TGA for the estimation of the polymer stabilization is common in literature and it has been widely used for different polymeric materials and experimental conditions [20]. Among all kinetic parameters calculated from the Arrhenius equation, apparent activation energy (Ea) is the most indicative one for comparison among materials in terms of their thermal stability. In this case, the Horowitz and Coats method has been used because they provide simple approaches to obtain information about the thermal and thermo-oxidative degradation of non-stabilized and stabilized-PP. Table 3 shows that both the Coats and Horowitz values increase significantly with the addition of recovered irganox 1010 and with pure irganox 1010. the comparison of the Ea between the pure irganox and the recovered one is not significant.

Conclusion

Industrial wastewater has been shown to be a source of various components that can affect the environment and people's health, but there is also evidence that it can be a source of compounds that are highly useful in the industry when they are extracted. Therefore, recovering this additive minimizes the environmental impact and becomes a good option for the circular economy. This study shows how the recovery of phenolic compounds (Irganox 1010) used as additives in PP production can recover more than 98% with high purity. The recovery and incorporation of Irganox 1010 in the PP matrix showed a significant improvement in the thermal and thermo-oxidative stability of PP. PP without thermal stabilizers does not have an important final application, since the material would completely degrade in the extrusion stages. Therefore, recovering this Irganox 1010 with these high levels of purity demonstrates an important methodology to apply in the industrial sector and promote sustainable sources of raw materials.

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Statements & Declarations

Conflict of Interest The authors declare that there is no conflict of interest and that the data presented is completely their own.

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

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