

Article

Quantification of Irgafos P-168 and Degradative Profile in Samples of a Polypropylene/Polyethylene Composite Using Microwave, Ultrasound and Soxhlet Extraction Techniques

Joaquín Hernández-Fernández ^{1,2,3,*} , Jaime Pérez-Mendoza ⁴ and Rodrigo Ortega-Toro ^{5,*}

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

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

³ Department of Natural and Exact Science, Universidad de la Costa, Barranquilla 080002, Colombia

⁴ Complex Fluid Engineering and Food Rheology Research Group (IFCRA), Food Engineering Department, Universidad de Cartagena, Cartagena de Indias 130015, Colombia; jperez@unicartagena.edu.co

⁵ Food Packaging and Shelf-Life Research Group (FP&SL), Food Engineering Department, Universidad de Cartagena, Cartagena de Indias 130015, Colombia

* Correspondence: jhernandezf@unicartagena.edu.co (J.H.-F.); rortegap1@unicartagena.edu.co (R.O.-T.)

Abstract: In polypropylene/polyethylene composite (C-PP/PE) production, stabilizing additives such as Irgafos P-168 are essential as antioxidant agents. In this study, an investigation was carried out that covers different solid–liquid extraction methods (Soxhlet, ultrasound, and microwaves); various variables were evaluated, such as temperature, extraction time, the choice of solvents, and the type of C-PP/PE used, and the gas chromatography coupled to mass spectrometry (GC-MS) technique was used to quantify the presence of Irgafos P-168 in the C-PP/PE samples. The results revealed that microwave extraction was the most effective in recovering Irgafos P-168. A recovery of 96.7% was achieved when using dichloromethane as a solvent, and 92.83% was achieved when using limonene as a solvent. The ultrasound technique recovered 91.74% using dichloromethane and 89.71% using limonene. The Soxhlet extraction method showed the lowest recovery percentages of 57.39% using dichloromethane as a solvent and 55.76% with limonene, especially when the C-PP/PE was in the form of pellets. The degradation products that obtained the highest degradation percentages were Bis (di-*tert*-butyl phenyl) phosphate and Mono (di-*tert*-butyl phenyl) phosphate using the microwave method with dichloromethane as a solvent and PP in film. Finally, the possible mechanisms for forming the degradation compounds of Irgafos P-168 were postulated.

Keywords: polypropylene/polyethylene composite (C-PP/PE); Irgafos P-168; extraction methods



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1. Introduction

In producing polypropylene/polyethylene composite (C-PP/PE) films, additives improve and modify the material's properties. These additives play a fundamental role in optimizing physical, chemical, and mechanical characteristics, allowing them to be adapted to the specific needs of various industrial applications, among which food packaging and packaging stand out [1–14]. Stabilizing additives, such as antioxidants and UV stabilizers, protect C-PP/PE from oxidation and degradation caused by environmental factors [14]. Fluidity and slip modifier additives improve film processing, reducing friction and facilitating slip in the production stages [14,15]. Plasticizers increase the flexibility and elasticity of the films, while reinforcing additives improve the mechanical resistance and rigidity of the material. Additionally, color additives and pigments provide a wide range of aesthetic options. These additives are essential to obtain high-quality, high-performance polypropylene and C-PP/PE films adapted to the needs of different industrial sectors [16–26].

One of the antioxidant additives in most significant demand in the production of C-PP/PE films is (tris (2,4-di-tert-butylphenyl) phosphite) known as Irgafos P-168; it is a trifunctional ester of phosphoric acid, which contains three phenyl groups substituted with butyl groups in specific positions [27]. This structural configuration (Figure 1) gives Irgafos P-168 antioxidant properties, allowing it to act as a free radical scavenger and delay oxidation processes that can lead to the degradation of C-PP/PE. Incorporating Irgafos P-168 in the molten polymer during the extrusion and thermomolding processes improves thermal stability, protecting it from oxidation and degradation [14]. These characteristics are essential to achieve optimal appearance and obtain stable physical properties, guaranteeing more excellent durability and useful life of the products [28].

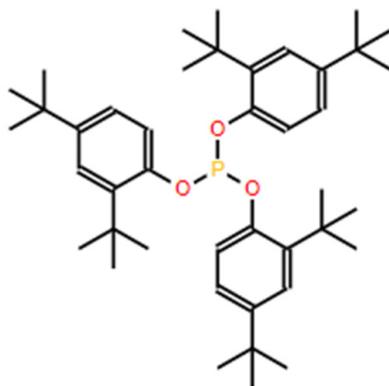


Figure 1. Molecular structure of the antioxidant additive Irgafos P-168.

Previously, various extraction techniques have been used for Irgafos P-168 and other antioxidant additives in C-PP/PE and PP films [29,30]. These techniques include Soxhlet extraction, ultrasound-assisted extraction (UAE), and more advanced techniques such as microwave-assisted extraction (MAE) and supercritical fluid extraction (SFE) [31–34]. Soxhlet extraction is a classic method where the sample is placed in a cell-shaped extraction cartridge, and a heating and cooling cycle is carried out. The solvent evaporates and condenses, efficiently extracting the antioxidant additives from the sample, but the method has certain limitations, such as long extraction times ranging from 6 h to 48 h and higher volumes of solvent required [35]. In contrast, the UAE uses ultrasonic waves to improve the extraction efficiency of antioxidant additives. This technique generates micro cavitation and turbulence in the solvent, accelerating extraction and offering promising results in shorter times [36]. Likewise, MAE, which stands out as a fast and efficient technique since it allows direct extraction in granulated or pelletized matrices using reduced volumes of solvent and without the need for exhaustive pretreatment of the samples, has proven to be effective in obtaining extraction results in significantly shorter times. In contrast, SFE uses a fluid in a supercritical state, which exhibits intermediate properties between a liquid and a gas. However, it offers better performance in selectivity and extraction efficiency; its application can be more complicated and expensive due to the need for specialized and expensive equipment [33–35].

It is essential to remember that solvents play a crucial role in extracting the additives in all these solid–liquid extraction techniques. Although organic compounds such as dichloromethane, cyclohexane, and chloroform are recognized for achieving high recovery percentages, their high toxicity represents a significant risk for the personnel involved in their handling and the environment in general [33–35]. Specifically, dichloromethane, also known as methylene chloride, is subject to use restrictions due to its harmful potential. Therefore, it is essential to select solvents that carefully ensure the extraction process's effectiveness, offer safety for human well-being, and minimize their environmental impact [28–32]. Limonene emerges as an up-and-coming option since its toxicity is considerably lower than that of traditional solvents [28–32].

Limonene C₁₀H₁₆ is a monocyclic hydrocarbon belonging to the class of terpenes. It has a highly aromatic structure, is hydrophilic, can dissolve a range of organic products, and is present in the peel of citrus fruits, especially lemons. There are two optical isomers of Limonene, d-Limonene and l-Limonene, and a racemic mixture that combines both isomers [28–32]. Its pleasant lemon aroma makes it an additive widely used in the food industry to add flavor and fragrance to various products. However, its applications go further, and it is also found in household, cosmetic, and pharmaceutical products, where it has been considered safe. In addition, studies have revealed that Limonene has anti-cancer properties [28–35]. In recent years, Limonene has also begun to be used as a green solvent since it is environmentally friendly and derived from natural sources. Limonene is biodegradable and non-toxic, which makes it an alternative to traditional solvents such as dichloromethane. It is safer and more ecological, minimizes the negative impact on ecosystems, and promotes more sustainable practices in the industry [28–33].

Unfortunately, the use of green solvents is still limited in the polymer industry for the extraction of additives such as Irgafos P-168, so in this research, extraction techniques assisted by microwaves, ultrasound, and Soxhlet will be used, using a method-sensitive microextraction coupled to gas chromatography, for the simultaneous determination of the concentration of Irgafos P-168 and degradation products in C-PP/PE samples. Three pretreatments of PP (ground, pellets, and films) will be carried out using a traditional solvent (dichloromethane) and a green solvent (Limonene). Multivariate analysis will evaluate performance, and the degradation products of Irgafos P-168 will be quantified to establish their relationship with the results of each extraction. The results of this research are essential to the scientific community, industry, and regulatory bodies involved in the extraction and characterization of Irgafos P-168 in polymeric matrices.

2. Materials and Methods

2.1. Reagents

The Irgafos P-168 was acquired from Shanghai Tixiai Co., Ltd. (Shanghai, China). Butylated hydroxytoluene (BHT) was also used as an internal standard provided by Campro Science GmbH (Berlin, Germany). Limonene (HPLC grade) was obtained from Scharlab (Barcelona, Spain). Hydrogen and nitrogen with 99.9999% purity were purchased from Linde (Cartagena, Colombia), and dichloromethane with 99.99% purity was used from Sigma Aldrich (Bangalore, India).

2.2. GC-MS Analysis

A specific method was designed using gas chromatography coupled with mass spectrometry (GC-MS) to evaluate the recoveries of the master mixture. The extracts obtained by solid–liquid extraction were analyzed by GC-MS, following the degradation products of each compound analyzed, together with an internal standard (BHT). These analyses were carried out using an Agilent 7890 gas chromatograph provided by Agilent JW Scientific (Diegem, Belgium). The chromatography was coupled to an Agilent 7000 GC-MS triple quadrupole (QQQ) mass spectrometer, equipped with an electron impact ionization (EI) source, and operated in selective ion monitoring (SIM) mode. The quadrupole and the ion source temperatures were maintained at 150 °C and 230 °C, respectively. The multiplier voltage was set to 2200 V. To improve the acquisition speed, three acquisition segments were programmed with different retention times (20, 15, and 20 ms, respectively). One microliter of extract was injected into a PTV injector in pulsed, splitless mode, with an injection temperature of 280 °C.

The column used in the gas chromatograph was a DB-5 ms of 30 m length, 0.25 mm internal diameter, and 0.25 µm film. The oven temperature was started at 60 °C for 3 min and then increased to 300 °C at a rate of 10 °C per minute, maintaining this temperature for 15 min. The total analysis execution time was 42 min. Helium was used as carrier gas at a constant flow of 1.0 mL per minute.

2.2.1. Prepare Irgafos 168 Calibration Standards and C-PP/PE Samples with Irgafos P-168 Preparation of the Curve for Calibration of the Chromatograph

Figure 2 shows how a stock solution of Irgafos P-168 at 10,000 ppm was prepared (by adding 10,000 mg of Irgafos P-168 in 1 L of Limonene) and an internal standard solution of butylated hydroxytoluene (BHT) at a concentration of 10,000 ppm. These solutions generated four samples with known concentrations of 500, 1000, 1500, and 2000 ppm.

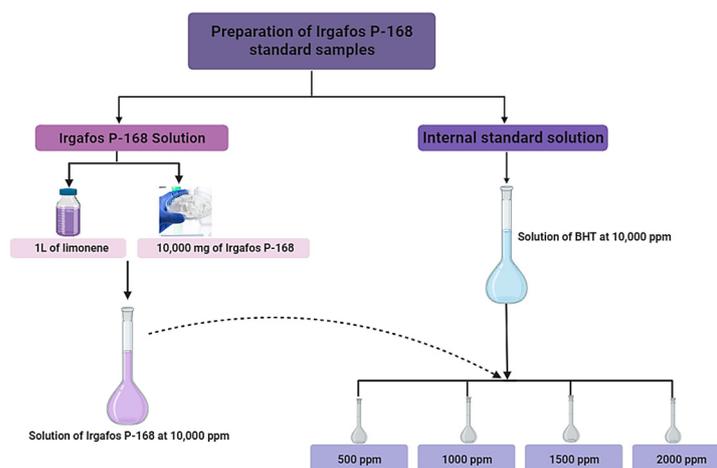


Figure 2. Preparation of Irgafos P-168 standard samples.

Preparation of the C-PP/PE Sample with Different Concentrations of Irgafos P-168

The C-PP/PE samples with Irgafos P-168 were prepared following the procedure described in Figure 3, which had the following stages: (1) 0.0, 0.5, 1, 1.5, and 2.0 g of Irgafos P-168 were weighed in quantities individually. (2) To each of the quantities of Irgafos P-168, 1 kg of virgin C-PP/PE resin was added. (3) Mixtures were premixed with a standard Prodex mixer, Henschel 115JSS, at 800 rpm for 7 min. (4) Next, each sample was mixed with a Welex-200 24.1 extruder equipped with five temperature zones in its path. The temperatures used were 190, 195, 200, 210, 210, and 220 °C. This process guaranteed uniform distribution of the mixture. (5) Finally, from each type of melt, 20 g of mass was fed into a CARVER 3895 hot press. In this CARVER machine, the samples were compressed until films 300 mm in diameter with a thickness of ≈ 100 μm were obtained. The resulting films in the experiment were identified as C-PP/PE (0 ppm of Irgafos P-168), C-PP/PE 2 (500 ppm of Irgafos P-168), C-PP/PE 3 (1000 ppm of Irgafos P-168), C-PP/PE 4 (1500 ppm of Irgafos P-168), and C-PP/PE 5 (2000 ppm of Irgafos P-168).

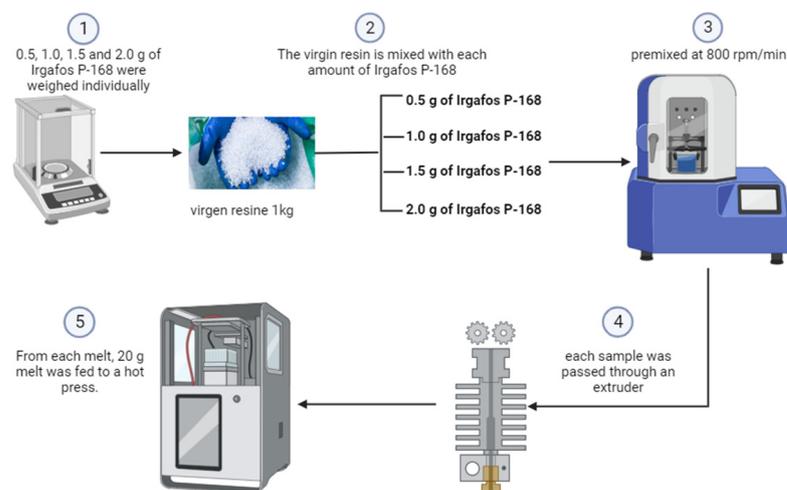


Figure 3. Preparation of C-PP/PE samples with different concentrations of Irgafos P-168.

Extraction of Irgafos P-168 in C-PP/PE Samples

Figure 4 presents the methodology used in this research to extract Irgafos P-168 from C-PP/PE samples in ground form, pellets, and films, to which Irgafos P-168 had been added. Solid–liquid extractions were carried out using two different solvents, dichloromethane and Limonene. These extractions were performed using three methods: Soxhlet, ultrasound (conventional laboratory sonic bath), and microwave oven (high-power programmable laboratory microwave oven), and a mass-coupled gas chromatograph was used to quantify the concentration of Irgafos P-168 and the degradation products present in the C-PP/PE film samples. In preliminary tests, it was identified that 90, 50, and 117 °C were the optimal temperatures for working with Soxhlet, ultrasound, and microwave, respectively. Therefore, this variable was left fixed in our experimental design, and thus, we could evaluate how other variables affect the extraction efficiency.



Figure 4. Extraction of Irgafos P-168 by Soxhlet, ultrasound, and microwave and quantification by GC-MS.

For microwave extraction, 5 g of C-PP/PE resin was extracted using a solution of dichloromethane and Limonene. It was determined that heating the solution in the microwave oven at 25–50% power for 45 min, stirring every 5 min, was sufficient to extract the antioxidant. Four different extractions were performed with the resin, pellets, and ground C-PP/PE, and the average results of the ultrasound, Soxhlet, and microwave extractions are presented in Table 1 and Figure 5. Concentrations are expressed in parts per million (ppm). Percentages indicate recovery relative to an initial concentration of 500 ppm.

Table 1. Experimental design of the extraction of Irgafos P-168 with different extraction techniques, different solvents, and different types of C-PP/PE.

Technique	Time (min)	Temperature	Solvent	Form of C-PP/PE	Irgafos 168 Recovery Rate (%)			
					C-PP/PE 2	C-PP/PE 3	C-PP/PE 4	C-PP/PE 5
					500	1000	1500	2000
Soxhlet	1440	90	Dichloromethane	Pellets	69.98	71.76	73.56	73.83
Soxhlet	1440	90	Dichloromethane	Film	72.44	76.38	76.04	77.42
Soxhlet	1440	90	Dichloromethane	Ground	77.4	79.92	77.35	79.88

Table 1. Cont.

Technique	Time (min)	Temperature	Solvent	Form of C-PP/PE	Irgafos 168 Recovery Rate (%)			
					C-PP/PE 2	C-PP/PE 3	C-PP/PE 4	C-PP/PE 5
					500	1000	1500	2000
Soxhlet	720	90	Dichloromethane	Pellets	47.52	61.14	61.15	59.75
Soxhlet	720	90	Dichloromethane	Film	54.68	64.42	64.67	62.81
Soxhlet	720	90	Dichloromethane	Ground	59.96	69.36	67.53	67.46
Soxhlet	1440	90	Limonene	Pellets	68.04	69.9	72.47	72.21
Soxhlet	1440	90	Limonene	Film	69.68	74.5	74.71	76.87
Soxhlet	1440	90	Limonene	Ground	74.44	77.92	75.13	79.14
Soxhlet	720	90	Limonene	Pellets	45.36	59.52	59.4	58.76
Soxhlet	720	90	Limonene	Film	51.84	61.96	63.41	61.15
Soxhlet	720	90	Limonene	Ground	56.56	67.76	65.59	66.09
Ultrasound	90	50	Dichloromethane	Pellets	73.84	76.2	79.25	77.83
Ultrasound	90	50	Dichloromethane	Film	75.84	79.62	84.72	82.36
Ultrasound	90	50	Dichloromethane	Ground	92.04	88.9	93.24	92.76
Ultrasound	60	50	Dichloromethane	Pellets	65.48	66.3	67.77	66.09
Ultrasound	60	50	Dichloromethane	Film	67.92	71.8	73.8	70.41
Ultrasound	60	50	Dichloromethane	Ground	78.84	75.46	78.89	78.96
Ultrasound	90	50	Limonene	Pellets	70	74.94	77.11	76.24
Ultrasound	90	50	Limonene	Film	72.84	78.24	82.65	80.23
Ultrasound	90	50	Limonene	Ground	89.56	87	92.05	90.23
Ultrasound	60	50	Limonene	Pellets	62.6	64.3	66.25	64.31
Ultrasound	60	50	Limonene	Film	65.56	69.86	71.88	69.87
Ultrasound	60	50	Limonene	Ground	75.88	73.08	76.73	76.25
Microwave	45	117	Dichloromethane	Pellets	77.4	78.32	82.73	79.74
Microwave	45	117	Dichloromethane	Film	83.6	83.66	88.8	83.91
Microwave	45	117	Dichloromethane	Ground	96.2	94.34	97.01	96.71
Microwave	25	117	Dichloromethane	Pellets	70.32	69.7	72.07	68.25
Microwave	25	117	Dichloromethane	Film	73.88	74.04	77.35	73.19
Microwave	25	117	Dichloromethane	Ground	84.72	78.54	80.64	81.86
Microwave	45	117	Limonene	Pellets	74.4	76.48	81.36	78.58
Microwave	45	117	Limonene	Film	80.32	81.84	87.09	82.48
Microwave	45	117	Limonene	Ground	91.88	89.78	94.72	94.94
Microwave	25	117	Limonene	Pellets	65.12	66.98	70.57	65.52
Microwave	25	117	Limonene	Film	68.4	71.48	75.32	71.23
Microwave	25	117	Limonene	Ground	78.44	75.44	78.91	80.09

For the ultrasonic bath, 3 g of C-PP/PE placed in a 20 mL vial were used. Next, 10.0 mL of an internal standard solution was added using a 5.0 mL micropipette, as shown in Figure 4. Each test was replicated five times, and sonication was carried out for three hours in an ultrasonic bath, keeping the temperature under control, below 50 °C. After completion of sonication, the vials were removed from the bath and allowed to stand for 10 min before filtration of the extracted Irgafos P-168 sample solutions using disposable PTFE syringe filters.

The extraction was carried out in three ways: ground C-PP/PE, pellets, and films. In the case of ground C-PP/PE, the extraction lasted for 90 min, while, for C-PP/PE pellets and films, it was carried out for 60 min in the ultrasonic bath. During extraction, the solution was shaken for at least 30 s every 10 min.

Notably, the microwave oven was revealed as a fast and effective method to extract Irgafos P-168 from the crushed resin, while the ultrasonic bath provided an economical and relatively fast alternative for extracting the additives. In contrast, the Soxhlet extraction method with these C-PP/PE resins required at least 7 h to extract most of the additives. In this study, Soxhlet extraction was extended for 1440 and 720 min, suggesting that it would possibly require more than 24 h to recover the additive completely.

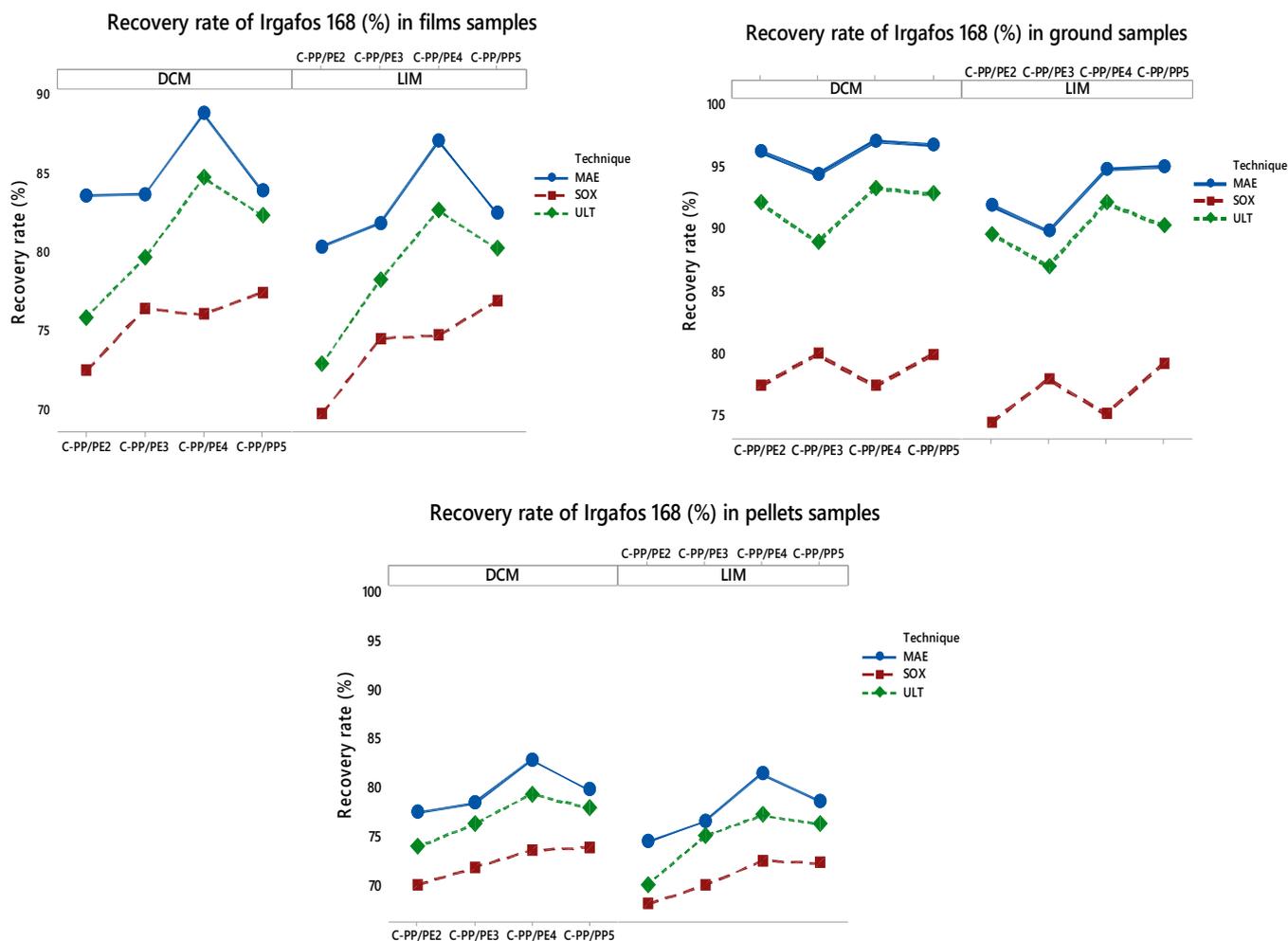


Figure 5. Graphic representation of the extraction of Irgafos P-168 with different techniques, different solvents, and different types of C-PP/PE.

2.3. Multivariate Graphical Analysis

This study conducted a graphical analysis to examine the recovery of the antioxidant Irgafos P-168 in the C-PP/PE samples. Minitab statistical software, widely recognized for its ability to perform advanced statistical analyses, was used to carry out this analysis. Since the study involves multiple variables, such as the different extraction techniques (Soxhlet, ultrasound, and microwave), the solvents used (dichloromethane and Limonene), and the types of C-PP/PE (ground, pellets, and films), a multivariate graphical analysis was performed. This made it possible to identify the existing relationships between the various extraction techniques, the solvents, and the C-PP/PE forms to extract Irgafos P-168.

3. Results and Discussion

3.1. Quantification and Recovery of the Additive Irgafos P-168 by GC

For the analysis of Irgafos P-168 in the C-PP/PE samples, an internal standard method was implemented to check the validity of the GC-MS method. It should be noted that both the standard solutions and the samples were analyzed in duplicate to guarantee the precision of the results. The calibration curve demonstrated excellent linearity within the established range, with a coefficient of determination greater than 0.999.

In the experimentation of this study, four different concentrations of Irgafos P-168 solutions were prepared using an internal standard (500, 1000, 1500, 2000 ppm). Following the procedure described in Section 2, GC-MS analyses were performed on Irgafos P-168

extracts obtained from C-PP/PE samples in various forms, such as ground C-PP/PE, C-PP/PE pellets, and C-PP/PE film.

Multiple extraction techniques were used to evaluate the recovery of Irgafos P-168, including Soxhlet, ultrasound, and microwave, along with two different solvents, dichloromethane, and Limonene. In addition, different forms of C-PP/PE were worked with, that is, ground, pellets, and film, and the extraction times were varied. To analyze the results effectively, a variability graph was constructed that allowed the identification of differences in the means and variations in antioxidant recovery at the combined levels (Figure 6).

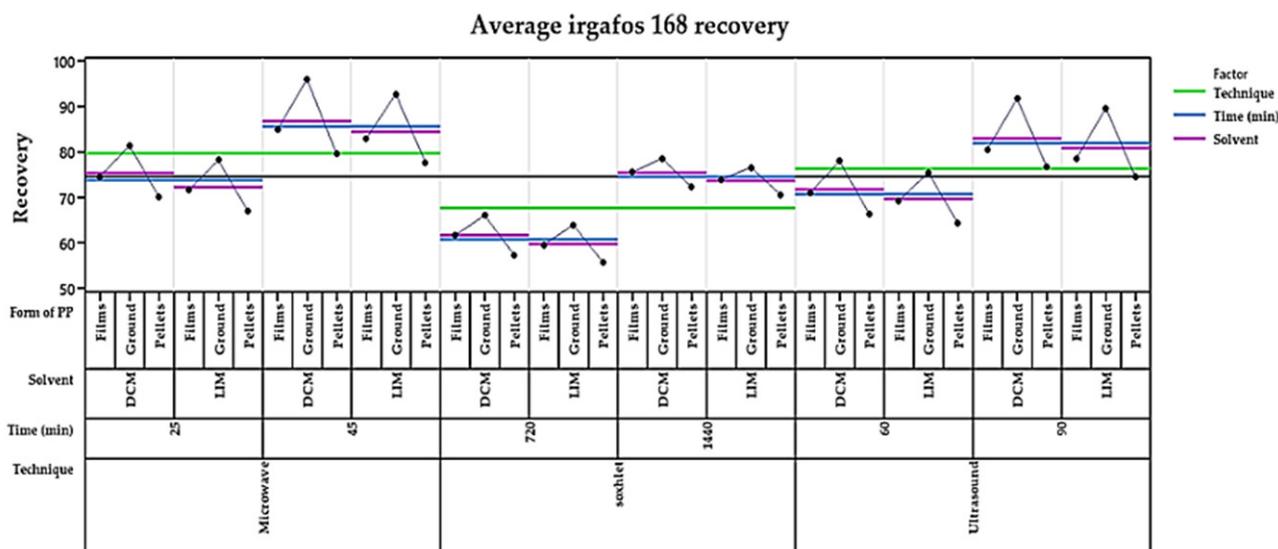


Figure 6. Average recovery of Irgafos P-168 for microwave, Soxhlet, and ultrasound with dichloromethane (DCM) and Limonene (LIM).

Figure 6 shows the relationship between the recovery percentage of Irgafos P-168 and the previously mentioned variables. The results highlight that the microwave extraction technique achieves the highest recovery percentages when applied for 45 min and ground C-PP/PE was used. Furthermore, no significant differences were observed between traditional and green solvents since the recovery percentages remained close. Specifically, dichloromethane recovered 96.07%, while Limonene obtained 92.83%.

The ultrasound technique obtained optimal results with an extraction time of 90 min, using ground C-PP/PE with the traditional solvent dichloromethane (91.74%) and Limonene (89.71%). The difference between these solvents remains minimal, regardless of the extraction technique used.

Lastly, the extraction performed by Soxhlet obtained lower recovery results than the microwave and ultrasound techniques. The highest percentages achieved with this technique occurred at 1440 min, 78.64% using dichloromethane as a solvent and ground C-PP/PE, and 76.66% with Limonene in ground C-PP/PE.

With everything mentioned above, it can be stated that using ground C-PP/PE instead of forms of C-PP/PE in films and pellets can improve the recovery results of Irgafos P-168 due to the larger contact surface, more excellent permeability, smaller size of particles, and greater homogeneity of the material. Furthermore, the results indicate that better recoveries were obtained using microwave extraction than ultrasound and Soxhlet techniques. This can be explained by the microwave extraction technique, which selectively heats the solvent and the sample. This allows for faster and more efficient heat transfer, speeding up the extraction process. By contrast, ultrasound and Soxhlet techniques may require more time to reach the appropriate temperature and achieve complete extraction, as demonstrated in the experimental design, since Soxhlet extraction requires 1440 min to achieve good recoveries. They are significantly below the recovery percentages obtained by microwave, which only

took 45 min. Another relevant aspect that supports the effectiveness of the microwave extraction technique is its ability to generate more intense agitation and turbulence in the sample. This improved agitation facilitates the interaction between the solvent and the analyte, thus simplifying the extraction of Irgafos P-168 and improving recovery efficiency. As is known, the microwave extraction technique achieved comparable or better results in a shorter extraction time compared to ultrasound and Soxhlet techniques. A shorter extraction time can minimize analyte degradation or loss and improve recovery, as seen in Section 2. In addition, it allows greater control of extraction conditions, such as temperature and pressure. This allows conditions to be optimized to maximize the recovery of Irgafos P-168 and minimize any possible interference or degradation of the analyte.

The dichloromethane solvent showed higher recovery percentages; however, the difference was insignificant enough to rule out Limonene as a green solvent option completely. In these cases, it is essential to consider Limonene's additional benefits, such as lower environmental impact and toxicity. The choice of solvent depends on other factors, such as current environmental regulations, specific application requirements, and personal or company preferences. Choosing a solvent such as Limonene is an ideal option for those who value sustainability and seek to minimize environmental impact.

In previous studies, Camacho et al. [36] have already used microwave extraction to evaluate the quality of resins such as polypropylene and low-density polyethylene (LDPE) in recycled resins and successfully extracted phenolic antioxidants such as Irgafos P-168 and Irganox 1010 using a mixture of 50/50 cyclohexane and isopropanol solvents, obtaining high recovery percentages of 97% for Irgafos P-168 and 93% for Irganox 1010. In addition, it is essential to mention that short extraction times of 30, 45, and 60 min were used with extraction temperatures of 70, 100, and 120 °C in the development of the method.

The previously mentioned study and the present research work have achieved high recovery percentages by applying various techniques and solvents. Within the framework of this research, some recovery percentages have been obtained that exceed the 90% threshold in the case of the conditions evaluated by microwaves and ultrasound, using both solvents, different extraction times, and different forms of the polymer. It is essential to highlight that the experimental conditions have differed between these studies, including aspects such as the type of polymer used, the particle size, the solvent combinations, and the time intervals used in the extraction process. These variations influence the results, making it difficult to compare the investigations directly.

3.2. Identification of Irgafos P-168 by Gas Chromatography Coupled to Mass Spectrometry (GC-MS) Analysis

The primary purpose of extracting Irgafos P-168 was to obtain the maximum possible amount of the original substance while minimizing the presence of relevant contaminants. However, it is crucial to consider that during this process, there is a possibility of Irgafos P-168 experiencing degradation, which could result in a decrease in recovery percentages. To address this concern, subsequent analyses of the Irgafos P-168 recovered in the extractions were conducted using gas chromatography coupled with mass spectrometry (GC-MS) to examine the potential formation of degradation products. The degradation products generated may pose challenges both in their recovery and detection during the analytical process. The application of the GC-MS technique allowed for the precise identification of these degraded products, thereby providing crucial information to assess whether Irgafos P-168 had undergone significant degradation. When interpreting the obtained data, previous knowledge that the analyzed compounds were specific degradation products of Irgafos P-168 was taken into account (Figure 7). These research findings are of paramount importance in understanding the potential effects of degradation on the quality and integrity of the compound. Furthermore, they significantly contribute to advancing knowledge in this field by providing a deeper understanding of degradation processes and their implications in the practical application of Irgafos P-168.

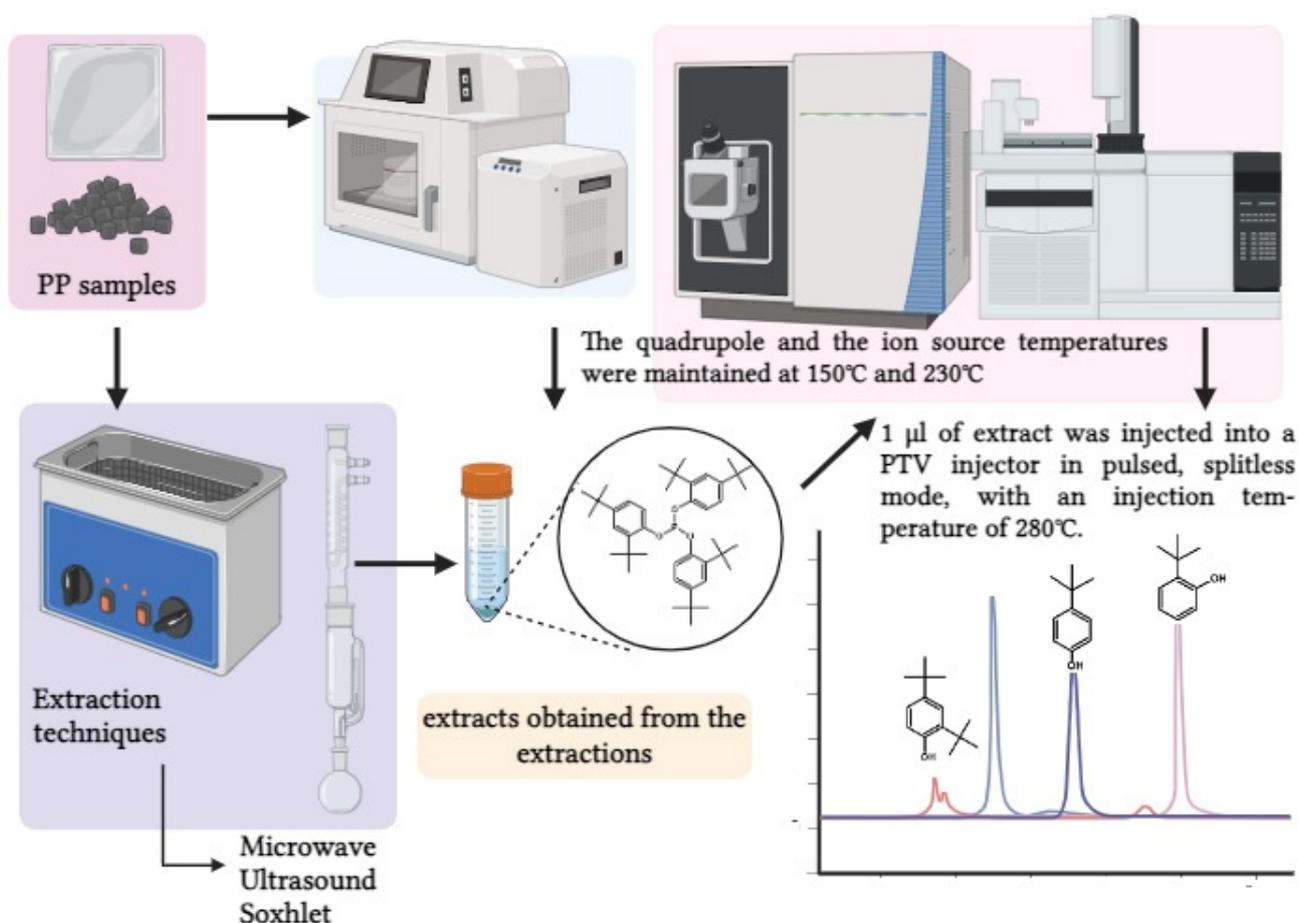


Figure 7. Identification of Irgafos P-168 by gas chromatography coupled to mass spectrometry (GC-MS) analysis.

Antioxidants play a crucial role in preserving copolymers like C-PP/PE, posing a significant challenge at the industrial level when they undergo thermo-oxidative degradation. This phenomenon not only compromises the durability and physical integrity of the polymer but also holds significant implications given its final application in direct food contact packaging. In this context, Irgafos P-168 is susceptible to oxidative degradation during solid–liquid extraction processes, especially in the presence of specific solvents such as Limonene and dichloromethane. This vulnerability arises from the chemical properties of Irgafos P-168 and its interaction with these mentioned solvents. During extractions, Irgafos P-168 may be exposed to environmental conditions conducive to oxidation, including the presence of oxygen and variations in temperature. Solvents like Limonene and dichloromethane can exacerbate this process by dissolving and transporting Irgafos P-168, thereby increasing its exposure to oxidative conditions. The oxidation or degradation of Irgafos P-168 during these extractions can have significant implications for its efficacy and quality. The resulting degradation products may be challenging to detect and recover, potentially impacting the purity and effectiveness of Irgafos P-168 in its final application.

Therefore, it is imperative to consider the susceptibility of Irgafos P-168 to oxidation or degradation when conducting solid–liquid extractions involving this compound along with solvents such as Limonene and dichloromethane. It is necessary to implement appropriate measures to minimize exposure to conditions that promote degradation and ensure the compound's integrity, both in industrial and research applications. Furthermore, it is important to note that the oxidative degradation of Irgafos P-168 can result in the formation of compounds with different properties, such as the generation of more polar compounds. These modified compounds may have a lower affinity for the solvents used

in extraction, which could hinder their separation from the C-PP/PE polymer and, consequently, reduce the extraction yield. Considering various factors that can influence the oxidative degradation of Irgafos P-168, such as temperature, the presence of catalysts, the duration of the extraction process, and the storage conditions of the C-PP/PE copolymer, is essential. Increased oxidative degradation of Irgafos P-168 may indicate a less efficient extraction process and, therefore, lower yield. Therefore, measures should be taken to minimize the oxidative degradation of Irgafos P-168 during the extraction process and the storage of the copolymer, in order to optimize extraction performance. The results of this study suggest that measuring the degree of oxidative degradation of Irgafos P-168 in the copolymer indirectly provides an assessment of the extraction performance of the compound in said polymer.

An illustration is provided in Figure 8 to clarify the degradation processes, showing how the breaking of the (PO) bond and the tert-butyl methyl diphenyl groups complicates the complete recovery of Irgafos P-168. This difficulty arises because a part of the molecule is lost due to fragmentation, leading to the formation of molecules with properties different from the original antioxidant. Additionally, Table 2 presents a detailed profile of the degradation of Irgafos P-168. This profile includes the recovery percentage of each compound obtained through the fragmentation of the crucial bonds present in the compound's structure. This detailed information provides a more comprehensive view of the resulting degradation products and their respective recovery rates, contributing to a deeper understanding of the effects of degradation on the original compound.

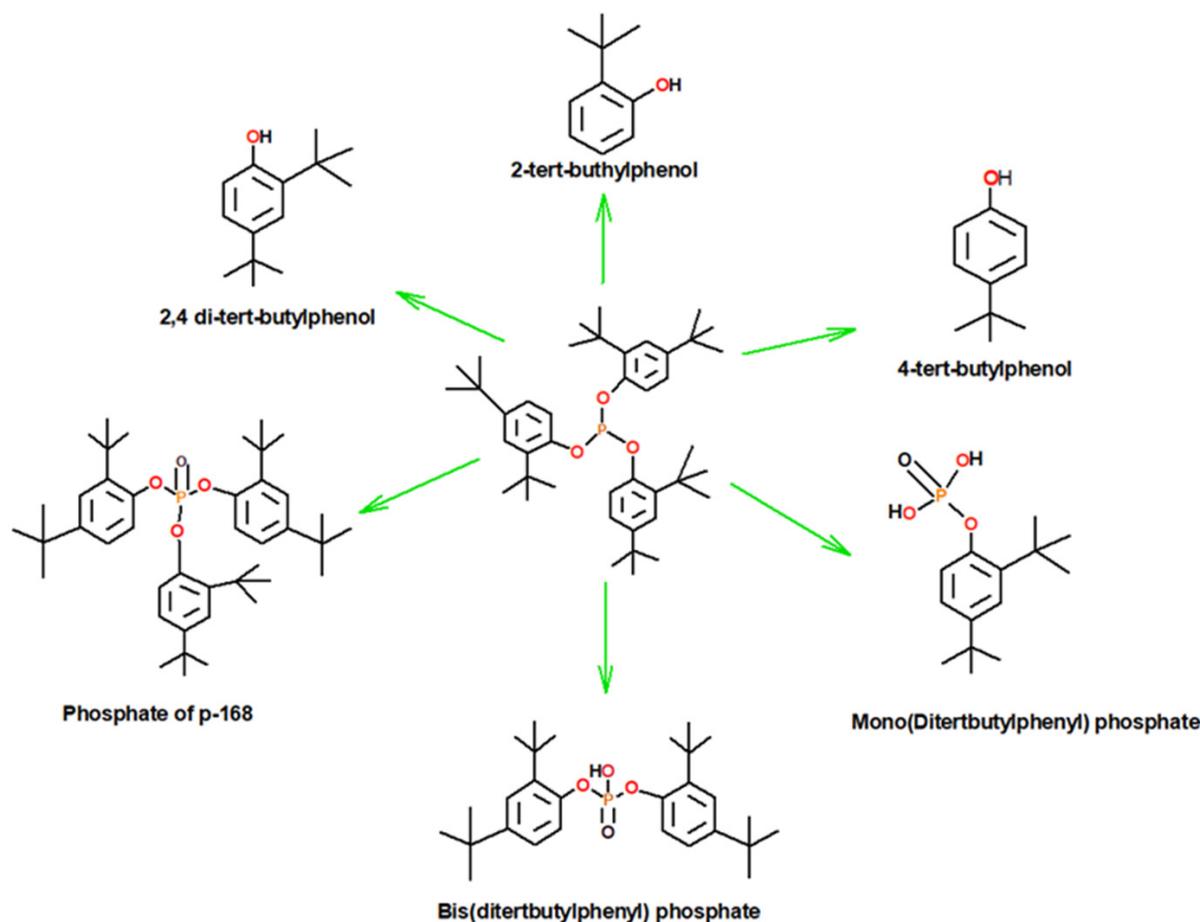


Figure 8. Recovered Irgafos P-168 fragmentation mechanism.

Table 2. Degradation profile of Irgafos P-168 in different solvents.

% Area under the Degradation by-Product Curve P-168											
Technique	Time (min)	Temperature	Solvent	Form of C-PP/PE	2,4-Di-tertbutylphenol	2-Tert-butylphenol	4-Tert-butylphenol	Phosphate of P-168	Bis(di-tertbutylphenyl) Phosphate	Mono(di-tertbutylphenyl) Phosphate	P-168
Soxhlet	1440	90	Dichloromethane	Pellets	0.6	0.5	0.1	0.4	0.7	0.9	72.28
Soxhlet	1440	90	Dichloromethane	Film	0.9	0.8	0.9	0.9	1.2	1.3	75.57
Soxhlet	1440	90	Dichloromethane	Ground	0.6	0.6	0.15	0.51	0.7	0.9	78.64
Soxhlet	720	90	Dichloromethane	Pellets	0.25	0.15	0.06	0.1	0.31	0.42	57.39
Soxhlet	720	90	Dichloromethane	Film	0.41	0.38	0.52	0.67	0.82	0.69	61.64
Soxhlet	720	90	Dichloromethane	Ground	0.28	0.17	0.1	0.11	0.33	0.46	66.08
Soxhlet	1440	90	Limonene	Pellets	0.42	0.38	0.84	0.31	0.62	0.82	70.65
Soxhlet	1440	90	Limonene	Film	0.82	0.76	0.84	0.79	0.95	1.12	73.94
Soxhlet	1440	90	Limonene	Ground	0.52	0.53	0.09	0.37	0.58	0.86	76.66
Soxhlet	720	90	Limonene	Pellets	0.18	0.07	0.01	0.08	0.19	0.31	55.76
Soxhlet	720	90	Limonene	Film	0.32	0.29	0.41	0.53	0.71	0.46	59.59
Soxhlet	720	90	Limonene	Ground	0.15	0.12	0.06	0.08	0.24	0.34	64.00
Ultrasound	90	50	Dichloromethane	Pellets	0.72	0.68	0.15	0.47	0.82	0.97	76.78
Ultrasound	90	50	Dichloromethane	Film	0.96	0.87	0.98	0.96	1.34	1.52	80.64
Ultrasound	90	50	Dichloromethane	Ground	0.68	0.71	0.24	0.64	0.82	1.12	91.74
Ultrasound	60	50	Dichloromethane	Pellets	0.29	0.19	0.12	0.18	0.41	0.46	66.41
Ultrasound	60	50	Dichloromethane	Film	0.52	0.42	0.67	0.72	0.86	0.72	70.98
Ultrasound	60	50	Dichloromethane	Ground	0.37	0.27	0.18	0.16	0.42	0.52	78.04
Ultrasound	90	50	Limonene	Pellets	0.52	0.47	0.96	0.41	0.76	0.92	74.57
Ultrasound	90	50	Limonene	Film	0.92	0.78	0.86	0.85	0.99	1.24	78.49
Ultrasound	90	50	Limonene	Ground	0.57	0.55	0.12	0.41	0.64	0.96	89.71
Ultrasound	60	50	Limonene	Pellets	0.23	0.12	0.08	0.14	0.23	0.41	64.37
Ultrasound	60	50	Limonene	Film	0.42	0.34	0.53	0.64	0.83	0.52	69.29
Ultrasound	60	50	Limonene	Ground	0.19	0.18	0.11	0.12	0.34	0.38	75.49
Microwave	45	117	Dichloromethane	Pellets	0.82	0.75	0.19	0.62	0.99	1.24	79.55
Microwave	45	117	Dichloromethane	Film	1.34	0.99	1.34	1.25	1.76	1.75	84.99
Microwave	45	117	Dichloromethane	Ground	0.82	0.96	0.37	0.75	0.96	1.34	96.07
Microwave	25	117	Dichloromethane	Pellets	0.38	0.41	0.33	0.42	0.66	0.67	70.08
Microwave	25	117	Dichloromethane	Film	0.71	0.57	0.81	0.96	1.12	0.96	74.61
Microwave	25	117	Dichloromethane	Ground	0.51	0.34	0.41	0.38	0.52	0.74	81.44
Microwave	45	117	Limonene	Pellets	0.57	0.51	1.08	0.48	0.82	0.99	77.71
Microwave	45	117	Limonene	Film	0.96	0.86	0.97	0.96	1.12	1.34	82.93
Microwave	45	117	Limonene	Ground	0.66	0.67	0.24	0.51	0.66	0.98	92.83
Microwave	25	117	Limonene	Pellets	0.29	0.18	0.11	0.16	0.29	0.47	67.05
Microwave	25	117	Limonene	Film	0.45	0.31	0.55	0.69	0.89	0.61	71.61
Microwave	25	117	Limonene	Ground	0.23	0.22	0.16	0.19	0.38	0.41	78.22

3.3. Determination of the Thermo-Oxidative Degradation Products of Irgafos P-168

Based on the results obtained previously, we present the possible mechanisms of the degradation of Irgafos P-168 in Figures 9–14, which exhibit the formation processes of each of the products resulting from the thermo-oxidative degradation. All these mechanisms share the characteristic of developing in conditions that involve the presence of hydrogen and oxygen radicals in abundance, which occur in the tertiary carbons present in the polypropylene structure [34–36].

3.3.1. Mechanism of the Phosphate Product of Irgafos P-168

In Figure 8, the mechanism carried out in the first two stages involves the typical steps of all the other degradation products since they show how the hydrogen radicals that cause the degradation of Irgafos P-168 are formed. The first thing that occurs is a homolytic cleavage in the tertiary carbon of C-PP/PE caused by temperature and the presence of the peroxide bond (OO), so said carbon undergoes oxidation, and at the same time, the hydrogen radical (H·) returns to stabilize by uniting this time with oxygen. Subsequently, a homolytic cleavage occurs again between the peroxy bond (OO), which on this occasion generates a hydroxyl radical (OH·) that attacks the phosphorus of Irgafos P-168, generating a double bond with it once again. It generates homolytic cleavage by hydrogen, stabilizing the polymer chain's carbon.

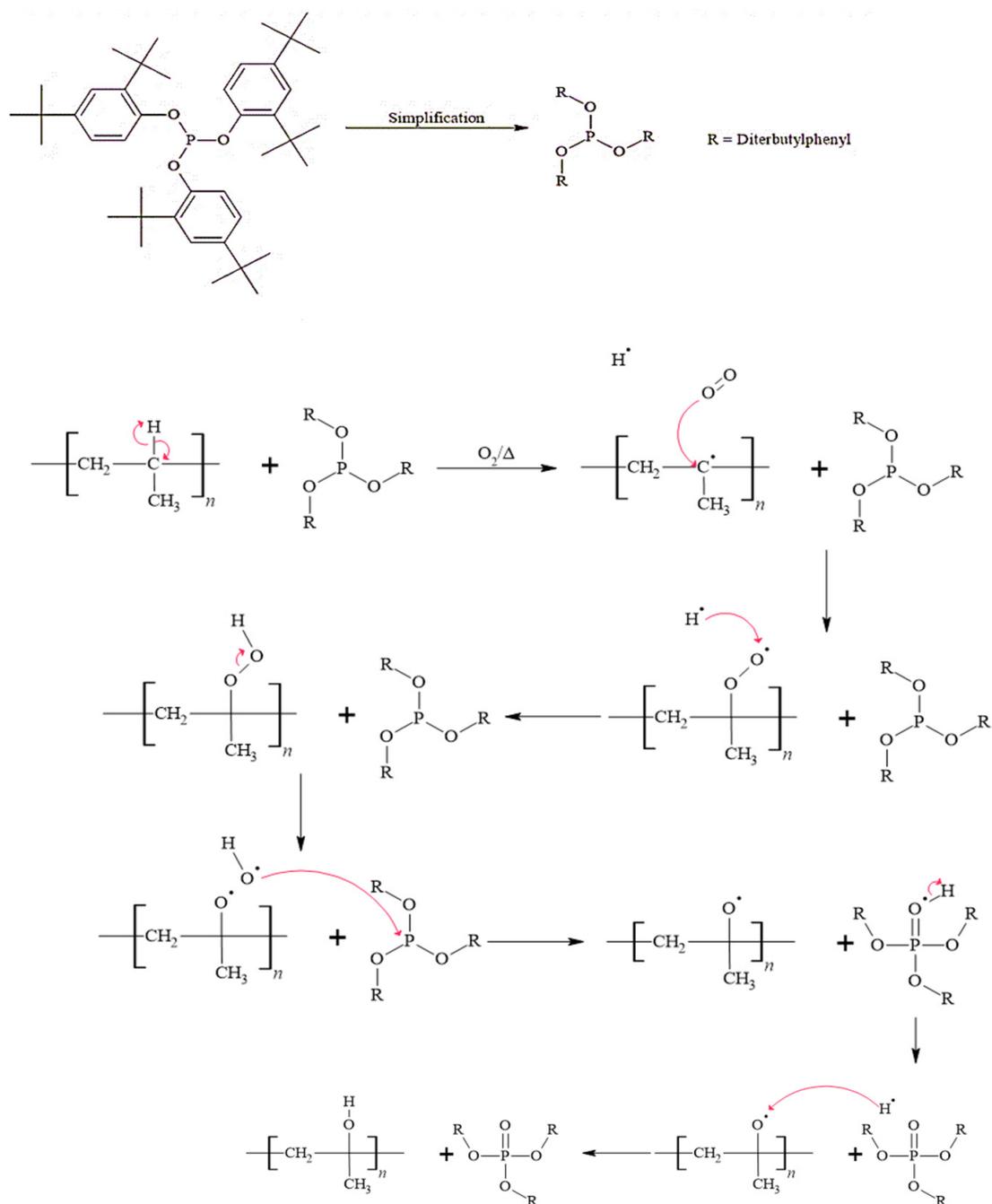


Figure 9. Formation mechanism of Irgafos P-168 Phosphate.

3.3.2. Mechanism of Formation of 2,4-Di-tert-butylphenol

Figure 10 represents the process by which the degradation product previously obtained, Irgafos P-168 Phosphate, undergoes a homolytic breakdown due to abundant hydrogen radicals (H^\cdot) and the influence of temperature. This cleavage occurs between the PO bond, forming an alkoxy radical (RO^\cdot). Simultaneously, this alkoxy radical (RO^\cdot) is stabilized by bonding with a hydrogen radical (H^\cdot), forming a new alcohol bond (ROH) that generates the product of interest. Furthermore, due to the complexity of this type of molecule, other possible degradation products result.

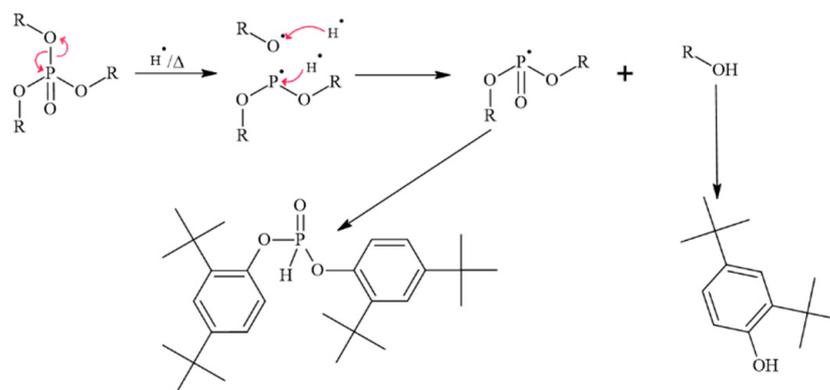


Figure 10. Mechanism of formation of 2,4-di-tert-butylphenol.

3.3.3. Mechanism of Formation of the Bis(di-tert-butylphenyl) Phosphate Product

In Figure 11, the degradation product (Irgafos P-168 Phosphate) is also the starting point. The process begins with a homolytic cleavage between the carbon of the R group and the oxygen, which leads to the release of the alkyl group in the form of a radical ($R\cdot$) and the oxygen attached to the phosphorus atom as another radical. At this point, hydrogen ($H\cdot$) radicals stabilize both radicals, forming Bis(di-tert-butylphenyl) phosphate.

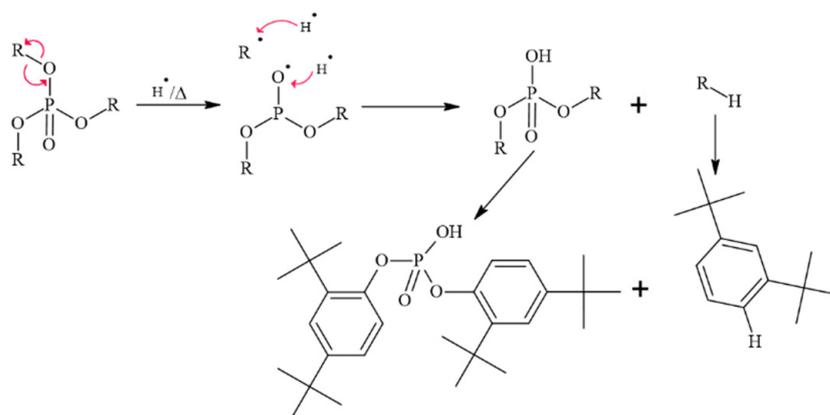


Figure 11. Mechanism of formation of Bis(di-tert-butylphenyl) phosphate.

3.3.4. Mechanism of Formation of the Mono(di-tert-butylphenyl) Phosphate Product

In Figure 12, the formation mechanism begins from the previous product Bis(di-tert-butylphenyl) phosphate; in the presence of the hydrogen radical and high temperature, a homolytic cleavage occurs between the C of the R group and the oxygen, releasing another R group, both of which are stabilized with hydrogen radicals. The degradation product of interest and a di-tert-butylphenyl are obtained.

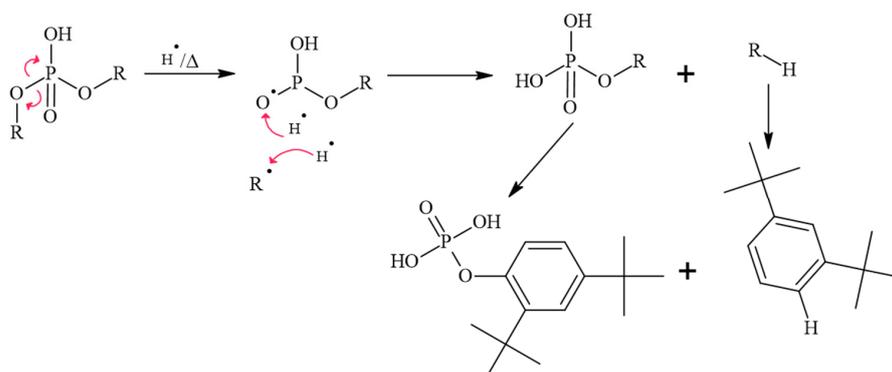


Figure 12. Mechanism of formation of Mono(di-tert-butylphenyl).

3.3.5. Mechanism of 2-Tert-butylphenol Product Formation

In Figure 13, this time in part of the product 2,4-di-tert-butylphenol, under the same conditions set out above, a homolytic cleavage occurs in the tert-butyl group in the position para, so the degradation product of interest and a tert-butyl group are obtained.

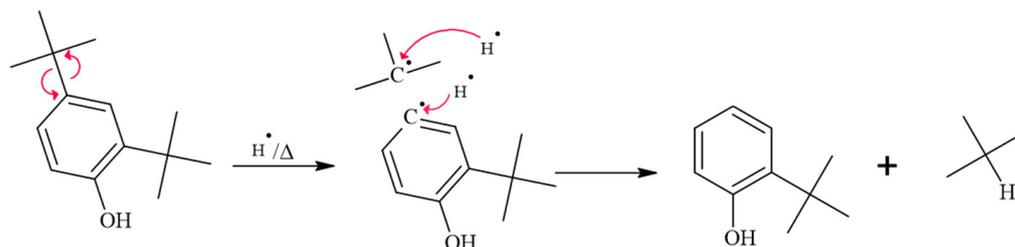


Figure 13. Mechanism of formation of 2-tert-butylphenol.

3.3.6. Mechanism for Obtaining the Product 4-Tert-butylphenol

The last mechanism illustrated in Figure 14 for the formation of the 4-tert-butylphenol product involves the loss of a tert-butyl group in the (ortho) position, so it begins with the 2,4-tert-butylphenol molecule, which undergoes a homolytic cleavage between the ring carbon bond and the tert-butyl carbon, resulting in the product of interest 4-tert-butylphenol and a tert-butyl group.

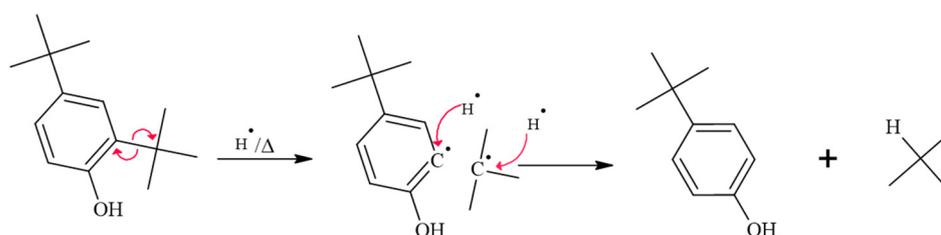


Figure 14. Mechanism of the formation of the 4-tert-butylphenol product.

3.4. Validation of Proposed Mechanisms

It is widely recognized in scientific circles that quantum chemistry offers an effective method for understanding processes occurring in chemical reactions. This allows for the calculation of charge distribution, molecular properties, and potential energy surfaces associated with these reactions. Numerous studies have supported the utility of Density Functional Theory (DFT) as a powerful tool for predicting trajectories, kinetics, and secondary products of compounds of interest under specific environmental conditions, as documented in the scientific literature. Therefore, we have chosen to employ computational tools to validate the formation of proposed degraded products in the preceding section. This will further support our conclusions and enhance our understanding of the underlying processes in the studied chemical reactions.

Based on the results provided in Table 3, it can be concluded that all analyzed formation mechanisms and products exhibit negative values for both the delta of Gibbs free energy (ΔG) and the delta of enthalpy (ΔH), indicating the favorable thermodynamic nature of the reactions under study. Significant differences are observed between the values of ΔG and ΔH among the different mechanisms, with the mechanism for obtaining the 4-tert-butylphenol product standing out as the most spontaneous with the most negative value of ΔG . The close relationship between ΔG and ΔH suggests that enthalpy plays an important role in the spontaneity of reactions, although other factors also have an influence.

Table 3. Gibbs free energy and enthalpy for the proposed degradation mechanisms.

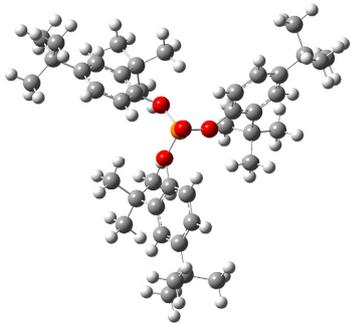
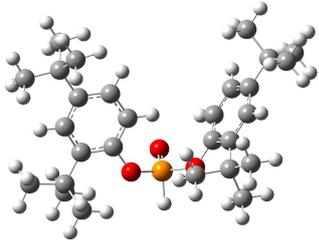
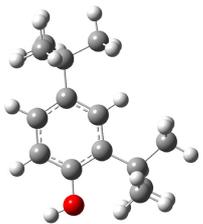
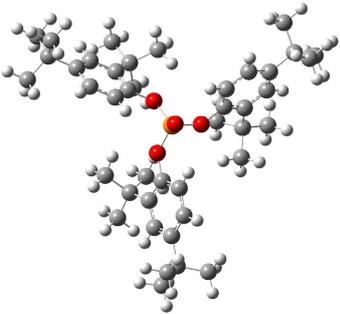
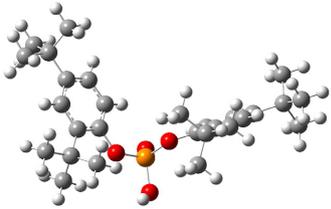
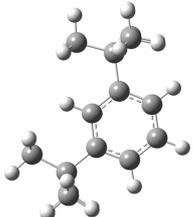
Mechanism	Structure	Gibbs Free Energy (Hartree)	Enthalpy (Hartree)	ΔG of the Reaction (kcal/mol)	ΔH of the Reaction (kcal/mol)
		-2279.760	-2279.614		
Mechanism of formation of 2,4-di-tert-butylphenol.		-1659.277	-1659.171	-744.23	-732.30
		-621.669	-621.610		
		-2279.760	-2279.614		
Mechanism of formation of the Bis(di-tert-butylphenyl) phosphate product		-1734.514	-1734.404	-761.17	-747.99
		-546.459	-546.402		

Table 3. Cont.

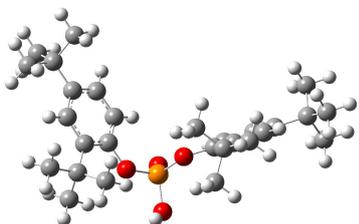
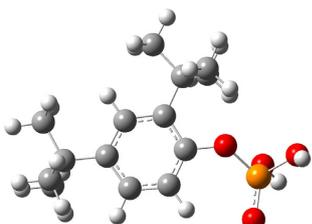
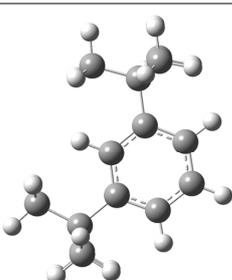
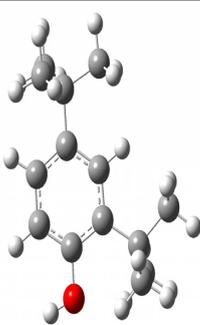
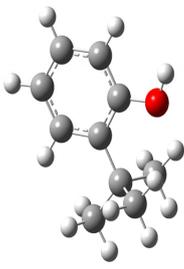
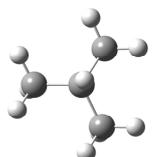
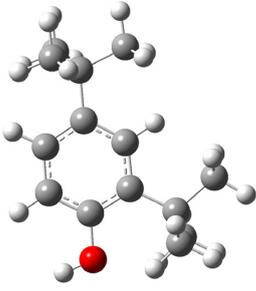
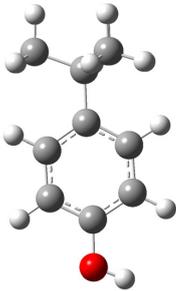
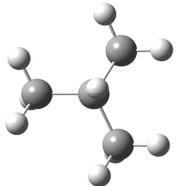
Mechanism	Structure	Gibbs Free Energy (Hartree)	Enthalpy (Hartree)	ΔG of the Reaction (kcal/mol)	ΔH of the Reaction (kcal/mol)
		-1734.514	-1734.404		
Mechanism of formation of the Mono(di-tert-butylphenyl) phosphate product		-1189.267	-1189.194	-760.54	-747.99
		-546.459	-546.402		
		-621.669	-621.610		
Mechanism for obtaining the product 4-tert-butylphenol		-464.665	-464.618	-878.51	-863.45
		-158.403	-158.368		

Table 3. Cont.

Mechanism	Structure	Gibbs Free Energy (Hartree)	Enthalpy (Hartree)	ΔG of the Reaction (kcal/mol)	ΔH of the Reaction (kcal/mol)
Mechanism for obtaining the product of 2-tert-butylphenol		-621.669	-621.610		
		-464.529	-464.482	-792.54	-778.11
		-158.403	-158.368		

3.5. Percentage Analysis of the Degradation Products of Irgafos P-168

Figure 15 provides an interpretation of the variations in Irgafos P-168 concentrations, illustrating the significant impact of different extraction methods, solvents, and forms of C-PP/PE. It was observed that all degradation products reached their highest percentages when the microwave extraction technique was used in combination with dichloromethane and C-PP/PE in the form of films. Although this technique involves short times and low temperatures, in theory, it should not cause significant structural changes; the greater extraction of degraded products may be because the samples were exposed to higher temperatures during the previous preparation stages, which could have contributed to the degradation of the Irgafos P-168. It is evident that the shape of the C-PP/PE also influences the number of degraded products. Notably, the highest percentages of degradation products were found in C-PP/PE films, while the pellet and ground forms showed lower concentrations of these products. The film structures are less dense and permeable, facilitating oxygen diffusion and, therefore, its reaction with Irgafos P-168. These films are also less protected against environmental elements such as sunlight and humidity, which can accelerate degradation processes. Furthermore, C-PP/PE films are more susceptible to mechanical stress during handling due to stretching or deformation processes during manufacturing, which increases their vulnerability to Irgafos P-168 degradation.

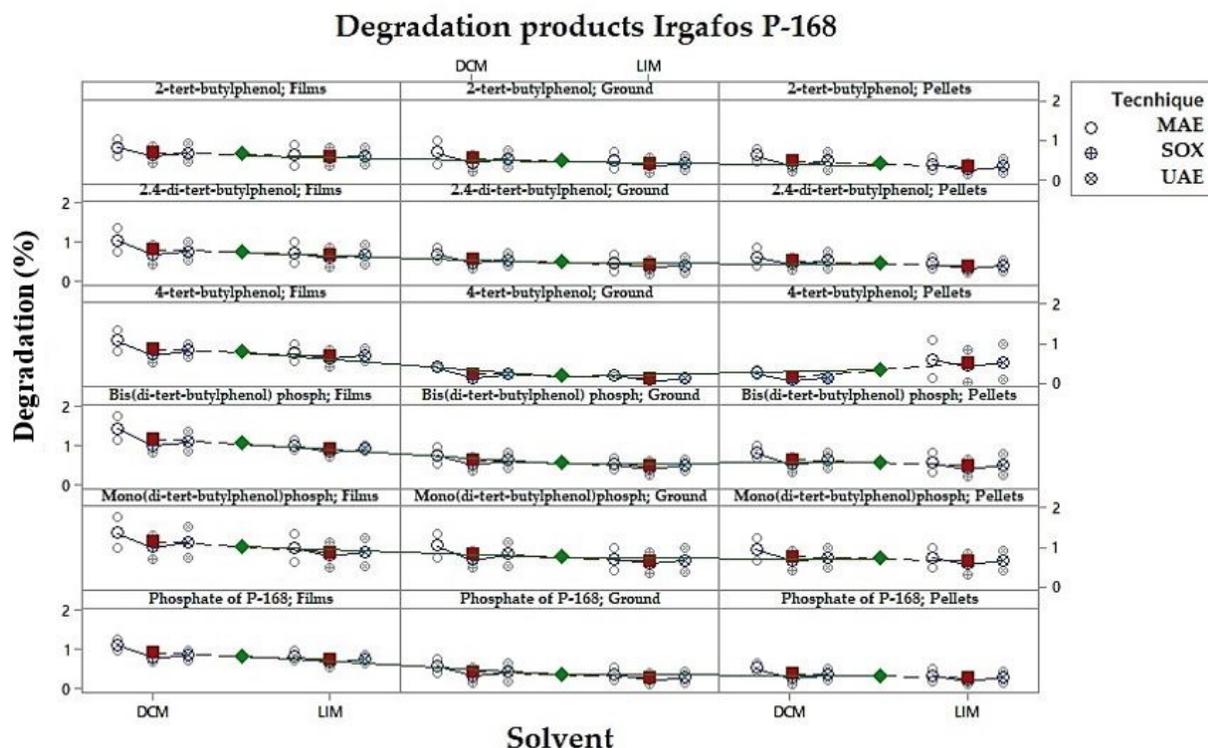


Figure 15. Degradation products of Irgafos P-168.

Interestingly, the most predominant degradation product was Mono(di-tert-butylphenyl) phosphate, followed by Bis(di-tert-butylphenyl) phosphate. This is interesting since, according to the literature, when the degradation of Irgafos P-168 occurs, Irgafos P-168 Phosphate and 2,4 di-tert-butylphenol are frequently the products with the highest percentage [36,37]. This discrepancy raises essential questions about the exact degradation mechanisms in the presence of different solvents. On the other hand, dichloromethane demonstrated notably higher recovery rates of degradation products compared to Limonene in all the techniques used. Again, Limonene, as a green solvent option, shows its effectiveness by providing lower percentages of degradation products and extracting acceptable amounts of Irgafos P-168. These results highlight the complexity of the interactions between Irgafos P-168, solvents, and extraction conditions and the urgency of finding an optimal balance between efficient additive recovery and minimal degradation. Furthermore, it highlights the critical importance of carefully selecting extraction conditions to preserve the integrity of the additive. These results also emphasize the urgency of continued research to constantly improve extraction techniques and minimize the degradation of the polymers and their additives.

4. Conclusions

The results obtained in this study show that the microwave extraction technique surpasses the ultrasound and Soxhlet techniques in terms of effectiveness, reducing extraction times and increasing the recovery efficiency of the compound of interest. Furthermore, ground C-PP/PE leads to notable improvements in the recovery of Irgafos P-168 compared to C-PP/PE presentations in the form of films and pellets. These improvements are attributed to the advantages inherent to using ground C-PP/PE, such as a substantial increase in the contact surface, more excellent permeability, the presence of smaller particles, and greater homogeneity in the composition of the material. To be more precise in the findings, by applying microwaves for 45 min, with the solvent dichloromethane and using ground C-PP/PE as a substrate, the maximum recovery of Irgafos P-168 is achieved, obtaining a percentage of 96.07%; with a duration of 45 min, using the solvent Limonene and ground C-PP/PE, a recovery of 92.83% is achieved; and by using the ultrasound extraction tech-

nique for 90 min, with the solvent dichloromethane and ground C-PP/PE, a recovery of 91.74% and 89.71% with Limonene is obtained. However, the Soxhlet extraction technique, with a duration of 1440 min and using ground C-PP/PE, entails the lowest recovery of 78.64% with dichloromethane and 76.66% with Limonene. These results underline that the microwave extraction technique is the best choice when combined with ground C-PP/PE, providing the highest recovery percentages at noticeably shorter extraction intervals. Although dichloromethane exhibits some advantages in terms of recovery, the choice of Limonene as an alternative solvent is viable. It provides additional benefits, such as lower toxicity and reduced environmental impact.

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