Antioxidants loss kinetics in polyethylene exposed to model ethanol based biofuels

Fatma Djouani, Bhavesh Patel, Emmanuel Richaud *, Bruno Fayolle, Jacques Verdu

Arts et Metiers ParisTech, CNRS, PIMM, 151 bd de l'Hôpital, 75013 Paris, France

Abstract

This work deals with a study of stabilizers loss by extraction in ethanol–cyclohexane mixtures simulating ethanol based biofuels. As theoretically predicted, cyclohexane has an extractive power considerably stronger than ethanol one and its effect predominates, even in fuels containing 50% ethanol. Antioxidant depletion displays first-order kinetics indicating that loss kinetics are extraction rather than diffusion controlled.

Keywords:
Biofuels
Polyethylene
Extraction
Irganox 1010
Irgafos 168

1. Introduction

Two recent trends in automotive industry, e.g. the increase of engine temperature and the increasing use of biofuels, lead to reconsider the problem of polymer–fuel interaction for all the polymer materials (polyolefins, polyamides, elastomers, etc.) used in motors and for tanks.

The new biofuel components e.g. essentially ethanol or unsaturated esters, can affect the polymer thermo-oxidative stability by chemical way through co-oxidation process or by physical way through stabilizer extraction. Published works on this topic are very scarce [1,2]. It has been observed that polyethylene (PE) displays a poor compatibility with biodiesel fuels. Most of the literature deals with elastomeric sealants swelling when exposed to miscible liquids, especially hydrocarbons [3,4]. It has been shown that the degree of swelling is a decreasing function of the crosslink density and of the polymer–fuel interaction parameter, this latter being an increasing function of the difference between polymer and fuel solubility parameters. In the case of HDPE, it has been shown that the tested fuels were absorbed by the polymer but without irreversible modification of the polymer structure [1].

To our knowledge, no paper was published on the eventual stabilizer extraction in PE exposed to biofuels. However, a stabilizer migration from polymer to environment is expected as illustrated by comparable studies in the field of food packaging or pipes industry [5–9]. Short-term effects of biofuels on PE are, no doubt, negligible, but a fast stabilizer extraction could significantly affect the long-term oxidative stability. The coupling of both chemical consumption of stabilizer and physical loss by evaporative process for instance can be simulated by a kinetic model in a case of oxidation [10] but it requires to know the values for kinetic parameters of elementary physical processes such as stabilizer extraction by the liquid (biofuel) medium.

Most of the previous studies devoted to stabilizer physical loss were focused on the diffusion phenomena [8]. In some cases, extraction was observed but not quantified [11] or quantified in the case of thick samples for which stabilizer loss is certainly controlled by diffusion [12] as it will be confirmed in the following. This is the reason why it seemed to us interesting to study antioxidant loss in the presence of biofuels in the case of thin films, which is for us the best way for determining extraction kinetics. It was chosen to study a PE commercial sample stabilized by a common mixture of hindered phenol (Irganox 1010) and phosphite (Irgafos 168). Experiments were also performed with laboratory mode samples containing only Irganox 1010 or Irgafos 168 as model systems. Ethanol based biofuels were simulated by ethanol–cyclohexane mixtures containing 10% or 50%, ethanol.

2. Experimental

2.1. Materials

2.1.1. Commercial polyethylene

Pellets made from a commercial grade of High Density PolyEthylene (HDPE in the following, density 949 kg m⁻³, $M_N = 18$ kg mol⁻¹ and $M_W = 228$ kg mol⁻¹) were compression molded using a Gibritte laboratory press (30 s, 200 °C, 24 MPa) in order to obtain films of

* Corresponding author.
E-mail address: emmanuel.richaud@ensam.eu (E. Richaud).
140 μm thickness of which melting temperature was c.a. 132 °C and crystalline ratio value estimated from melting enthalpy was close to 50% using 290 J g⁻¹ as melting enthalpy for an infinite crystal.

2.1.2. Model polyethylene

Laboratory made samples were prepared using:

- a stabilizer free PE powder (supplied by Borealis, density 935 kg m⁻³, average molar mass \( M_N = 8 \text{ kg mol}^{-1} \) and \( M_W = 143 \text{ kg mol}^{-1} \)). The absence of stabilizer was checked by absence of induction period in oxidation kinetics at 180 °C (see below).
- Irgafos 168 (CAS No. 31570-04-4, supplied by Ciba SC, melting temperature of 185.5 °C and melting enthalpy close to 73.0 J g⁻¹) having the following structure:

![Structure of Irgafos 168](image)

- Irganox 1010 (CAS 98584-37-3, supplied by Ciba SC, melting temperature close to 117.6 °C a melting enthalpy close to 58.6 J g⁻¹).

Stabilized PE samples were prepared by pouring a dichloromethane solution of the stabilizer onto PE. The stabilizer concentration and the solution volume are adjusted in order to obtain the desired stabilizer concentration in PE. After evaporation of the solvent at room temperature, about 100 μm thick films containing 0.1–0.4% Irgafos 168 and 0.1–0.5% Irganox 1010 were prepared by compression molding. They exhibit melting point close to 123 °C (crystallinity ratio estimated from melting enthalpy \( x_C \approx 40\% \).

The initial stabilizer concentration in the PE (used for FTIR or UV calibration) was calculated using:

\[
[\text{Stab}] = \frac{\rho_{\text{PE}}}{M_{\text{Stab}}} \cdot x_{\text{Stab}} \cdot f_{\text{Stab}}
\]

where \( \rho_{\text{PE}} \) is the polymer density (935 g l⁻¹), \( M_{\text{Stab}} \) is the stabilizer molar mass (g mol⁻¹), \( x_{\text{Stab}} \) is the global stabilizer weight ratio in the polymer and \( f_{\text{Stab}} \) is the stabilizer functionality, i.e. the number of active groups per molecule: 4 for Irganox 1010 and 1 for Irgafos 168.

2.2. Exposure condition

A 3 cm x 2 cm films (thickness being c.a. 140 μm) were immersed in 100 ml model fuel under reflux at c.a. 80 °C (refluxing temperature of the mixture), 60 and 40 °C and periodically analyzed. After exposure, sample was quickly removed, air dried at atmospheric pressure and ambient temperature, analyzed and re-immersed. We paid attention to systematically analyse the same “zone” of the sample (i.e. the sample center) to avoid discrepancies due to possible slight fluctuations of stabilizer local concentration or sample thickness. Three model fuels were studied: Ethanol 100%, ethanol–cyclohexane (50/50) and ethanol–cyclohexane (10/90).

2.3. Analytical methods

2.3.1. FTIR spectroscopy

IR spectra in transmission mode were obtained on a Bruker IFS28 apparatus in standard conditions with averaging 32 scans at a minimal 4 cm⁻¹ resolution. Residual stabilizer concentration in polymer was determined from absorbance values measured at peak maximum by subtracting the baseline value and using Beer Lambert law with molar absorptivity values given in Table 1.

2.3.2. Differential scanning calorimetry under oxygen

Samples (about 5 mg mass) were placed in open aluminum pans. The oxidation induction time (OIT) was determined on a Q10 apparatus (TA Instruments) in the following conditions:

1. Sample are rapidly heated until 180 °C and kept 5 min at this latter temperature to reach thermal equilibrium under nitrogen.
2. The cell atmosphere was switched to 100% oxygen (supplied by a 50 ml min⁻¹ flow) and the heat flow was recorded in isothermal condition (180 °C). The end of the induction period is taken at the onset of the exotherm corresponding to the degradation. It has been shown that oxidation induction time (OIT) is almost proportional to the stabilizer concentration for binary mixtures PE + antioxidant [13] as illustrated in Fig. 1a and b, but this is not necessarily true for PE stabilized with synergistic mixtures of antioxidants [14,15].

Let us mention that differential scanning calorimetry under oxygen has many common features with Rancimat. Principle of measurement is to submit virgin or aged hydrocarbon samples (fats, lubricants, oil, polymers) to accelerated ageing whose induction period duration is related to the residual oxidative stability (expressed, in our case, by the residual stabilizer concentration). It is noteworthy that after the end of induction period, all substrate characteristics change suddenly (carbonyl build-up, hydroperoxides concentration, mass loss, elongation at break, residual elongation, etc.) and corresponding induction period values are generally very close. Here the choice of DSC was made for the following reasons:

- According to literature [16,17], Rancimat apparatus is designed for experiments at 100–120 °C (which is actually a moderate temperature for polymer oxidation). It is particularly well adapted for fats or oil because these ones are very volatile and would quickly evaporate at higher temperatures. For PE + Irgafos 168 or PE + Irganox 1010, the induction period would be respectively on the order of 50 h and 3000 h at 120 °C, which is much too long for a rapid stabilizer concentration analysis.
- OIT at 180–200 °C is not adapted to low molecular mass substrates because of their evaporation. However, for unoxidized PE + stabilizers blends, a linear relationship between OIT value and residual stabilizer concentration permits a fast and fairly precise measure of stabilizer concentration (Fig 1 and [10,13]).

2.3.3. Liquid chromatography

Residual stabilizers and their by-products were removed from polymer films by solvent extraction procedure. Let us mention that several extraction methods (differing by solvent choice and temperature) exist in literature [18–23]. We have chosen chloroform [23] with 16 h refluxing time but without using an ultrasonic bath. About 0.5 mg of commercial HDPE was reflux-extracted in 50 ml chloroform. The complete extraction was checked by the disappearance of FTIR signals ascribed to stabilizers (see Section 3 part and Table 1) and by the vanishing of OIT at 180 °C. Solution was then filtered and directly analyzed by HPLC using a Waters
717 + apparatus. Stationary phase was silane grafted C18 thermo-
stationed at 35 °C. The mobile phase was acetonitrile (HPLC plus
grade, supplied by Carlo Erba) at 1 ml min⁻¹ flow. Detection was
performed by Waters 2414 Refractive Index (Tdetector = 40 °C) and
Photo Diode Array Waters 2998 allowing to monitor UV spectra
of mobile phase in the 200–400 nm wavelength range every sec-
ond. We have focused on the absorption at 270 nm which permits
to monitor aromatic rings of both phosphites [24] and phenols
[25].

Table 1
Wavenumber, vibration mode and molar absorptivity of characteristics groups of stabilizers main peaks.

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Compound</th>
<th>ε (1 mol⁻¹ cm⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgafos 168</td>
<td>772</td>
<td>– (P–O–C)</td>
<td>318</td>
<td>0.5513</td>
</tr>
<tr>
<td>Irgafos 168</td>
<td>850</td>
<td>– (PIII)–O–Ar</td>
<td>333</td>
<td>0.9385</td>
</tr>
<tr>
<td>Irgafos 168</td>
<td>1080</td>
<td>–</td>
<td>379</td>
<td>0.8055</td>
</tr>
<tr>
<td>Irgafos 168</td>
<td>1191</td>
<td>– (P–O)</td>
<td>440</td>
<td>0.9401</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>1743</td>
<td>–O–C–O–O</td>
<td>322</td>
<td>0.8846</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>3650</td>
<td>Ar–OH</td>
<td>117</td>
<td>0.5478</td>
</tr>
</tbody>
</table>

UV
Irganox 1010 | 269              | Ar–O     | 1355            | 0.6979 |

Fig. 1. Initial oxidation induction time values for laboratory made samples stabilized with Irgafos 168 (a) and Irganox 1010 (b).

3. Results

3.1. Calibration of analytical methods

3.1.1. FTIR

FTIR spectra of samples prepared with a single stabilizer are shown in Fig. 2a (Irgafos 168), b and c (Irganox 1010). The absorbances of peaks corresponding to Irgafos 168 and Irganox 1010 increase almost linearly with stabilizers concentration. Their molar absorptivities are listed in Table 1. These results confirm thus a limited oxidation during sample processing.

For Irgafos 168, many bands could be used to monitor stabilizer loss: 720, 855, 1080 and 1191 cm⁻¹. Their advantages or limits for monitoring stabilizer loss are the following:

- A 720 and 1080 cm⁻¹ overlap with bands of PE matrix that induces scatter in quantitative determinations. Furthermore their assignment is not trivial especially for 1080 cm⁻¹ peak.
- Peak at 1191 (P–O in phosphate) is clearly identified. Even if it slightly overlaps with 1211 cm⁻¹ (P–O in phosphate [26]), it was preferred to the peak at 850 cm⁻¹ because it is less scattered.

For phenols, stabilizer loss can be monitored by 1740 and 3650 cm⁻¹ (see Fig. 2b and c). Ester absorption at c.a. 1740 cm⁻¹ has two advantages: first, it has a higher molar absorptivity than 3650 cm⁻¹, and second, it does not overlap with PE matrix absorption meanwhile OH signal does (which is certainly the reason why scatter is higher for ester than for phenols (Table 1)).

UV analysis (not shown here) were also performed. UV spectra displayed a band at 269 nm for PE + Irganox 1010 but quantitative analysis was undoubtedly less reliable from UV data than from OIT or FTIR data so that it will not be used in this study. Beer–Lambert plots for peaks at 1191 cm⁻¹ (Irgafos 168) and 1743 cm⁻¹ (Irganox 1010) will be used in the following to monitor the stabilizer loss kinetics during exposure.

The Irgafos 168 bands are clearly distinguishable in the commercial sample. In contrast, Irganox 1010 bands are too weak to allow quantitative measurements, despite the fact that the presence of the stabilizer is confirmed by HPLC (see below).

3.1.2. HPLC analysis of commercial PE

Overlapping of stabilizer chromatograms obtained in separate runs is shown in Fig. 3a. Irganox 1010 displays a peak at 8.2 min and a shoulder at 9 min and several small peaks between 2 and 7 min.

Irgafos 168 displays a predominating peak at 28 min and a shoulder at 31–32 min. In both cases, secondary peaks indicate the existence of isomers and/or impurities, which is not surprising for commercial grades.

The chromatogram of removed materials (stabilizers together with their impurities and process induced by-products) by chloro-
form extraction from commercial PE reveals the presence of both stabilizers (Fig. 3b). The additional peak observed at 15 min corresponds to the phosphate generated from Irgafos 168 oxidation (as shown in [24] by reacting Irgafos 168 with tert-butyl hydroperox-
ide). These results confirm thus a limited oxidation during sample processing.

In conclusion, the commercial PE is suspected to contain both Irgafos 168 and Irganox 1010 which is not surprising since this is a very common stabilizer blend characterized by a strong synergis-
tic effect [14,15].

3.2. Physical loss kinetics

Commercial PE samples of 140 μm thickness were exposed in the three model fuels containing respectively 100% (ethanol), 50%
(E50) and 10% (E10) ethanol at reflux (80 °C). The decrease of
residual stabilizer concentration was monitored by OIT measurement. The kinetic curves of OIT change are shown in Fig. 4. These results call for the following comments:

(1) Extraction is considerably slower in pure ethanol than in cyclohexane containing fuels. Concerning these latter, there is practically no difference between E10 and E50 and, presumably pure cyclohexane. It has been already shown that the extractive power of liquids decreases when the polarity difference between the polymer and the liquid increases [27], but there was, to our knowledge, no proposal for a quantitative relationship between the extraction rate and the polymer, the additive and the liquid characteristics.

(2) It has been tried to fit the OIT decay curves by a simple first-order model (Eqs. (2) and (3)). The agreement with experimental data is satisfying provided an asymptotic (residual) OIT value (denoted by OIT<sub>1</sub>) is taken into account:

\[
\frac{d\text{OIT}}{dt} = -\beta (\text{OIT} - \text{OIT}_1)
\]

(2)

\[
\text{OIT} = \text{OIT}_1 + (\text{OIT}_0 - \text{OIT}_1) \cdot \exp(-\beta \cdot t)
\]

(3)

OIT<sub>0</sub> being the initial OIT value before exposure and \(\beta\) a pseudo first-order rate constant characterizing the stabilizer loss.

4. Discussion

Cyclohexane is especially efficient in extracting stabilizers from PE since its solubility parameter (\(\sim 16.7 \text{ MPa}^{1/2}\)) is very close to the...
polymer one (15.8–17.1 MPa\(^{1/2}\)) [27]. It is thus able to swell PE and to favor the stabilizer transport through the polymer matrix. Ethanol, of which the solubility parameter (26.3 MPa\(^{1/2}\)) is far from PE one, does not swell PE and displays thus a considerably lower extractive power.

Our results reveal an apparent discrepancy. According to the data of Fig. 4 and Table 3, Irgafos 168 is expected to be predominantly lost in the first hours of exposure in the commercial PE sample containing a binary stabilizer mixture. According to the OIT values obtained with unextracted single stabilizer systems (Fig. 1a for Irgafos 168, Fig. 1b for Irganox 1010), and supposing a linear dependence of OIT with stabilizer concentrations, the loss of Irgafos 168 in the first hour of exposure in ethanol at 80 °C (Fig. 3) would be expected to have a little influence on OIT provided Irganox 1010 and Irgafos 168 contributions are additive. This is contradicted by experimental results: OIT decreases by more than 40% of its initial value after 1 h of exposure. It can be also noticed that the pseudo-first order rate constant \( b \) for OIT decrease is considerably higher than the first-order rate constants \( b \) for single stabilizers physical loss. The explanation is obvious: Irgafos 168

Table 2

<table>
<thead>
<tr>
<th></th>
<th>EtOH</th>
<th>50% EtOH</th>
<th>10% EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>OIT(_{\infty}) (min)</td>
<td>7</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>( \beta ) (h(^{-1}))</td>
<td>0.449</td>
<td>4.459</td>
<td>4.713</td>
</tr>
</tbody>
</table>

(Fig. 3) would be expected to have a little influence on OIT provided Irganox 1010 and Irgafos 168 contributions are additive. This is contradicted by experimental results: OIT decreases by more than 40% of its initial value after 1 h of exposure. It can be also noticed that the pseudo-first order rate constant \( b \) for OIT decrease is considerably higher than the first-order rate constants \( b \) for single stabilizers physical loss. The explanation is obvious: Irgafos 168

Table 3

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \beta ) (h(^{-1}))</th>
<th>( \tau ) (s)</th>
<th>( R^2 )</th>
<th>( D_{\text{max}} ) (m(^2) s(^{-1}))</th>
<th>( D_{\text{min}} ) (m(^2) s(^{-1}))</th>
<th>( \epsilon ) (m)</th>
<th>( h_{\text{max}} )</th>
<th>( h_{\text{min}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>8.0E-01</td>
<td>1.3E+01</td>
<td>0.9963</td>
<td>7.4E-13</td>
<td>5.9E-14</td>
<td>1.0E-04</td>
<td>1.2E+01</td>
<td>9.4E-01</td>
</tr>
<tr>
<td>40</td>
<td>8.4E-01</td>
<td>1.3E+01</td>
<td>0.9964</td>
<td>7.4E-13</td>
<td>5.9E-14</td>
<td>1.0E-04</td>
<td>1.2E+01</td>
<td>9.4E-01</td>
</tr>
</tbody>
</table>

Fig. 4. OIT\(_{200}\) variation for the commercial sample exposed in ethanol (\( \bullet \)), E10 (\( \square \)) and E50 (\( \diamond \)) at 80 °C (a) and OIT\(_{180}\) changes for commercial sample exposed in ethanol (b).

Fig. 5. Exposure of laboratory made samples containing Irganox 1010 (a) and Irgafos 168 (b) stabilizer loss at 40 °C (\( \bullet \)), 60 °C (\( \bigcirc \)) and 80 °C (\( \blacklozenge \)) in pure ethanol.

Fig. 6. Exposure of laboratory made samples containing 0.2% (\( \bullet \)), 0.3% (\( \square \)) and 0.4% (\( \blacklozenge \)) Irgafos 168 at 60 °C in pure ethanol.
systems. In such systems, it can be assumed that: 

Two extreme cases can be imagined:

1. Interface crossing is considerably faster than diffusion, then, diffusion controls the whole stabilizer loss kinetics.
2. Diffusion is fast enough to redistribute homogeneously the stabilizer in the whole sample thickness at every time.

It remains to try to justify the apparent first-order character of extraction kinetics in the case of Irgafos 168 and the fact that it is less obvious in the case of Irganox 1010. It can be recalled that this phenomenon results from the sequence of two physical processes: first the diffusion of additive molecules from their initial location to the surface, second the interface crossing and the passage of the molecule from polymer into the media. This process is called evaporation in gaseous media and extraction in liquid media.

Two extreme cases can be imagined:

1. “Interface crossing” is considerably faster than diffusion, then, diffusion controls the whole stabilizer loss kinetics.
2. Diffusion is fast enough to redistribute homogeneously the stabilizer in the whole sample thickness at every time. Loss kinetics is hence controlled by “interface crossing”. In the initial steps of a fickian diffusion process, the stabilizer concentration is expected to decrease proportionally to the square root of time.

The competition between both processes was first modeled by Crank [28]. The criterion proposed by this author was then used by Calvert and Billingham [12] in the case of polymer-stabilizer systems. In such systems, it can be assumed that:

- Stabilizer concentrations are low enough (generally lower than 0.5% [14]) to neglect the plasticizing effects so that diffusion is really Fickian and the diffusion coefficient is concentration independent [29].
- Extraction could obey the same type of kinetic law as evaporation. This latter is usually derived from two hypotheses:

  1. The first hypothesis states that the loss rate of additive in a saturated sample \( r_{Sat} \) is equal to the loss rate of pure additive \( r_{pure} \) in liquid state:

\[
\left( \frac{dn_A}{dt} \right)_{Sat} = -r_{Sat} = -r_{pure} \]

\[ r_{Sat} \text{ and } r_{pure} \text{ being in mol m}^{-2} \text{ s}^{-1}, \text{ and } n_A \text{ being the number of molecule A lost per area unit.} \]

  2. The second hypothesis states that, in a non saturated sample, for a given additive concentration \( [A] \), the lost rate is proportional to \([A]\) so that:

\[
\left( \frac{dn_A}{dt} \right)_{Sat} = \frac{[A]}{[A]_{Sat}} \]

so that:

\[
\frac{dn_A}{dt} = \frac{r_{Sat}}{[A]_{Sat}} \cdot [A] \]  

If interface crossing controls the whole kinetics, this means that diffusion is fast enough to redistribute homogeneously the stabilizer in the whole sample thickness (denoted by \( L \)) at every time. The decrease of additive concentration obeys thus a first-order law:

\[
\frac{d[A]}{dt} = -\frac{1}{L} \cdot \frac{dn_A}{dt} = -\beta [A] 
\]

in which:

\[
\beta = \frac{1}{L} \cdot \frac{r_{Sat}}{[A]_{Sat}} 
\]

\( \beta \) being a first-order rate constant characteristic of the sample thickness under consideration.

Since loss kinetics obeys effectively first-order law in the case of Irgafos 168, the analogy between extraction and evaporation is confirmed. Then, the lack of correlation between experimental data and first-order kinetic curves in the case of Irganox 1010 can be tentatively explained by the fact that this system is on the other side of the boundary between extraction controlled and diffusion controlled kinetic regimes for the sample thickness under consideration (~140 μm).

A simple reasoning aimed to determine the rate controlling step for physical loss can be made from:

1. A characteristic time for interface crossing \( \tau_I \):

\[
\tau_I = \beta^{-1} = \frac{L}{r_{Sat}} \cdot [A]_{Sat} \]  

2. A characteristic time of diffusion \( \tau_D \):

\[
\tau_D = L^2/D 
\]

\( D \) being the diffusion coefficient of stabilizer through the polymer.

3. An adimensional number \( h \) analogous to a Deborah number by the ratio of characteristic times:

\[
h = \frac{\tau_D}{\tau_I} = \frac{L}{D} \cdot \frac{r_{Sat}}{[A]_{Sat}} 
\]

- if \( h > 1 \) (\( \tau_I < \tau_D \)), diffusion is the rate controlling process, the profile of additive concentration into the sample thickness will display a strong gradient in the superficial layer, the concentration being almost zero at the surface.


- if \( h < 1 (t_i > T_0) \), the interface crossing is slow and, then, diffusion is fast enough to redistribute homogeneously the additive into the whole thickness, the concentration profile is flat.

A more or less wide transition exists around \( h = 1 \). It can be also seen that the boundary between both regimes depends on the sample thickness. Using Crank’s equation, Calvert and Billingham [12] reached the same criterion as the above one and determined its value for two sample geometries (e.g. foils or cylindrical fibers). In the case of foils, they have shown that the process is extraction controlled for \( h > 0.6 \) and diffusion controlled for \( h > 10 \).

It seemed interesting to us to try to determine the ratio of characteristic times using experimental data reported by Moisan [30], Limm and Hollifield [31] for Irganox 1010, and by Begley et al. for Irgafos 168 [8], together with values estimated from models [32] (Table 4 and 5). According to its crystallinity ratio (~50%), the polyethylene under investigation is closer to LDPE than to HDPE. In the following only LDPE characteristics will be used in the polyethylene under investigation is closer to LDPE than to HDPE (Table 4 and 5). According to its crystallinity ratio (50%) for which loss kinetics would be extraction controlled. It is interesting to note that this latter case is already known that the choice of a stabilizer depends on its chemical efficiency in the considered temperature range [14,24], and that, in a given stabilized family, the performances of two stabilizers (for example two phenols differing by their para-substituent nature) could be described by functions of diffusivity and solubility in polymer matrix [33]. This work suggests that, for more complex applications (here in presence of fuels), their relative compatibility with polyethylene, hydrocarbon fuel and ethanol has also to be taken into account.

**Acknowledgements**

This work has been accomplished in the frame of the “contract BioCarbMat” and sponsored by the competitiveness pole MOV’E O which is gratefully acknowledged.

**References**


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**Table 4**

Diffusion coefficient for Irganox 1010.

<table>
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<tbody>
<tr>
<td>LDPE</td>
<td>40 4.84E−15</td>
<td>3.10E−15</td>
<td>5.80E−15</td>
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</tr>
<tr>
<td></td>
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<td>2.30E−14</td>
<td>5.83E−14</td>
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<td></td>
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<td>HDPE</td>
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<td>8.95E−16</td>
<td>2.92E−15</td>
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**Table 5**

Diffusion coefficient for Irgafos 168.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Begley et al. [8] min</th>
<th>Begley et al. [8] max</th>
<th>Limm et al. [31]</th>
<th>Brandsch et al. [32]</th>
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</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>40 2.21E−14</td>
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</tr>
<tr>
<td></td>
<td>60 1.64E−13</td>
<td>4.25E−13</td>
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<td>80 9.71E−13</td>
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