

## MATHEMATICAL AND COMPUTATIONAL MODELING TO PREDICTION OF PVC AGING

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**Abstract.** Photobioreactors are closed systems for microalgae cultivation, and they have been studied by many research institutes, once these microorganisms are the promise of biofuels. Many studies have been developed about better design to photobioreactors, but it still missing studies with materials that lower the cost of these equipments. The systems at the lowest cost are those that use the sun as light source. It has to be designed with transparent materials, and polymeric materials such as polycarbonate and crystal PVC are good choices. However, prolonged exposure of polymers to light triggers degradation by thermal effects and ultraviolet radiation, once polymers are very sensible to ultraviolet light, causing discoloration and yellowing of materials. That process would shorten the usable life of the equipment. With this article we present a mathematical and computational model to prediction of the aging of PVC for photobioreactors. The model combines theoretical concepts of polymer thermodynamics and empirical correlations of Heat Transfer. We considered the mechanisms of degradation by photochemistry degradation, and it will happens when the light absorption generates an excited state of polymers molecules and theses excited molecules, when they come back to their normal state, will dissipate energy emitting light, which may results in a chemical reaction. The degradation in this way depends on the wavelength, glass transition temperature, a reaction rate constant and temperature. These equations form a system of time dependent ODE's, which are not dependent on space. The resulting ODE's set was solved using a fourth order Runge-Kutta method with fixed time step.

**Keywords:** photobioreactor, polymer degradation, mathematical model, PVC

### 1. INTRODUCTION

Photobioreactors are flexible systems that can be optimized according to the biological and physiological characteristics of the microalgae species being cultivated. These equipments offer better control over culture conditions and growth parameters, prevent evaporation, reduce gas losses, allow to attain higher microalgae densities or cell concentrations, higher volumetric productivities and offer a more easily preventing contamination (Mata *et al.*, 2010). However, photobioreactors are so much expensive, and this makes the final price of microalgae products not competitive.

The type of material used is of fundamental importance for a suitable photobioreactor construction. Materials such as plastic or glass sheets, collapsible or rigid tubes, must lack toxicity, have high transparency, high mechanical strength, high durability, chemical stability and low cost (Richmond, 2004). The ease of cleaning and loss of the plastics transparency exposed outdoors are operational issues to consider (Mata *et al.*, 2010). The most common used materials are acrylic, polycarbonate, low-density polyethylene and crystal PVC (Burgessa, G.; Fernández-Velasco, 2007). The poly(vinyl chloride) (PVC) has the advantage of low cost, long-term stability and flame resistance with compared with other commodity plastic and the mechanical properties of PVC are controllable by varying the amount of plasticizer (Ito and Nagai, 2007).

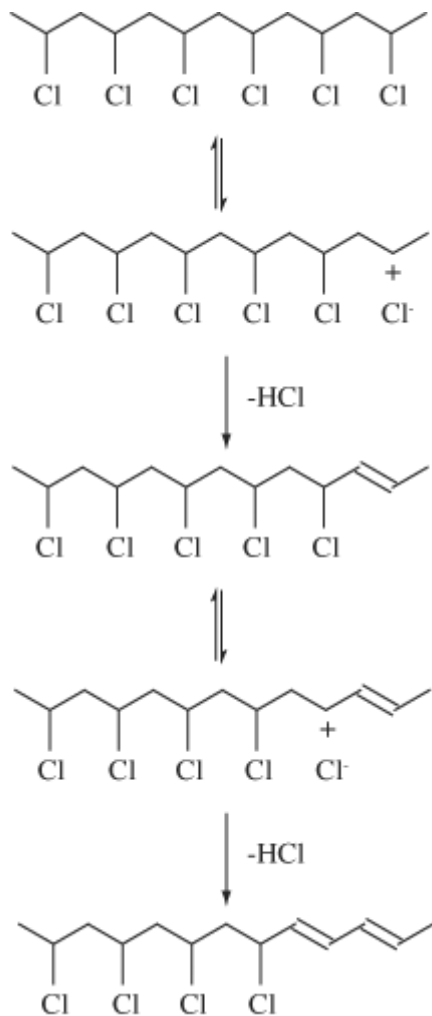
However, in outdoor applications all polymers degrade. The degradation rate depends on the environment (especially sunlight intensity, temperature and humidity) and on the type of polymer (Gijsman, Meijers and Vitarelli, 1999). If we could manufacture a perfect PVC molecule, it would be a totally linear with all vinyl chloride monomer units linked in a head-to-tail fashion. But according to studies, processing creates defects caused by chain scission. Because this, the PVC molecule contains many structural defects in the form of long and short chain branches, terminal and internal unsaturation, unusual end groups, and both initiator and emulsifier residues (Wilkes, Summers and Daniels, 1943). These defects makes the molecules absorb wavelengths in the UV region and this cause the photodegradation. The mechanism of photodegradation is well known, but is controversial the effect in the lifetime of polymer, mainly to applications like ours, where the light is one of the most important factors to success.

In this context, the mathematical modeling of photodegradation becomes at an indispensable tool for helps on prediction of lifetime of this polymer when exposed in outdoor conditions. So, the aim of this paper is proposed an initial mathematical model to describe the PVC consumption when exposed to a constant light intensity with controlled

temperature and absence of oxygen. As a differential, a consideration of the chemical energy accumulation was proposed.

### 1.1. Degradation mechanism

The effect of these processing irregularities may occur to the breakup of polymer chain, forming free radicals that can initiate the process of dehydrochlorination of the polymer and formation of allylic chlorides sites, generating a self-catalytic reaction (Michel and Hoang, 1981), as shown in Figure 1.



**Figure 1.** Simplified mechanism of the dehydrochlorination process (Rodolfo Jr. and Mei, 2007).

## 2. MODEL SCHEME

### 2.1. Balance of chemical species

According the reaction presented on Figure 1, we used the ionic mechanism equation, proposed by Starns (2002), where the radical  $Cl\cdot$  processes are responsible for transfer process that generates new labile defect and leads to autoacceleration:



The rate of given equations depends of the constant of reaction values  $k_1$  and  $k_2$ , the initial luminous intensity ( $I_0$ ) and of the constant of reaction inverse ( $k_{-2}$ ) in a lower proportion, once  $k_{-2} \ll k_2$ .

This mathematical model we present the result of degradation according to the consumption of chemical species by the following differential equations:

$$\frac{d[HCl]}{dt} = k_2 \cdot [PVC\bullet] \cdot [Cl\bullet] - k_{-2} \cdot [\sim CH_2CH_2 \sim] \cdot [HCl] \quad (2)$$

$$\frac{d[\sim CH_2CH_2 \sim]}{dt} = k_2 \cdot [PVC\bullet] \cdot [Cl\bullet] - k_{-2} \cdot [\sim CH_2CH_2 \sim] \cdot [HCl] \quad (3)$$

$$\frac{d[Cl\bullet]}{dt} = k_1 \cdot [PVC] \cdot [I_0] - k_2 \cdot [PVC\bullet] \cdot [Cl\bullet] + k_{-2} \cdot [\sim CH_2CH_2 \sim] \cdot [HCl] \quad (4)$$

$$\frac{d[PVC\bullet]}{dt} = k_1 \cdot [PVC] \cdot [I_0] - k_2 \cdot [PVC\bullet] \cdot [Cl\bullet] + k_{-2} \cdot [\sim CH_2CH_2 \sim] \cdot [HCl] \quad (5)$$

According the Eq.(1) we propose that the degraded PVC may be given in function of HCl generated. Therefore, we can obtain a first order process in polymer mass not degraded, luminous intensity and the constant of reaction  $k_1$ .

$$\frac{d[PVC]}{dt} = - \frac{d[HCl]}{dt} = -k_1 \cdot [PVC] \cdot [I_0] \quad (6)$$

Equation (6) is dependent of  $k_1$  that may be given in function of the energy activation, the process temperature and of the HCl generation:

$$k_1 = t_0 \cdot \exp\left(\frac{E_a}{RT}\right) \cdot \frac{E_q^n}{S^n + E_q^n} \quad (7)$$

Where:

$t_0$  = time to onset the degradation ( $h^{-1}$ )

$E_a$  = energy activation (kJ/mol)

$R$  = Regnault constant (kJ/mol.K)

$T$  = temperature (K)

$E_q$  = chemistry energy (kJ)

$n$  = adjustment coefficient

$S$  = saturation constant (kJ)

## 2.2. Energy Balance

Whereas in the control volume the energy input is in form of light, and accumulates only as chemical energy in molecules, we have the energy balance is given as follows:

$$\frac{dE_T}{dt} = \frac{dE_q}{dt} + \frac{dE_{luz}}{dt} \quad (8)$$

It is known that the luminous energy does not accumulate in control volume, so:

$$\frac{dE_{luz}}{dt} = I_0 - E_{qabs} - I_s = 0 \quad (9)$$

With this, we consider that luminous energy that enters may accumulate in the form of chemical energy ( $E_{qabs}$ ) or exits of the control volume. The luminous intensity that leaves the control volume ( $I_s$ ) may be given by the Lambert-Beer law:

$$I_s = I_0 \cdot e^{-\alpha \cdot \ell \cdot [PVC]} \quad (10)$$

Where,

$\alpha$  = absorption coefficient ( $M \cdot m^{-1}$ )  
 $\ell$  = control volume thickness (m)  
 $[PVC]$  = PVC concentration ( $mol \cdot L^{-1}$ )

The chemical energy balance is given by:

$$\frac{dE_q}{dt} = Y \cdot k_1 \cdot [PVC] + E_{qabs} \quad (11)$$

This balance considers that the chemical energy in the control volume will be used to PVC degradation, which is dependent on the yield coefficient ( $Y$ ), or will accumulate in the system.

To obtain the chemical energy accumulate in the system, we may combine the Eqs. (9) and (10):

$$E_{qabs} = I_0 \cdot (1 - e^{-\alpha \cdot \ell \cdot [PVC]}) \quad (12)$$

### 3. COMPUTATIONAL SIMULATION

The ordinary differential equations (2), (3), (4), (5), (6) and (11) form a system time dependent and not dependent of space. They were implemented in the Fortran program to observe the behavior of production and consumption of chemical species involved in the reaction present in Fig. 1 and the production of chemical energy during the development. The resulting set of ODEs was solved using Runge-Kutta fourth order with fixed time step.

**Table 1.** Parameters used.

Parameter	Value
$t_0$ ( $h^{-1}$ )	1
$E_a$ (kJ/mol)	108.26 <sup>(1)</sup>
$R$ (kJ/mol.K)	8.314
$T$ (K)	293.15
$n$	10
$S$ (kJ)	500
$\alpha$ ( $M \cdot m^{-1}$ )	0.001 <sup>(2)</sup>
$\ell$ (m)	0.015
$Y$ (kJ/M)	100
$k_2$	10
$k_{-2}$	0.001

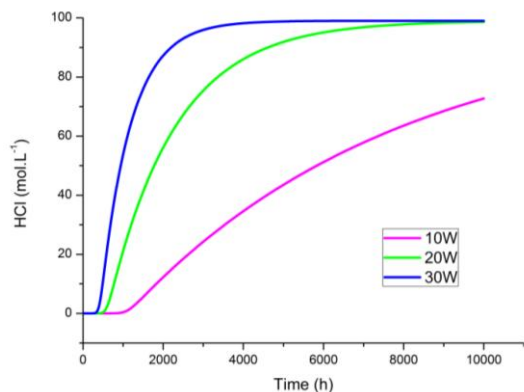
<sup>(1)</sup> Nunes *et al.*, 2006.

<sup>(2)</sup> Singh *et al.*, 2010.

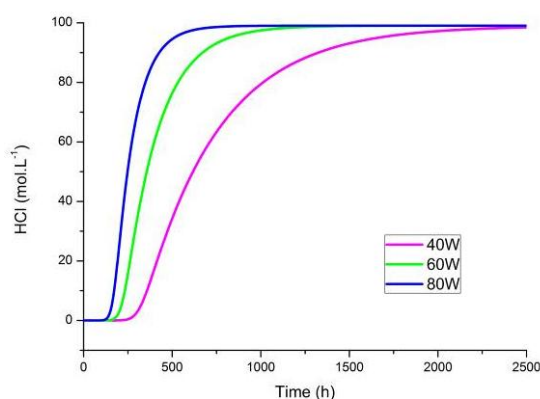
### 4. RESULTS AND DISCUSSION

The graphs were generated to compare the behavior under different luminous intensities, ranging from 10W to 80W, as can be seen in the results below.

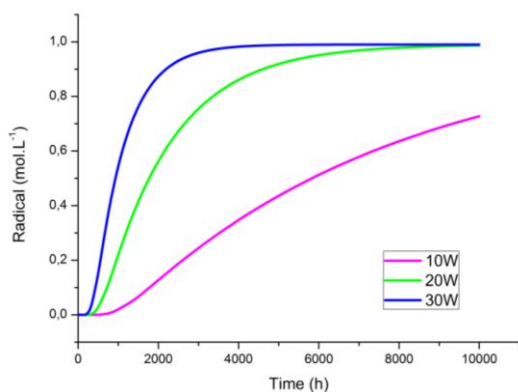
The variation of chemical species concentration poly(chloride vinyl) according the generated program has been shown graphically for low light intensities and for high light intensities.



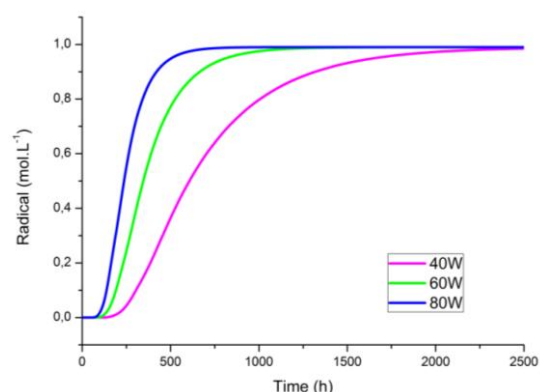
**Figure 2.** Variation of HCl concentration with low light intensity.



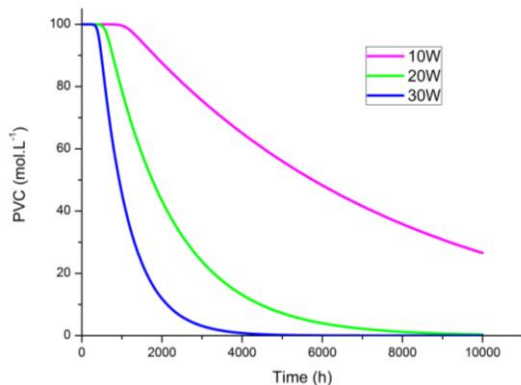
**Figure 3.** Variation of HCl concentration with high light intensity.



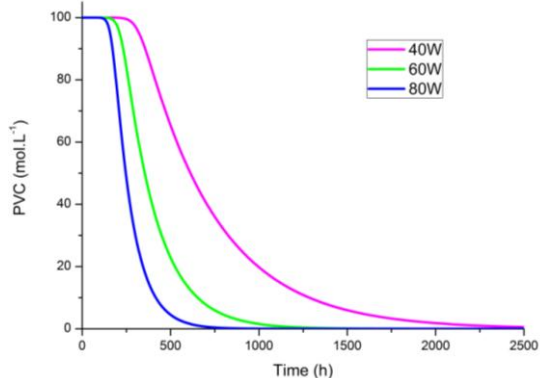
**Figure 4.** Variation of PVC· concentration with low light intensity.



**Figure 5.** Variation of PVC· concentration with high light intensity.



**Figure 6.** Variation of PVC concentration with low light intensity.



**Figure 7.** Variation of PVC concentration with low light intensity.

The kinetic curves of mass change of HCl are shown in Figs. 2 and 3, where the first one simulates de concentration change under conditions of low light intensity and Fig. 3 shows the simulation under high light intensity. The concentration changes correspond to HCl formation during the photodegradation. Compared with curves presented by Fig. 6 and 7, it is observed that the PVC consumption is directly proportional to HCl production. A sigmoid curve is observed to all species concentration changes. This is expected once it is necessary that the system absorbs a certain amount of energy required to form the excited state. How shown on the graphs, has a stationary state at begin to the curve, in this phase, the system is accumulating chemical energy provides by the light energy that arrives into the control volume.

A comparison of mathematical kinetic models with experimental observations indicated that the well-known autocatalysis of dehydrochlorination by HCl begins with an interaction of HCl with a polyene sequence, and this interaction facilitates the photodegradation.

How expected, the degradation it is initiated more quickly when the polymer is exposed to higher light intensities. To low light intensity, the stationary phase lasts for 600 hours for an intensity of 10 watts. While to 20 watts and 30 watts, this phase lasts about 290 and 180 hours, respectively. The difference between 10-20 watts it is much larger than 20-30 watts of exposure. This is a pattern observed when the light intensity is increased, like observed in graphs of high intensities too. With this it is possible conclude that above some intensities, isn't proportional the increasing of degradation.

To high intensities, the stationary phase lasts for 130 hours for an intensity of 40 watts, while it falls drastically to 85 hours to 60 watts and 62 hours to 80 watts.

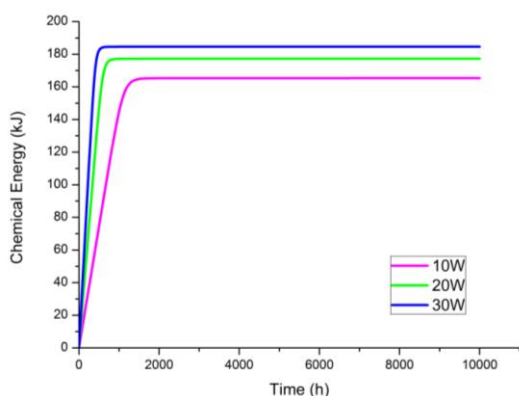
It is important note that the PVC is a fraction of undegraded poly(vinyl chloride). When the constants of reaction come to equilibrium, the degradation reaction will tend to stop, but as noted, this happens only when the PVC concentration is very low (Table 2).

**Table 2.** Duration of stabilization phase and life-time of PVC under different light intensities

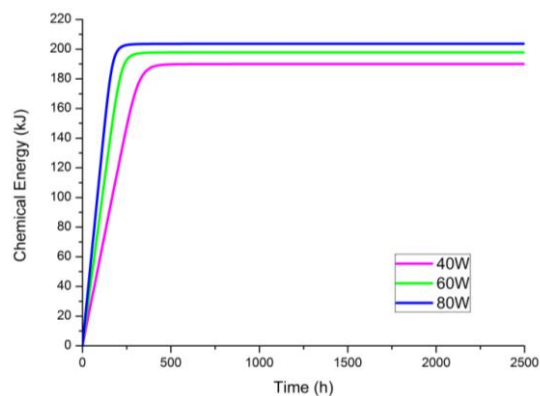
Light Intensity (W)	Stabilization phase (h)	Lifetime (h)
10	600	31 858
20	290	19 801
30	180	8 968
40	132	4 171
60	85	2 363
80	62	1 379

With increase of intensity, the percentage of stationary phase compared with the lifetime increases too. To low intensities this relation is 1.8%, 1.4% and 2% to 10, 20 and 30 watts. While to high intensities, this relation is 3.2%, 3.6% and 4.5% to 40, 60 and 80 watts. With these dates we suppose that how higher the light intensity, higher will be the stationary phase too. This is due to the chemical energy accumulated during the reaction that has different values to different intensities.

The chemical energy evolution may be observed in the Figs. 8 and 9. Differently that the other curves presented, the chemical energy it is accumulated during the initial phase. When the absorbed energy it is sufficient to break the double bond it is initiated an accelerated process of degradation.



**Figure 8.**



**Figure 9.**

After this, the chemical energy is constant. This happens because the chemical energy absorbed ( $E_{qabs}$ ) decreases according the degradation occur. Considering that the chemical energy is the energy of bond of molecules, as a degradation progress, the number of bond decrease. It is expected this behavior of chemical energy, especially when the reaction reaches the equilibrium.

According the increment of light intensity, the chemical energy stabilization happens before and with a smaller value. To low intensities, the chemical energy stabilizes in 165.32 kJ, 177.21 kJ, and 184.55 kJ to 10, 20 and 30 watts. While to high intensities this values are 189.94 kJ, 197.81 kJ and 203.55 kJ. To major values of light intensity, the chemical energy accumulated is major too, because of this the degradation happens before, once the energy supplied is major.

## 5. CONCLUSIONS

Many authors proposed models to thermal degradation of PVC, but in their results are usually given to very high temperatures what isn't interesting to this paper, once our aim it is obtain the degradation profile in environmental conditions.

The results demonstrate presented good curves, with the expected behavior of chemical species, but still miss studies about the coefficients of reaction, and the composition influence in their values.

It is known that the absorption coefficient ( $\alpha$ ) changes with the increase light intensity, but was not found in literature studies with these relations.

This model may be a initial model. Still have to consider the alfa change and the relation with absorbance. Obtain the absorbance profile during the degradation it is interesting once most article presents results with this relation.

The including of chemical energy profile during the degradation was an innovation that comes to help to understand the energy behavior during the process, and proved as a good tool to compare different results.

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