

## **A STUDY ON THE KINETICS OF OXYGEN REDUCTION FOCOAR**

**Le Quoc Khanh<sup>1,\*</sup>, Vo An Quan<sup>2</sup>, Nguyen Thi Hao<sup>2</sup>, Do Tra Huong<sup>3</sup>,  
Nguyen Van Duong<sup>1</sup>, Le Xuan Que<sup>2</sup>**

<sup>1</sup>*Tay Bac University, Quyet Tam Ward, Son La*

<sup>2</sup>*Institute for Tropical Technology, VAST, 18 Hoang Quoc Viet Road, Ha Noi*

<sup>3</sup>*Thai Nguyen University of Education, 20 Luong Ngoc Quyen Street, Thai Nguyen*

\*Email: *khanhle80@gmail.com*

Received: 11 August 2017; Accepted for publication: 6 October 2017

### **ABSTRACT**

In poor oxygenated environments the oxidation and growth of the living organisms are slowed or stopped, so that food is better preserved. The most appropriate method for oxygen depletion in the air-tight minienvironment is oxygen reduction with iron-based reducing agent, which can reduce the air oxygen concentration to about 0 %, and maintain this low oxygen concentration long during storage. This paper studies the kinetics of oxygen reduction by reducing agent FOCOAR in an airtight minienvironment under isobaric conditions. The kinetics of the reduction process calculated according to the relation  $v_{av} = [21 \% - C_{O_2}(\text{end})] / t_{\text{end}}$ , in which  $v_{av}$  is average reduction rate,  $C_{O_2}(\text{end})$  is oxygen concentration at the end of the experiment,  $t_{\text{end}}$  is total time needed for the oxygen reduction experiment. Instantaneous reduction rate  $v_{\text{red}}$  was calculated according to equation  $v_{\text{red}} = \Delta C_{O_2} / \Delta t$ , in which  $\Delta C_{O_2}$  is oxygen concentration reduced in time  $\Delta t$ , and  $\Delta t = t_{i+1} - t_i$  is time interval for oxygen reduction. It is found that  $v_{av}$  depends on the quantity of reducing agent FOCOAR, and in certain time interval varies as linear function of reduction time, corresponding to constant  $v_{\text{red}}$ . The kinetic result allows an estimating the amount of the reducing agent FOCOAR needed for a preserve minienvironment.

*Keywords:* tropical preservation, corn grain, hermetic poor oxygen, FOCOAR deoxidizer.

### **1. INTRODUCTION**

Metals produced from oxide ore tend to be oxidized by oxygen in the air to form a stable oxide that originally exists in nature [1]. This is known as corrosion, a process that occurs in almost every field of technology, industry and life, causing tremendous economic harm, especially for coastal tropical countries. In terms of thermodynamics the process of metal

corrosion is a natural process of force majeure. Kinetically, the rate of metal corrosion depends on many factors, in which catalysts and metal surfaces play an important role [1].

The general chemical equation for this corrosion - oxidation is:



where M denotes the metals.

The catalyst makes the process (1) more favorable, the surface effect acting on the speed of the general reaction (3), can increase the speed many times, even to millions of times. With the theoretical model in which the corrosion rate  $v_{\text{corr}}$  is proportional to the surface area S of the M metal by the formula

$$v_{\text{corr}} = k.S_M \quad (4)$$

where k is the coefficient, and the metal material M is in form of  $1 \text{ cm}^3$ , which will allow to calculate the relative rate of corrosion increasing with decreasing particle size (Figure 1).

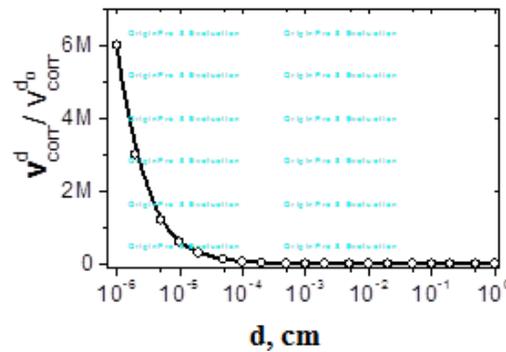


Figure 1. The rate of corrosion increases with decreasing particle size,  $v_{\text{corr}}^d$ : the rate of corrosion at size d;  $v_{\text{corr}}^{\text{do}}$ : the rate of corrosion in dimensions by  $1 \text{ cm}^3$ .

Thus, it is possible to produce some selected powdered metal materials with suitable particle size for an air deoxygenator. In a hermetic minienvironment the deoxygenator can reduce the concentration of oxygen to zero, creating an oxygen-poor minienvironment for antioxidant tropical preservation [2, 3].

In fact, this is a very suitable micro-environment for storage and prevention of oxidation, which can be applied in many industrial sectors, including tropical preservation for technical materials, agro-forestry postharvest, cereals, food, pharmaceutical etc. [3].

Deoxidizer FOCOAR is researched and manufactured at the Institute for Tropical Technology with the major component of iron powder, zinc and some additives, used to reduce the air oxygen in the air-tight minienvironment under normal temperature, pressure and humidity. In other words, FOCOAR works under normal microclimate conditions, which have the effect of modifying microclimate with 21 % (rounded) oxygen concentration to the controllable lower oxygen, even up to zero, for the long time [3].

The deoxidization of FOCOAR in an air-tight micro-medium has been investigated initially for tropical preservation [3]. There is, however, no in-depth study of kinetics towards modeling,

thereby facilitating more proactive control of the deoxygenation process in the microenvironment. This article presents the deoxidization kinetics of the deoxidizer FOCOAR.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Material

PET plastic bottle: Polyethylene terephthalate, transparent 100 % pure, 38 cm high, diameter 23 (cm), surface area of 0.234 m<sup>2</sup>, capacity of 15.78 liters; 5 Valve lock ¾, PVC pipe φ 44, PVC resin glue; Corn seeds F1 hybrid NK7328. Deoxidizer FOCOAR manufactured by the Institute for Tropical Technology, is a dark pigment, packaged in 20×20×5 size, weighing 10 g, 20 g and 30 g / pack.

### 2.2. Equipment

Grain moisture meter: Farmcomp, Wile 55, ± 0.5 % error, Air Hygrometer: Hair Hygrometer, error ± 1 %; Gauge of oxygen concentration (percentage by volume of oxygen in air), error of ± 0.1 %.

Study layout: The deoxydiser FOCOAR (1. in Fig. 2) is placed at the bottom of the tank with a plastic lining to adjust the mouth of the bag to control the concentration of oxygen from the outside, Plastic. The oxygen sensor is placed in the neck of the device,

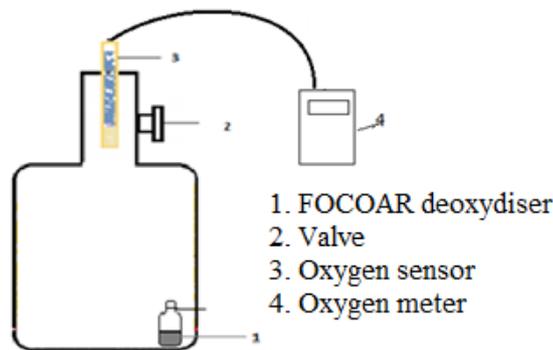


Figure 2. Hermetic bag (PET) for poor oxygen.

### 2.3 Methodology

#### *Evaluation of the deoxidation rate of the FOCOAR in microenvironment*

The deoxidation rate of the FOCOAR deoxidizer was evaluated using the oxygen meter to measure the change in oxygen concentration over time. The oxygen content in the air was considered to be of 21 %.

Average oxygen reduction rate  $v_{av}$  for the total reduction process, from original oxygen concentration 21 % up to the end nearly at 0 %, was calculated as follows:

$$v_{av} = [21 \% - C_{O_2} (\text{end})] / t_{\text{end}} \quad (5)$$

where:  $C_{O_2} (\text{end})$ : Oxygen concentration at the end of the experiment;  $t_{\text{end}}$ : Total time needed for the oxygen reduction experiment.

Oxygen reduction rate  $v_{\text{red}}$  was calculated as follows:

$$v_{\text{red}} = \Delta C_{\text{O}_2} / \Delta t \quad (6)$$

where:  $\Delta C_{\text{O}_2}$  : Oxygen concentration reduced in time  $\Delta t$ ;  $\Delta t$ : Time for oxygen reduction.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of FOCOAR content on the deoxidation rate in PET

The amount of FOCOAR in PET was 20 g, 40 g, and 60 g, respectively. The results of the study on the variation of oxygen concentration over time are presented in Figure 3.

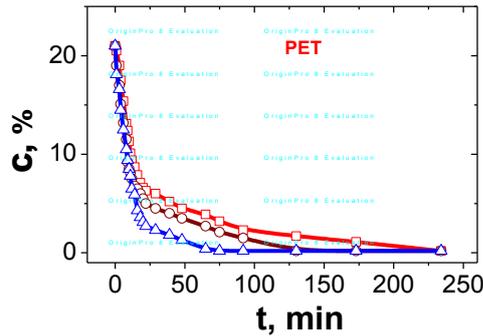


Figure 3. The process of reducing oxygen levels in PET over time, with three quantities 20, 40 and 60 g of deoxygenation FOCOAR.

Calculated data of average rate of oxygen reduction in PET  $v_{\text{av}}$  according to equation (5) is presented in Table 1. Varying this average deoxidation rate in PET as a function of the content of FOCOAR in the interval of 20 g – 60 g is described in Figure 4.

Table 1. Average rate of oxygen reduction  $v_{\text{av}}$  (% / min) depends on FOCOAR mass  $m_{\text{FOCOAR}}$  (g).

No,	$m_{\text{FOCOAR}}$ , g	$V_{\text{av}}$ , % / min
1	20	0,00566
2	30	0,00802
3	40	0,01009
4	50	0,01402
5	60	0,01749

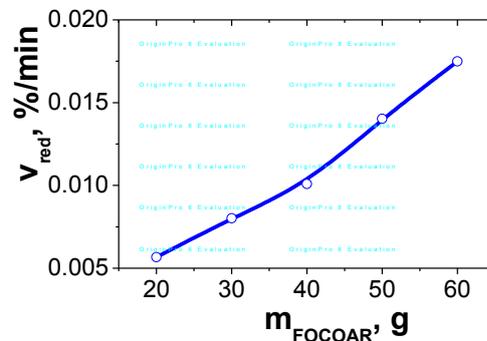


Figure 4. Variation of average rate of oxygen reduction  $v_{\text{red}}$  as a function of FOCOAR mass  $m_{\text{FOCOAR}}$ .

With FOCOAR mass of 60 g the highest reduction rate of oxygen reduction results decreasing in the time needed to take oxygen concentration down to 0, with a required duration within 100 minutes, in line with the experimental requiring.

Consequently, the amount of FOCOAR 60 g was chosen in subsequent experiments.

### 3.2. Oxygen reduction in PET containing corn seeds

Two PET bottles of the same capacity: empty (PET1), containing 10 kg of corn grain at a moisture content of 13% (PET2).

The 60 g FOCOAR bag was placed at the bottom of the tanks, Oxygen sensor placed on the neck of PÉT, and conducted to the test and to determine the variation in oxygen concentration from 21 % to approximately 0 % over time.

Experimental data of the variation of oxygen concentration by time are shown in Tables 2.

Table 2. Changes in oxygen concentration over time in PET1 and PET2 microenvironments.

Without corn grain (PET1)				With 10 kg of corn grain (PET2)			
t (min)	Oxy, %	t (min)	Oxy, %	t (min)	Oxy, %	t (min)	Oxy, %
0	21,0	18	6,0	0	21,0	407	6,0
1	19,0	20	5,5	28	19,0	454	5,5
3	17,0	22	5,0	59	17,0	511	5,0
4	15,0	25	4,5	100	15,0	572	4,5
6	13,0	26	4,0	155	13,0	638	4,0
8	11,0	28	3,5	217	11,0	714	3,5
9	9,0	31	3,0	286	9,0	805	3,0
10	8,5	35	2,5	307	8,5	969	2,5
11	8,0	52	1,5	324	8,0	1550	1,5
12	7,5	59	1,1	343	7,5	1869	1,1
14	7,0	72	0,5	365	7,0	2229	0,5
16	6,5	84	0,2	385	6,5	2403	0,2

For better visualization the decreasing of oxygen concentration in PET as a function of experimental time t are represented in Figure 5 and 6.

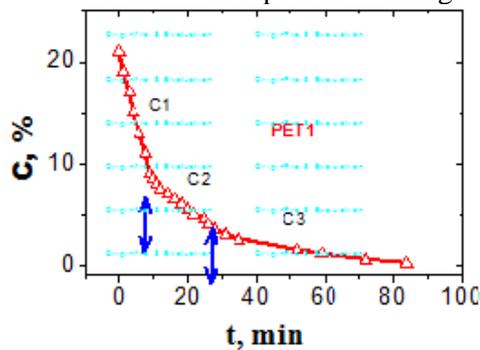


Figure 5. Oxygen concentration in PET1 variation over time as a function of time t, C is volumic concentration of oxygen (%)

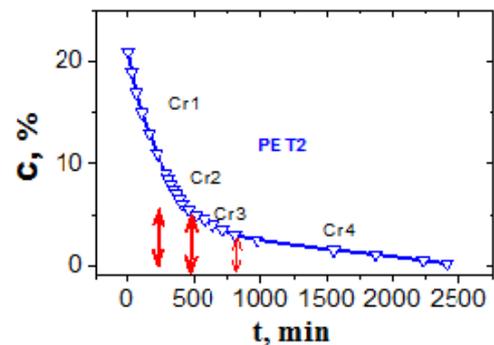


Figure 6. Oxygen concentration in PET2 variation over time as a function of time t, C is volumic concentration of oxygen (%)

The average deoxidation rate from the oxygen concentration of internal 21 % to 0.2 % was calculated using equation (5) in 2.3 paragraph. For the PET1 micro-environment, the average deoxidation rate for the total test time is  $v_{av} = 0,2476 \text{ \% / min}$  and PET2 microenvironment is  $v_{av} = 0,0086 \text{ \% / min}$ . Deoxidation rates in PET2 microarrays are about 29 times slower than in PET1. Because in the microenvironment, PET2 contains 10 kg of maize with a small grain of corn grain, slowing the diffusion of oxygen to the reducing agent's surface, leading to a slower rate of deoxygenation.

It is evident that in both experiments the oxygen concentrations were decreased but not linearly with test time during the total reduction process Fig. 5 and 6. However in certain section the concentration decrease linearly varied with the test time which can be described as linear equation:

$$C_i = -kt_i + C_{i_{t_{i0}}} \quad (7)$$

where  $k$  is linear coefficient  $k > 0$ ,  $t_i$  is time interval in section  $i$ ,  $C_i$  is oxygen concentration in section  $i$  and  $C_{i_{t_{i0}}}$  is oxygen concentration section  $i$  but at time starting this section  $t_{i0}$ , off course section  $i = 1$  is just original atmosphere oxygen concentration  $C_{1_{t_{10}}} = 21 \text{ \%}$ .

Specifically, for PET1 microarrays there are 3 linear intervals resulting 3 equations  $C_1$ ,  $C_2$ ,  $C_3$  with reliability  $R$  over 0,989, with PET2 environment there are 4 linear intervals  $Cr_1$ ,  $Cr_2$ ,  $Cr_3$ ,  $Cr_4$  with degrees  $R$  confidence above 0,985, Table 3.

*Table 3.* Linear Equation  $C_i = -kt_i + C_{i_{t_{i0}}}$  in different section of curves  $C - t$  of oxygen reduction in PET1 and PET2. (Note there is an error occurred during linearization due to which  $C_{1_{t_{10}}}$  is only approximately equal original atmosphere oxygen concentration).

PET1		PET2	
Linear equation	$R^2$	Linear equation	$R^2$
$C_1 = -1,239t_1 + 20,850$	0,9962	$Cr_1 = -0,052t_1 + 20,900$	0,9852
$C_2 = -0,249t_2 + 10,562$	0,9973	$Cr_2 = -0,0268t_2 + 16,797$	0,9972
$C_3 = -0,051t_3 + 4,155$	0,9595	$Cr_3 = -0,007t_3 + 8,650$	0,9921
		$Cr_4 = -0,0016t_4 + 3,999$	0,9965

From the experimental results (Table 2) there is possible to calculate the correlation ( $v_{red} - t$ ) according to equation (6). Using certain mathematical smoothing for the curve, original from rough results calculated according to equation (6), with differential expression  $\Delta C_{O_2} / \Delta t$ , 3 sections of constant  $v_{red}$  are occurred which is very well corresponding to the linearity of the equation  $C - t$  described in Table 3. The results obtained from this calculation and smoothing for the case of oxygen reduction in PET1 are described using curves  $v_{red}$  versus  $t$  (Figure 7).

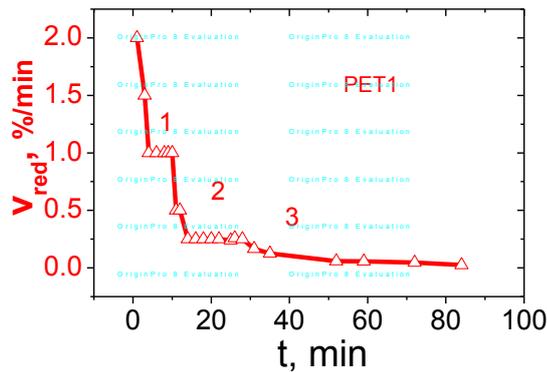


Figure 7. Variation of oxygen reduction rate  $v_{red}$  (% / min) as a function of  $t$ , PET1, different reaction phases 1 to 3.

Using this graph (Figure 7) one can well distinguish 3 different sections (different phases) of the oxygen reduction process from 1 to 3. It is interesting that the constant level of  $v_{red}$  well expresses the linearity of the equation  $C_i = -kt + C_{i_{TiO}}$  (Table 3).

On the other hand, the transition of each phase to other of the deoxygenation process represents a passivation of metals [1] in FOCOAR deoxidizer which are oxidized to reduce the atmosphere oxygen in the minienvironment PET. The metal oxidation product  $M_nO_m$  forms oxidation products layer that covers the surface to reduce decay attainment. This layer is passivation layer but usually is unstable, then swollen due to the volume of oxide being higher than that of the metal [1]. Each time the passive layer breaks open, it causes a new deoxygenation phase, until the next passive layer could be formed covering the surface [1, 4].

#### 4. CONCLUSIONS

Deoxygenated kinetics was studied using 20 g to 60 g FOCOAR deposited in PET minienvironments. The obtained result shows that all the tests have deoxygenated approximately to the end of up to 0% which manifest a possibility to form poor oxygen minienvironments for the antioxidant preservation. The greater the amount of reducing agent FOCOAR, the higher the reduction rate, the container containing 60 grams of reducing agent has a maximum average reduction rate  $v_{av} = 0.2476$  % / min. When comparing deoxidation in PET bottles of 10 kg of corn kernels and the deoxidization in empty PET flasks, the deoxidation rate is highly dependent on the diffusion through the corn kernels.

The kinetics of the oxygen reduction using FOCOAR deoxydiser depends on the different phases of the oxidation – passivation of the metals in the deoxydiser. Initial oxidation kinetics is found being linear but gradually becomes slow down due to a passivation formed by reaction product layer covering the active metal surface. This passivation layer is usually unstable, then swollen due to the volume of oxide being higher than that of the metal. Each time the passive layer breaks open, it causes a new deoxygenation phase, until the next passive layer could be formed covering the surface

**Acknowledgement.** This research is funded by Institute for Tropical Technology - VAST.

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