



Research/Technical Note

Esterification Between Citric Acid and *Callistemon citrinus*, Rice-Husk, *Garcinia dulcis* Catalysed by Citric Acid's-H⁺-Monomers and Polymers Formation Mechanism

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Abstract: Esterification between citric acid molecules and molecules of *Callistemon citrinus*, rice husk and *Garcinia dulcis* (pulp-peel and pips) were carried out such as the citric acid molecules quantities (moles) were negligible against to these raw materials' reactive molecules quantities (moles). Results showed generally an important initial, total conversions (after 60 minutes) of citric acids molecules which confirmed the essential role of raw materials' aromatics molecules characterized by their alkene organic-function titrated with HF-0.00261N (Hydrofluoric acid) as support of citric acid's protonic acid H⁺ catalyst (a portion of the carboxylic acids' citric acid molecules used), support of non-ionic citric acid's carboxylic acid (a portion of the carboxylic acids' citric acid molecules used) and support of raw materials molecules reagents. So, the citric acid partial order of esterification of these used raw materials (*Callistemon citrinus*, rice husk and *Garcinia dulcis* (pulp-peel and pips)) with citric acid molecules were determined. Also, the brown citric acid equivalent monomers formed during esterification were calculated and their evolution were followed for all raw materials and results allowed to determine the citric acid's protonic acid activities. In the same time, relationship between raw materials' external specific surfaces, estimated by calculated and measured densities, and conversion or brown citric acid equivalent formed were established to conduct finally at the catalyst turnover. The variation of alkene organic-function concentration and/or quantities not only in solution but also in all by-products allowed to an ionic mechanism of these esterification with citric acid catalyzed by citric acid's protonic acid H⁺ (a portion of the carboxylic acids' citric acid molecules used) supported on all raw materials' aromatics molecules and fiber structures in glass-flask where not only carbonic acids molecules but also hydrogens molecules gas were emitted. Finally, seeing that a non-negligible alkene organic-function quantities were titrated on all by-products, their valorization as catalytic support of citric acid molecules polymerization were carried out and a procedure constituted principally with estimation of dichloromethane and hexane insoluble/soluble products, titration with HF-0.00261N of the unsaturated organic-function in hexane soluble products and titration with NaOH-0.05N of the black citric acid equivalent quantities evolutions were established and the results confirmed the ionic mechanism of esterification with citric acid molecules during which not only carbonic gas and hydrogen gas were emitted but also new monomers and each equivalent saturated products (characterized by their globally white color and unsaturated organic-function titrated with HF-0.00261N), new polymers and poly-polymers (characterized by their globally black color and titrated with NaOH-0.05N) different to that obtained with radical mechanism catalyzed by Lewis acid sites were formed.

Keywords: Esterification, Citric Acid's Protonic Acid H^+ , Catalyst, Support, *Callistemon citrinus*, Rice-husk, *Garcinia dulcis*, Hexane, Dichloromethane, Soluble Products, Insoluble Products, Monomers, Polymers

1. Introduction

The first step the characterizations of raw materials such as their compositions and also their sieving-characteristics as such as specific diameter, calculated volumetric mass (density), calculated external specific surfaces, measured density, measured external specific surfaces deduced by measured density. The second step was the esterification reaction with citric acid molecules [1] which consisted not only to esterify the acid function of the citric acid molecules by rice husk's, *Garcinia dulcis*' and *Callistemon citrinus*' organic molecules but also to esterify the acid functions of their organic molecules by the citric acid molecules' alcohol functions. Thus, citric acid polymers and esters of citric acid molecules with rice husks', *Garcinia dulcis*' (pips – pulp-pell) and *Callistemon citrinus*' organic molecules in glass-balloon auto-catalysed by citric acids' protonic acids H^+ were obtained with each by-products according to a mechanism. So, not only the quantifications of citric acids' protonic acid catalysts were done but also the quantification of formed esters was made by measuring out with 0.05N-NaOH solution the rest of citric acid molecules' acid functions not having been esterified [1]. Also, the quantifications of alkene-equivalent content of raw materials, esters solutions and by-products were done to evaluate their aromatics' functions on surfaces and structures contributions as catalytic support of citric acid molecules esterification, citric acid protonic acid H^+ -catalyst and polymerization. Finally, by-products valorization was made as catalytic support to polymerize citric acid molecules in the same time a control-procedure was established to evaluate the polymerization evolution, to confirm and established the citric acid molecules polymerization on glass-material auto-catalyzed by citric acids' protonic acid H^+ .

2. Esterification Between Citric Acid Molecules and Organic Molecules

2.1. Citric Acid Generalities

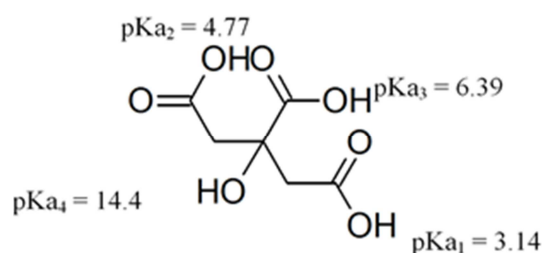


Figure 1. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid).

Citric acid $C_6H_8O_7$ is a tricarboxylic acid α -hydrolyzed. It contains three acids with pKa such as $pK_{a1} = 3.14$, $pK_{a2} = 4.77$ and $pK_{a3} = 6.39$ and a α -alcohol function with $pK_a = 14.4$ [2, 3, 4] (Figure 1). By its reactivity, the citric acid was the object of several studies and was used in several fields like the cosmetics, the food one, the chemistry and others [5, 6]. Noticed that the acid form is AH with $pK_a(AH)$. It was shown that if the $pH \leq [pK_a(AH) - 2]$, the quantity of basic A^- associated to the acid/base couple AH/A^- is negligible in comparison with the AH quantity. And if the $pH \geq [pK_a(AH) + 2]$, the quantity of acid AH associated to the acid/base couple AH/A^- is negligible in comparison with the A^- quantity [6]. For $[pK_a(AH) - 2] \leq pH \leq [pK_a(AH) + 2]$, the basic A^- and the acid AH forms coexist but if $[pK_a(AH) - 2] \leq pH \leq pK_a(AH)$ the acid form AH dominate and if $pK_a(AH) \leq pH \leq [pK_a(AH) + 2]$ the basic form A^- dominate [7]. Consequently, for the citric acid, the acids and basics forms according to the pKa and pH were showed in the following Table 1:

Table 1. Dominant Forms of "Citric Acid" According to the pH.

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
$pH \leq 3.14$	AH_3/AH_2^-	3.14	$AH_3 \rightleftharpoons AH_2^- + H^+$	AH_3	Citric Acid
$3.14 \leq pH \leq 4.77$	AH_2^-/AH^{2-}	4.77	$AH_2^- \rightleftharpoons AH^{2-} + H^+$	AH_2^-	Di-Hydrogenocitrate
$4.77 \leq pH \leq 6.39$	AH^{2-}/A^{3-}	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	AH^{2-}	Mono-Hydrogenocitrate
$6.39 \leq pH$	AH^{2-}/A^{3-}	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	A^{3-}	Citrate

2.2. Esterification with Citric Acid Molecules Principles

Fischer-Speier esterification also called carboxylic acids esterification is generally a liquid phase chemical reaction between an alcohol function and a carboxylic acid function catalyzed by H^+ ions from acids functions on solution (Figure 2). This reaction is accompanied with water molecules formation according to the general reaction (Figure 3).

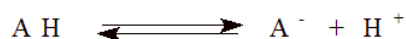


Figure 2. H^+ ions catalysts from acids functions on solution.



Figure 3. Esterification reaction general equation.

Thus, tricarboxylic acids of citric acid could be esterified with three alcohol functions of species' organic molecules (Figure 4) and also species' organic molecules carboxylic acids could be esterified by the alcohol function of citric acid (Figure 5) if the solution pH is respected [1, 7] according to the general equations:

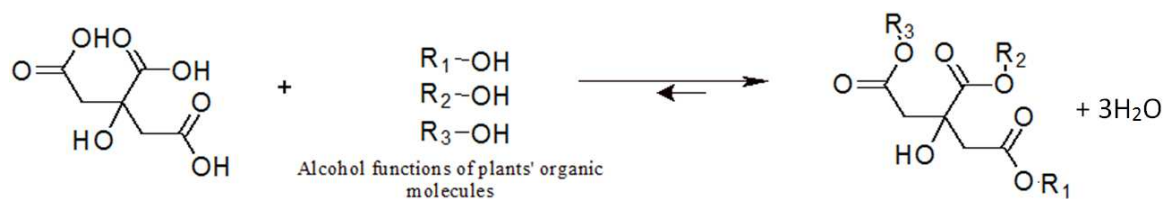


Figure 4. Tricarboxylic acids of citric acid esterification with three alcohol function of species' organic molecules.

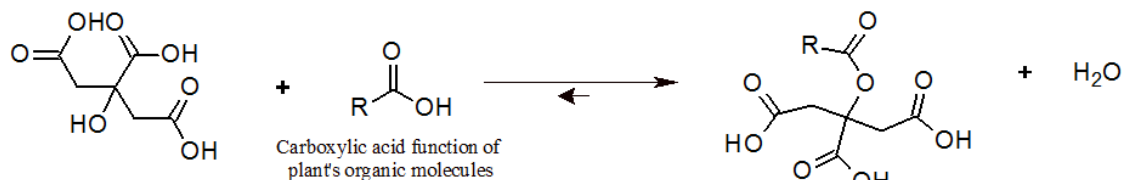


Figure 5. Acid of species' organic molecules esterification with the citric acid alcohol function.

Also, tricarboxylic acids of citric acid could be in reaction with three amino-acids or amines functions of organic molecules if the solution pH is respected [1, 7] to obtain amide molecules according to the general equations (Figure 6 – Figure 7):

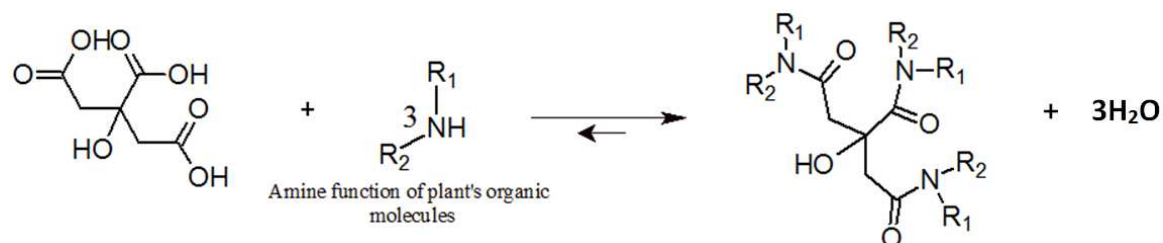


Figure 6. Amide formation by amine function and tricarboxylic acids of citric acid molecule reaction.

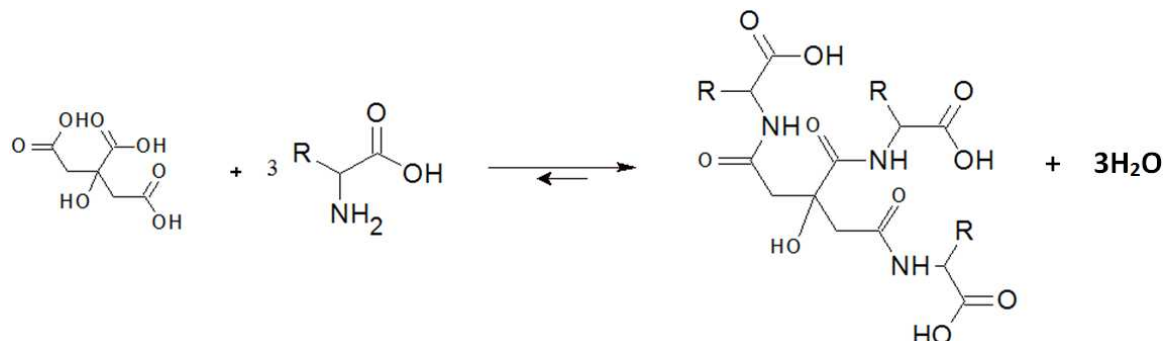


Figure 7. Amide formation by amino-acid and tricarboxylic acids of citric acid molecules.

In the present manuscript, esterification between citric acid molecules and rice husk's, *Garcinia dulcis*' and *Callistemon citrinus*' organic molecules was done. The esterification experimental conditions will be described in the following paragraphs §2.3. But above all touch on about these species' physico-chemical characteristics.

2.2.1. Rice Husk

Rice husk is the external part of rice grain which should be peeled mechanically or manually due to its inedible. Rice grain is made up approximatively of 17% to 23% rice husk according its variety. The constituent parts of rice husk varied according its variety, the geographic area of plantation, the

season and cultivation method. But generally, rice husk is constituted of 84% to 87% of organic compounds and 13% to 16% of non-organic compound such as 12% to 13% of silica (SiO₂), manganese, copper, and zinc with other oxides like MgO, K₂O, Na₂O and CaO. Organic compounds are principally cellulose, lignin, pentosane and few quantities of proteins and vitamins. The rice saponification index is 190 and it contains approximatively 0.026 (wt/wt%) of fatty acid, and 0.0498 (wt/wt%) of proteins [8, 9, 10]. The rice husk refusals size characteristics after blinder-mix (§2.3.2), used during experimentations, were shown in the following table 2.

Table 2. Mixed rice husk refusal characteristics.

Refusal Characteristics (RC)	Formulas	Rice husk
Superior sieve-Ts [mm]	0.8 (module-30)	-
Inferior sieve-Ti [mm]	0.63 (module29)	-
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	1.2698
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	0.7610
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	0.7690
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	1.8180
Rice husk total units (a)	-	32
Rice husk total units weight [g]	-	0.0235
Rice husk unit weight [g]	-	7.34E-4
Calculated Total specific volume unit [cm ³]	$V_s = \left[\frac{4}{3} \times \pi \times \left(\frac{\phi_s}{2} \right)^3 \right] \times 32_{(a)}$	7.38E-3
Rice husk calculated Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	3.1859
Rice husk calculated specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	2.48E-3
Rice husk calculated specific surface [cm ² .g ⁻¹] (1)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	24.76
Rice husk measured density [g.ml ⁻¹]	-	1.285
Rice husk measured specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	6.41E-3
Rice husk measured specific surface [cm ² .g ⁻¹] (2)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	61.38
Medium rice husk calculated specific surface [cm ² .g ⁻¹] (3)	$(3) = [(1)+(2)]/2$	43.07

2.2.2. Garcinia Dulcis

Garcinia dulcis is a tropical fruit tree native to Southeast Asia. Then, it was planted in Indochina, Malesia, Philippines through to New Guinea, Queensland and Australia [11, 12, 13]. It is also found in Africa and Madagascar such as the *Garcinia dulcis* used was gathered in the southeast of Madagascar at Ankaramalaza region. The scientific classification of *Garcinia dulcis* is shown in the following table 3 [11]. *Garcinia dulcis* is an evergreen tree with horizontal branches and a dense, pyramidal crown. A *Garcinia dulcis* fruit is composed with a green peel which is rough due to the presence of sticky liquids from its interior; a yellow fibrous-juicy pulp comestible which taste bitter-acid and pips composed with brown-husk and a buttered white cotyledon which taste bitter and spicy at the end.

Table 3. *Garcinia dulcis* scientific classification.

Kingdom	Plantae
Clade	Tracheophytes
Clade	Angiosperms
Clade	Eudicots
Clade	Rosids
Order	Malpighiales
Family	Clusiaceae
Genus	<i>Garcinia</i>
Species	<i>G. dulcis</i>
Binomial name	<i>Garcinia dulcis</i>

The refusal characteristics of *Garcinia dulcis*-pips after blinder-mix used during experimentations was given in the following table 4.

Table 4. Mixed *Garcinia dulcis* pips refusal characteristics.

Refusal Characteristics (RC)	Formulas	<i>Garcinia dulcis</i> pips
Superior sieve-Ts [mm]	2.5 (module-35)	-
Inferior sieve-Ti [mm]	2.00 (module34)	-
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	1.25
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	2.3880
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	2.4090
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	17.910
<i>Garcinia dulcis</i> pips total units (a)	-	5
<i>Garcinia dulcis</i> pips total units weight [g]	-	0.0245
<i>Garcinia dulcis</i> pip unit weight [g]	-	4.90E-3
Calculated Total specific volume unit [cm ³]	$V_s = \left[\frac{4}{3} \times \pi \times \left(\frac{\phi_s}{2} \right)^3 \right] \times 5_{(a)}$	3.56E-2
<i>Garcinia dulcis</i> pips calculated Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	0.6875
<i>Garcinia dulcis</i> pips calculated specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	1.15E-2
<i>Garcinia dulcis</i> pips calculated specific surface [cm ² .g ⁻¹] (1)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	114.72
<i>Garcinia dulcis</i> pips measured density [g.ml ⁻¹]	-	0.8033
<i>Garcinia dulcis</i> pips measured specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	9.82E-3
<i>Garcinia dulcis</i> pips measured specific surface [cm ² .g ⁻¹] (2)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	98.19
Medium <i>Garcinia dulcis</i> pips calculated specific surface [cm ² .g ⁻¹] (3)	$(3) = [(1)+(2)]/2$	106.45

The refusal characteristics of mixed *Garcinia dulcis*' pulp and peel fibrous used during experimentations was shown in the following table 5.

Table 5. Mixed *Garcinia dulcis* pulp-peel refusal characteristics.

Refusal Characteristics (RC)	Formulas	<i>Garcinia dulcis</i> pulp-peel
Superior sieve-Ts [mm]	1.00(module-31)	-
Inferior sieve-Ti [mm]	0.80 (module30)	-
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	1.25
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	0.9550
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	0.9640
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	2.8660
<i>Garcinia dulcis</i> pulp-peel total units (a)	-	97
<i>Garcinia dulcis</i> pulp-peel total units weight [g]	-	0.0104
<i>Garcinia dulcis</i> pulp-peel unit weight [g]	-	1.07E-4
Calculated Total specific volume unit [cm ³]	$V_s = \left[\frac{4}{3} \times \pi \times \left(\frac{\phi_s}{2} \right)^3 \right] \times 97_{(a)}$	6.91E-1
<i>Garcinia dulcis</i> pulp-peel calculated Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	0.0150
<i>Garcinia dulcis</i> pulp-peel calculated specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	5.24E-1
<i>Garcinia dulcis</i> pulp-peel calculated specific surface [cm ² .g ⁻¹] (1)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	5242.85
<i>Garcinia dulcis</i> pulp-peel measured density [g.ml ⁻¹]	-	0.0861
<i>Garcinia dulcis</i> pulp-peel measured specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	9.16E-2
<i>Garcinia dulcis</i> pulp-peel measured specific surface [cm ² .g ⁻¹] (2)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	916.37
Medium <i>Garcinia dulcis</i> pulp-peel calculated specific surface [cm ² .g ⁻¹] (3)	(3)=[(1)+(2)]/2	3079.61

Research on the phytochemical constituents and biological activities of *Garcinia dulcis* [13] have demonstrated that various parts of the plant contain an abundance of bioactive organic compounds mainly xanthenes and flavonoids, with significant pharmacological properties such as anti-atherosclerosis, anti-bacterial, anti-cancer, anti-hypertension, and anti-malarial. Also, it has a long history of use as a traditional medicine for the treatment of ailments such as lymphatitis, parotitis, struma, scurvy, cough and sore throat. *Garcinia dulcis* contains generally 0.4 (wt/wt%) of proteins and 0.5 (wt/wt%) of lipids with only 1 (wt/wt%) of fibrous [14].

2.2.3. *Callistemon Citrinus*

Callistemon citrinus also called “bottle brush”, because of

its form was from Australia and New-Caledonia. Etymologically, *Callistemon citrinus* was from Greek “kallos”- beauty and “stêmôn” – filament. During flowering period, this bush is composed with a long etamine like a bottle-brush followed by fruits to seed capsules formations which were spherical whose peel was brown and the interior green-white delicately perfumed. Its saponification index was 202 and contains approximatively 0.3(wt/wt%) fatty acids.

The refusal characteristics of mixed *Callistemon citrinus* fruits-seeds capsules used during experimentations was shown in the following table 6.

Table 6. Mixed *Callistemon citrinus* seeds capsule refusal characteristics.

Refusal Characteristics (RC)	Formulas	<i>Callistemon citrinus</i>
Superior sieve-Ts [mm]	2.50(module-35)	-
Inferior sieve-Ti [mm]	2.00 (module34)	-
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	1.25
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	2.3880
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	2.4090
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	17.9100
<i>Callistemon citrinus</i> total units (a)	-	7
<i>Callistemon citrinus</i> total units weight [g]	-	0.0595
<i>Callistemon citrinus</i> unit weight [g]	-	8.50E-3
Calculated Total specific volume unit [cm ³]	$V_s = \left[\frac{4}{3} \times \pi \times \left(\frac{\phi_s}{2} \right)^3 \right] \times 7_{(a)}$	4.99E-2
<i>Callistemon citrinus</i> calculated Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	1.1927
<i>Callistemon citrinus</i> calculated specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	6.61E-3
<i>Callistemon citrinus</i> calculated specific surface [cm ² .g ⁻¹] (1)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	66.13
<i>Callistemon citrinus</i> measured density [g.ml ⁻¹]	-	0.5823
<i>Callistemon citrinus</i> measured specific surface [m ² .g ⁻¹]	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	1.35E-2
<i>Callistemon citrinus</i> measured specific surface [cm ² .g ⁻¹] (2)	$S_s = 3 / \left(\frac{\rho \times \phi_s}{2} \right)$	135.44
Medium <i>Callistemon citrinus</i> calculated specific surface [cm ² .g ⁻¹] (3)	(3)=[(1)+(2)]/2	100.79

The scientific classification of *Callistemon citrinus* is shown in the following table 7 [15].

Table 7. *Callistemon citrinus* scientific classification.

Kingdom	Plantae
Clade	Tracheophytes
Clade	Angiosperms
Clade	Eudicots
Clade	Rosids
Order	Myrtales
Family	Myrtaceae
Genus	<i>Melaleuca</i>
Species	<i>M. citrina</i>
Binomial names and synonyms	
<i>Melaleuca citrina</i>	
<i>Callistemon citrinus</i>	
<i>Metrosideros citrina</i> Curtis	
<i>Callistemon citrinus</i>	

Noticed that there are about fifty (50) species of callistemon [16] but they have commonly been referred to as bottlebrushes because of their cylindrical, brush like flowers resembling a traditional bottle brush.

2.2.4. Equivalent-alkene Rate of Raw Materials Rice Husk, *Garcinia Dulcis* and *Callistemon Citrinus*

Equivalent-alkene (C^-) organic function rate of raw materials rice husk, *Garcinia dulcis* and *Callistemon citrinus* was measuring-out by HF-0.00261N titration according to the procedure described on the bibliography [17]. The results were showed in the following table (Table 8) such as the on surface equivalent-alkenes of raw materials was obtained at the first color variation from blue to transparent and their total equivalent-alkene was obtained at the second variation to yellow-green. The inside-structure equivalent-alkene corresponded to alkenes of organic functions like insoluble and soluble fiber which is located and constituted the internal-structure-microstructure of each raw materials [18, 19].

Table 8. Equivalent-alkenes rate of rice-husk, *Garcinia dulcis* and *Callistemon citrinus*.

	Rice-husk	<i>Garcinia dulcis</i> – pulp-peel	<i>Garcinia dulcis</i> - pips	<i>Callistemon. Citrinus</i>
On surface (1) equivalent-alkene [mol.g ⁻¹]	-	2.40E-4	2.667E-4	8.897E-4
Total (2) equivalent-alkene [mol.g ⁻¹]	9.03E-4	1.034E-3	1.567E-3	3.29E-3
Inside-structure (3) equivalent-alkene [mol.g ⁻¹] (3)=(2)-(1)	9.03E-4	7.94E-4	1.30E-3	2.40E-3

2.3. Esterification Between Citric Acid Molecules and Organic Molecules of rice husk – *Garcinia Dulcis* and *Callistemon Citrinus* Experimental Conditions

2.3.1. Esterification Between Citric Acid Molecules and Species' Organic Molecules Experimental Conditions

Three parameters were taken into account to optimize the esterification between citric acid molecules and organic molecules of rice husk – *Garcinia dulcis* and *Callistemon citrinus* such as:

- 1) The pH of mixed solution which were previously calculated (Table 9) [20]. Notice that all pH were less than 3.14 that is to say dominant forms were AH_3 and AH_2^- (Di-Hydrogenocitrate) (Table 1-§2.1.). That doesn't exclude the presence of AH^{2-} (Mono-Hydrogenocitrate) and possibly A^{3-} (Citrate) when citric acid molecules located in the vicinity of basic-organic functions molecules of raw materials [1].
- 2) At 60 [mn], the moles ratio between citric acid and estimated lipids or fatty acids and/or proteins of raw materials was chosen so that all the time they were around and superior to 1 to make sure that there were enough citric acid molecules for each esterification. But, for all the other times less than 60[mn], this ratio was chosen so that the lipids or fatty acids were in excess and/or in certain cases around once and maximally twice than citric acid moles (Table 9) except for *Garcinia*

dulcis this ration was very important because the ratio-evaluation was done by taking into account of only lipids or fatty acids and proteins rate. However, noticed that for *Garcinia dulcis*, lipid's or fatty acids-equivalent and proteins estimated rate reflect only 0.99% (wt/wt%), in the same case for respectively *Callistemon citrinus* and rice husk estimated rate reflect only 30% (wt/wt%) and 2.61% (wt/wt%). Consequently, these estimated ratios were undervalued and really they should be largely inferior to zero. Also, the moles ratio between total equivalent-alkene and citric acid were deduced and showed in the following Table 9; noticed that this ratio is more than three. Finally, the weight ratio between raw material and citric acid was all the time more than three. That is to say, it's possible to consider that generally the reactive organic functions, which certainly depend on each raw material alkenes titrated, is in excess than citric acid molecules. In this case, the aim was to study the citric acid esterification kinetics and the contribution of raw materials' alkene-structure functions as catalytic support as said on the bibliography [21].

- 3) The mixed solution esterification temperature which were more than 373 [°K] at its ebullition temperature. Noticed that esterification was also done with pips of *Garcinia dulcis* and all experimental conditions were shown in the following table 9.

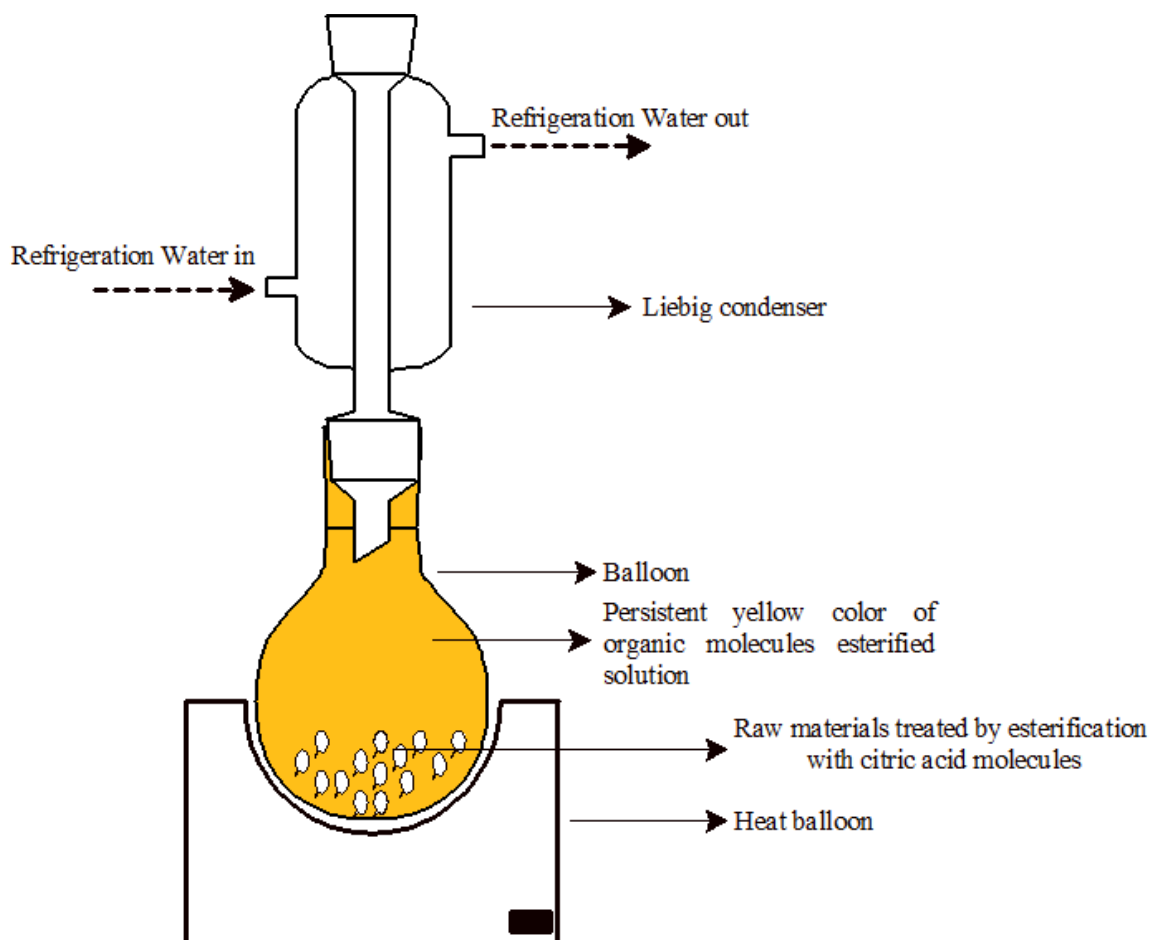
Table 9. Experimental conditions of esterification between citric acid and organic molecules of rice-husk, *Garcinia dulcis* and *Callistemon dulcis*.

	Reaction time [mn]	Raw material weight [g]	Water volume [ml]	Expected Calculated pH	Exp. pH	Citric acid weight [g]	Citric acid [moles]
Rice-husk	60	20.02	101.25	1.95	3.2	2.7849	1.45E-2
	1-5-15	20.02	90	2.45	3.2	0.85	4.4E-3
<i>Garcinia dulcis</i> – pulp – peel	60	27.95	101.25	2.31	2.73	1.856	0.0097
	1-5-15	25.03	66.5	2.31	2.73	1.2205	0.0064
	60	13.98	101.25	1.79	2.01	20.0179	0.1042
<i>Garcinia dulcis</i> – pips	1	13.98	20	2.10	2.09	1	0.0052
	2	09.19	12.9	2.10	2.09	0.6431	0.0033
	5	13.98	20	2.10	2.09	1.0095	0.0053
<i>Callistemon</i>	60	13.2520	150	2.16	2.24	2.7849	0.0290
<i>Citrinus</i>	2-5-15	13.2520	59	2.16	2.47	0.85	0.0109

Table 9. Continue.

	Reaction time [mn]	Estimated fatty acids and/or protein [moles]	Estimated Citric acid/fatty acids and/or protein moles ratio	Total Alkene-equivalent/Citric acid moles ratio	Raw material/ Citric acid/Weight ratio
Rice-husk	60	1.7760E-3*	8.1619	1.2471	7
	1-5-15	1.7760E-3*	2.4911	4.0861	24
<i>Garcinia dulcis</i> – pulp – peel	60	5.5118E-4*	17.5271	2.9910	15
	1-5-15	4.9376E-4*	12.8663	4.0745	21
	60	2.7563E-4*	378.018	0.2101	0.7
<i>Garcinia dulcis</i> – pips	1	2.7564E-4*	18.8835	4.2063	14
	2	1,8116E-04*	18.4771	4.2988	14
	5	2,7563E-04*	19.0634	4.1666	14
<i>Callistemon</i>	60	1.434E-2*	2.02	1.5053	2.5
<i>Citrinus</i>	2-5-15	1.43E-2*	0.7605	4.0001	6.5

*Estimation deduced by taking account of lipids or fatty acids and proteins rate of each raw materials given by webographies.

**Figure 8.** Raw materials' organic molecules extraction by citric acid esterification assembly.

2.3.2. Esterification Between Citric Acid Molecules and Species' Organic Molecules Procedure

Firstly, raw materials were mixed with a blender and their size were estimated using sieves. The refusals sizes were characterized and each mixed-raw materials characteristics were shown in the table 2, table 4, table 5 and table 6 (§2.2.1-§2.2.2-§2.2.3) respectively for rice-husk, *Garcinia dulcis* pips and *Callistemon Citrinus*. But, mixed product of *Garcinia dulcis* pulp-peel were so fluid with thins heterogeneous filaments and it was practically impossible to estimate their corresponding size and characteristics as sphere or cylinder. In any case, all raw materials equivalent-alkene rates were shown in table 8. Equipments accessories and chemical products used for the esterification with citric acid molecules were: balloon (250[ml]) – Liebig-condenser – heat balloon – screen - balance – magnetic stirrer – refractometer. So, secondly took and weight the citric acid and raw materials to be esterified. Prepare the citric acid solution for the esterification in the balloon and put in the raw materials. Complete the extraction assembly (Figure 8) and finally heat the balloon inside the heat balloon at the reaction temperature. When the experimental duration has passed, stop the heat balloon without stopping the Liebig-condenser water refrigeration not only to reduce the balloon-temperature but also to eliminate the light gas leak risk. Immediately, as soon as possible change the heat balloon to a beaker containing iced-cube which not only stop the esterification-reactions but also it stop the opposite reaction –hydrolysis of the obtained esters. When the balloon temperature was carried out to room temperature, stop the refrigeration water of Liebig

condenser and we obtained a homogeneous brown extracted-liquid and/or by-products (according to the experimental conditions) which was the residual of raw materials. Thus, pass the obtained solution in the balloon through the screen to recover not only the brown esters solutions of raw materials' organic molecules in a beaker which allowed to suggest a mechanism of alkene formation by citric acid molecules decarboxylation on glass flask catalyzed by its own protonic-acid- H^+ (§3.) but also the by-products (retained on the screen) whose all characterizations by HF-0.00261N titration allowed to suggest a global mechanism of esterification between citric acid molecules and organic molecules – Alkene's organic molecules as heterogeneous catalytic support (§4.) and the by-products valorization as catalytic support for citric acid polymerization §5.

3. Esterification Between Citric acid Molecules and Organic Molecules of Raw Materials Global Results

As described previously, the pH during esterification between citric acid and organic molecules of rice husk, *Garcinia dulcis* and *Callistemon citrinus* on glass flask were in the vicinity of]1.14 – 3.14[that is to say, on these conditions the dominant forms were AH_3 (citric acid) and AH_2^- (Di-Hydrogenocitrate) (Table 1-§2.1.). The global results of these esterification were shown in the following table 10.

Table 10. Global results of rice husk, *Garcinia dulcis* and *Callistemon citrinus* esterification with citric acid molecules.

	Reaction time [mn]	Raw material weight [g]	Water volume [ml]	Exp. pH	Citric acid weight [g]	Conversion [%]	By-product weight [g]
Rice-husk	60	20.02	101.25	3.2	2.7849	75.64	63.7514
	1	20.02	90	3.2	0.85	19.61	62.598
	5	20.02	90	3.2	0.85	23.57	58.332
	15	20.02	90	3.2	0.85	24.23	59.44
<i>Garcinia dulcis</i> – pulp – peel	60	27.95	101.25	2.73	1.856	62.77	67.02
	1	25.03	66.5	2.73	1.2205	25.08	23.94
	5	25.03	66.5	2.73	1.2205	38.23	18.14
	15	25.03	66.5	2.73	1.2205	45.19	23.94
<i>Garcinia dulcis</i> – pips	60	13.98	101.25	2.01	20.0179	90.90	21.80
	1	13.98	20	2.09	1	61.51	22.99
	2	09.19	12.9	2.09	0.6431	73.64	21.43
	5	13.98	20	2.09	1.0095	96.37	26.6516
<i>Callistemon Citrinus</i>	60	13.25	150	2.24	2.7849	30.63	53.7020
	2	13.25	59	2.47	0.85	04.37	28.14
	5	13.25	59	2.47	0.85	06.40	34.105
	15	13.25	59	2.47	0.85	15.93	27.305

Table 10. Continue.

	By-product increased ratio [%]	Extracted solution volume [ml]	Extracted solution odor and color	Extracted solution density [g/ml]	Total extracted weight [g]
Rice-husk	218.44	50	Rice-husk-odor Brown-yellow	0.80	103.75
	212.68	48.10		0.8200	102.04
	191.37	47.50	Rice-husk-odor White-brown	0.8000	96.332
	196.90	45.00		0.8000	95.44
<i>Garcinia dulcis</i> – pulp – peel	139.79	39.50	Pungent-odor Pungent-taste Yellow-pale ~ slightly-brown	0.8772	101.665
	-4.35	62.50	Pungent-odor	0.9815	85.29
	-27.53	64.20	Pungent-taste	0.9810	81.12
	-4.35	61.00	Yellow	0.8772	77.45
			Pungent-odor		
	55.94	95.50	bitter-taste Yellow-brown-gluey	0.8700	104.89
<i>Garcinia dulcis</i> – pips	64.45	11	Pungent-odor bitter-taste Yellow-gluey	0.9177	33.0797
			Pungent-odor		
	133.19	-	bitter-taste Yellow-brown-gluey	-	21.43
			Pungent-odor		
	90.64	≈ 0.29	bitter-taste Yellow-brown-gluey	≈ 0.8700	26.9024
			Pungent-odor		
<i>Callistemon Citrinus</i>	305.30	92	Pungent-taste Red-brick-brown	0.6105	109.87
	112.38	45	Pungent-odor	0.9700	71.79
	157.40	38.50	Pungent-taste	0.9625	71.16
	106.08	42.10	Yellow-brown	0.9593	67.69

3.1. Citric Acid Conversions Evolution in Terms of Time (Extracts and by-Products Qualities)

According to the previous table 10, the extracted solutions colors, odors and tastes; the increasing of all by-products weight versus the initial weight of used raw materials indicates that there were not only esterification between raw materials organic functions with citric acid molecules but also polymerization of citric acid molecules occurred on raw

materials' organic functions structure and/or eventually inside the porous generated by these structures [21]. Thus, the citric acid conversion increased all the time with reaction duration (Figure 9). For *Garcinia dulcis* pips, the citric acid conversion decrease slightly with time seeing that *Garcinia dulcis* contains esters of citric acid whose quantities increased with time and in the same time contributed to decrease slightly its global conversion by NaOH-0.05N titration.

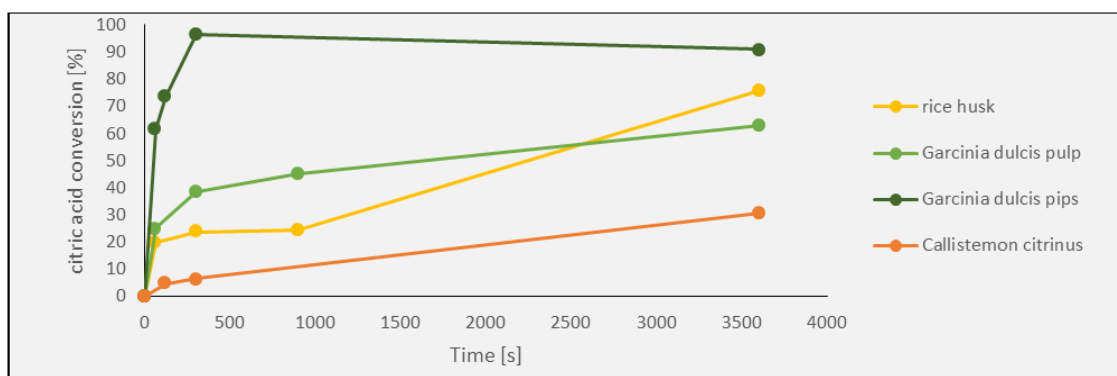


Figure 9. Citric acid conversion evolution in terms of time.

3.2. Quantification of Brown Citric acid Polymers Equivalent (bp-equivalent) Formed During Esterification

Noticed that during the esterification between citric acid

molecules and raw materials organic functions there was formations of not only esters but also citric acid molecules polymers such as yellow, red brick and brown citric acid polymers located on the raw materials structures and/or

eventually inside its structure porosity. In these cases of experimental conditions (table 9), the polymerization of citric acids molecules were certainly catalyzed by their own protonic acid-H⁺ seeing that any catalyst like H⁺/H₂SO₄ or Fe [6, 11] were used during the esterification. Thus, a mechanism of alkene formation by citric acid molecules decarboxylation on glass flask catalyzed by their own protonic acid-H⁺ is described in the following paragraphs leading to the formations of not only citric acid polymers but also hydrogen (H₂) and other molecules. Also, seeing that all citric acid polymers [6] were formed during all esterification reactions, their quantifications was done by NaOH-0.05N titration and the results was given as brown citric acid polymers equivalent (bp-equivalent) which is the greatest form of polymers noticed.

3.2.1. Proposal Mechanism of Citric Acid Molecules

Polymerization by Alkene Formation Through Citric Acid Molecules Dehydration and Decarboxylation

The first step was all the time citric acid molecules dehydration catalyzed in this case by their own protonic acid-H⁺ (figure 10); water molecules and alkene functions of citraconic acid (prop-1-ene-1,2,3-tricarboxylic acid) were formed. Then, two citraconic acids reacted to form 2,3-bis(carboxymethyl)but-3-ene-1,2,4-tricarboxylic acid [figure 11-(I)] whose four acid functions reacted each other to form water molecules and 2,4,7,9-tetraoxo-1,4,5,6,7,9-hexahydrooxepino[4,5-d]oxepine -5a(2H)-carboxylic acid [figure 12-(A)] which is constituted

with two hydracids functions and one carboxylic acids function. Then, the decarboxylation of 2,4,7,9-tetraoxo-1,4,5,6,7,9-hexahydrooxepino[4,5-d]oxepine -5a(2H)-carboxylic acid (A) catalyzed by citric acid molecules protonic acid-H⁺ occurred according to the mechanism described on the following figure (figure 13-decarboxylation-mechanism) with formation of carbon dioxide gas (CO₂), hydrogen gas (H₂), citric acid's protonic acid-H⁺ catalyst regeneration and the products [Figure 14-(B-yellow monomers)]. Hydrogenations of these B-yellow monomers obtained by glass flask catalyzed with citric acid protonic acid-H⁺ in solution gave [Figure 15-(D-new monomer)] and [Figure 15-(C-new products)] according to whether respectively one or two of alkene functions were hydrogenated. Finally, B- yellow monomers polymerizations occurred also in solution catalyzed by the citric acid's protonic acid-H⁺ according to the previous mechanism [Figure 11(I)] to form red-brick, brown and eventually black citric acid polymers [6, 20]. Noticed that in the same time, (D)-new monomers can reacted together in solution to form a new organic products-compounds without alkene functions (E) catalyzed by the citric acid's protonic acid-H⁺ according to the previous mechanism [Figure 11(I)] (Figure 16). Finally, noticed that (E) could reacted together and/or reacted with another (D)- new monomers to form polymers like black citric acid polymer (F) for example (Figure 17) and their alkene functions could be hydrogenated to form each equivalent saturated organic molecules.

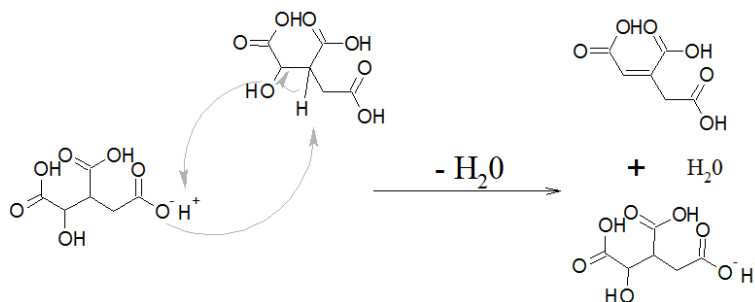


Figure 10. Citric acid molecule dehydration catalyzed by citric acid protonic acid H⁺.

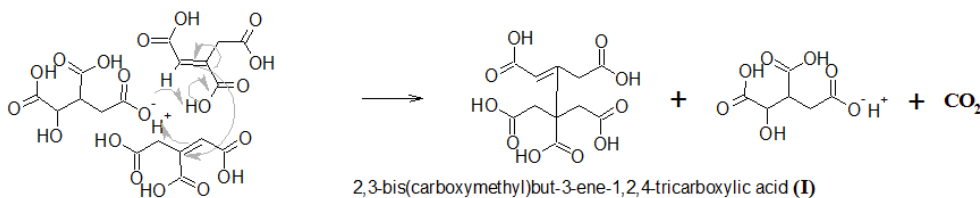


Figure 11. (I). Citraconic acid dimerization to form (I).

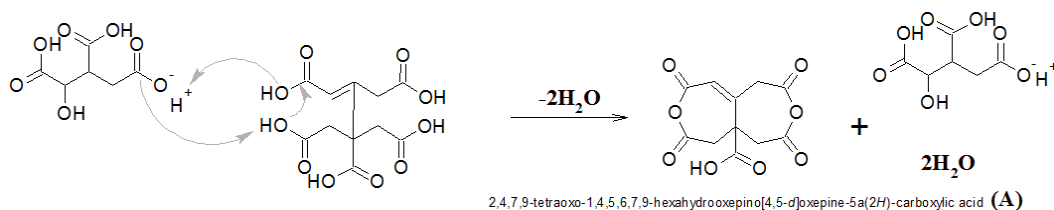


Figure 12. (A). (I) dehydration to form (A).

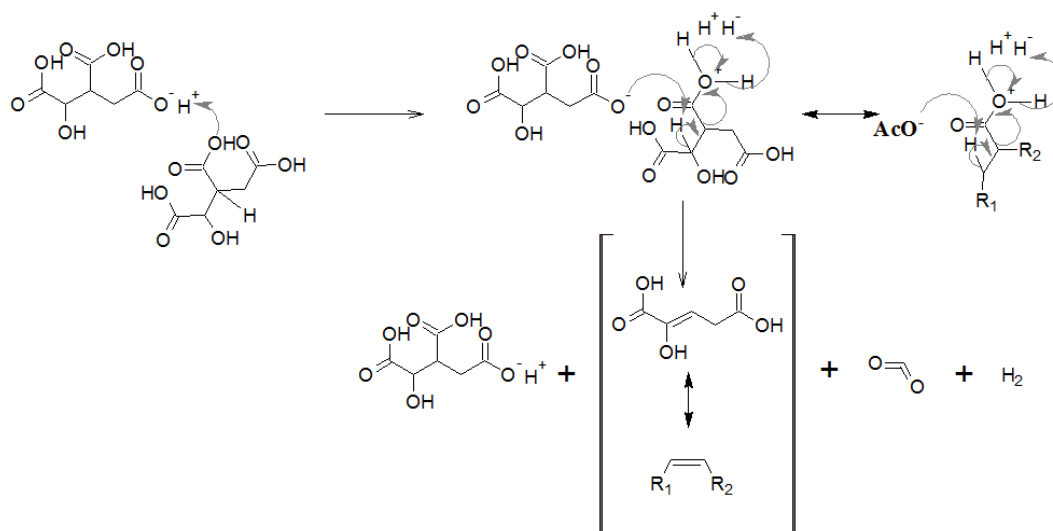


Figure 13. Decarboxylation mechanism.

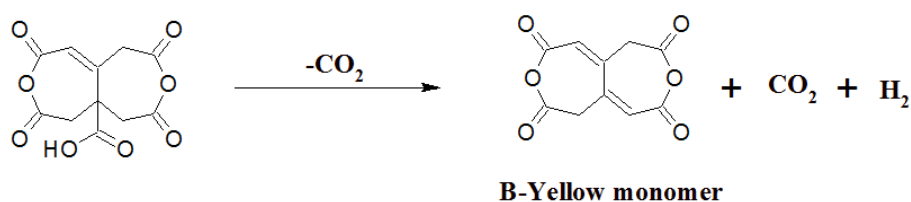


Figure 14. B-yellow monomer formation.

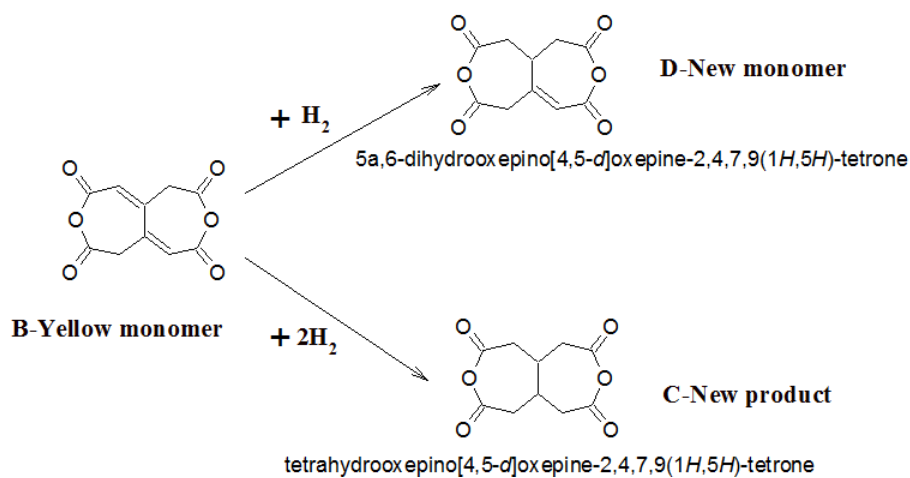


Figure 15. B- Yellow monomer hydrogenation to D-new monomer and -C-new products.

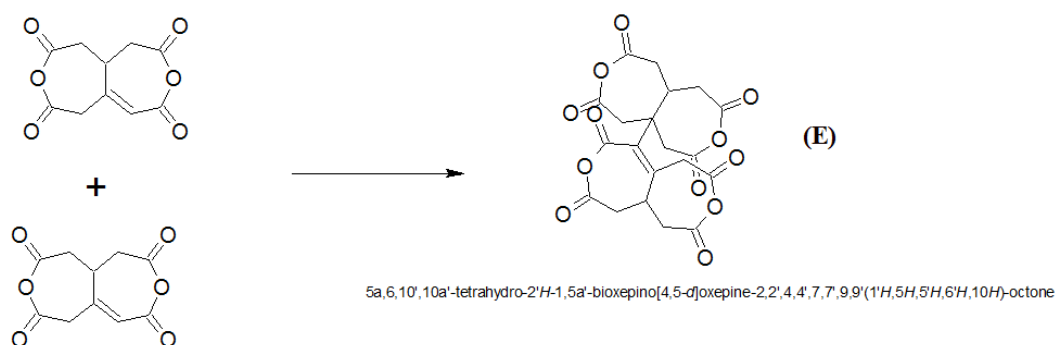


Figure 16. (E) formation by D-new monomers dismutation.

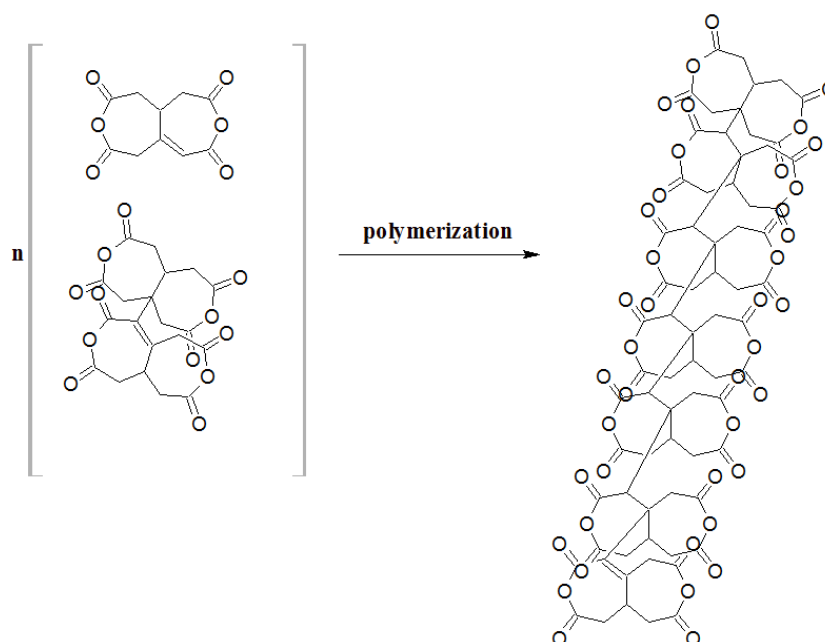


Figure 17. (E) and/or (D) monomers polymerization to form polymers as (F).

3.2.2. Brown Citric Acid Equivalent Polymers

(bp-equivalent) Quantification During esterification

According to the mechanism described Above (figure 13 decarboxylation mechanism), it was possible to quantify the carbon dioxide gas (CO_2) emitted during the esterification reaction. In order to ensure this, the law of mass conservation was used assuming that the water mass condensed on the assembly was counted as negligible. Then, the brown citric acid polymers equivalent (bp-equivalent) quantification during esterification was offset seeing that according to the global brown citric acid polymer formation (bp) mechanism, the moles carbon dioxide gas emitted and brown citric acid polymer ratio was 10. The following table 11 shows these results. Notice that total extracted weight was the weight of esters solution (deducted by its volume and density-Table 10)

plus by-product weight (Table 10). Also, noticed that at 60[mn], the carbon dioxide conversion calculated by carbon dioxide emitted weight and citric acid with raw materials weight ratio were too high confirming not only the water molecules elimination to form alkene functions and/or esters and/or hydracids of citric acid polymers synthesized with their possible condensations on the assembly during the reactions and also the other carbon dioxide formed by raw materials' carbonic acid decarboxylation. These results confirmed also the high values of by-products increased ratio (Table 10). Assuming that all carbon dioxide emitted were from citric acid polymerization seeing that decarboxylation of raw materials' carboxylic acid functions were also possible according to the previous mechanism (§3.2.1.), the equivalent-brown citric acid calculated.

Table 11. Global results of rice husk, *Garcinia dulcis* and *Callistemon citrinus* decarboxylation and equivalent-brown citric acid polymers formation.

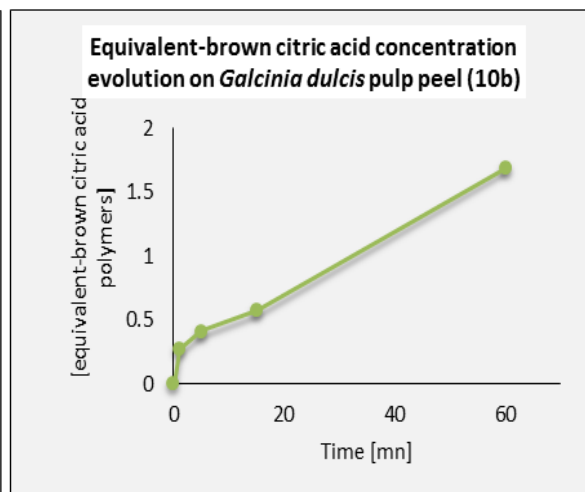
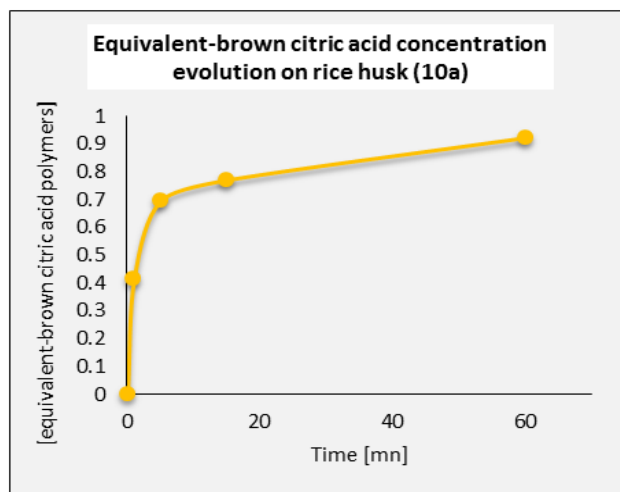
	Reaction time [mn]	Total reagent and solvent-water weight [g]	Total extracted weight [g]	Carbon dioxide weight [g]	Carbon dioxide Conversion [%]
Rice-husk	60	124.0549	103.7514	20.3035	89.03
	1		102.04	8.83	42.31
	5	110.87	96.332	14.538	69.66
	15		95.44	15.43	73.93
<i>Garcinia dulcis</i> – pulp – peel	60	131.0508	101.665	29.3858	98.61
	1		85.2878	7.4658	28.44
	5	92.7536	81.1204	11.6363	44.32
	15		77.4532	15.3136	58.30
<i>Garcinia dulcis</i> – pips	60	135.2424	104.89	30.3574	89.31
	1	34.9749	33.0797	1.8952	12.66
	2	22.7280	21.43	1.3009	13.24
	5	34.9840	26.9024	8.0816	53.93
<i>Callistemon Citrinus</i>	60	168.8201	109.868	58.9521	-
	2		71.79	2.5573	16.66
	5	74.3473	71.1613	3.1861	20.76
	15		67.6915	6.6558	43.37

Table II. Continue.

	Carbon dioxide [moles]	Equivalent-Brown citric acid polymers [moles]	Equivalent-brown citric acid polymers concentration [mol.l ⁻¹]	Extracted solution odor and color
Rice-husk	0.4614	0.4614E-1	0.9229	Rice-husk-odor
	0.2007	0.2007E-1	0.41722	Brown-yellow
	0.3304	0.3304E-1	0.6956	Rice-husk-odor
	0.3507	0.3507E-1	0.7703	White-brown
<i>Garcinia dulcis</i> – pulp – peel	0.6679	0.6679E-1	1.6908	Pungent-odor
				Pungent-taste
				Yellow-pale ~ slightly-brown
	0.1697	0.1697E-1	0.2715	Pungent-odor
	0.2645	0.2645E-1	0.4119	Pungent-taste
	0.3480	0.3480E-1	0.57055	Yellow
				Pungent-odor
<i>Garcinia dulcis</i> – pips	0.6899	0.6899E-1	-	bitter-taste
				Yellow-brown-gluey
				Pungent-odor
	0.0431	0.0431E-1	0.2292	bitter-taste
				Yellow-gluey
	0.0296	0.0296E-1	0.2422	Pungent-odor
				bitter-taste
<i>Callistemon Citrinus</i>				Yellow-brown-gluey
	0.1837	0.1837E-1	0.9513	Pungent-odor
				bitter-taste
				Yellow-brown-gluey
	1.3398	1.3398E-1	0.7282	Pungent-odor
				Pungent-taste
				Red-brick-brown
	0.0581	0.0581E-1	0.1292	Pungent-odor
	0.0724	0.0724E-1	0.1881	Pungent-taste
	0.1513	0.1513E-1	0.3593	Yellow-brown

These results confirmed that not only there were esterification between citric acid molecules and raw materials' organic functions but also polymerization between citric acid molecules and eventually decarboxylation of raw materials' carboxylic acid. Indeed, the following figures (figure 18a-18b-18c-18d) showed that the concentration of equivalent-brown citric acid polymers increased rapidly all the time for all raw materials. That allowed to study the kinetic

against citric acid seeing that they were negligible in comparison with raw materials' organic molecules constituted mainly of alkenes organic functions (Table 3) and/or carboxylic acids and its derivatives in the following paragraphs on chapter 4. Also, effects of alkenes-organic molecules of raw materials as heterogeneous support contribution will be study in the following paragraph §.3.2.3.



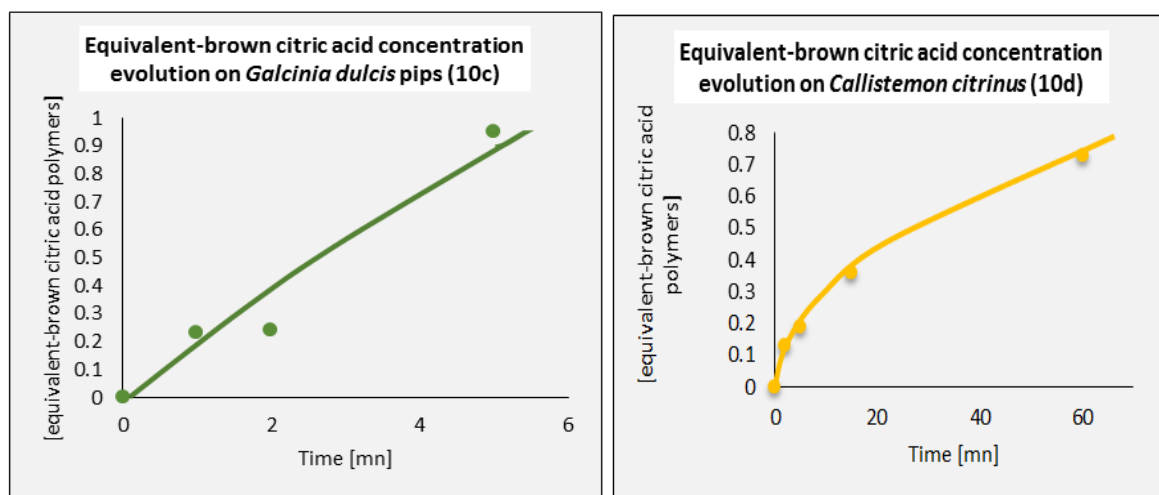


Figure 18. Equivalent-brown citric acid concentration evolution in terms of time for rice husk (18a) – *Garcinia dulcis* pulp – peel (18b) – *Garcinia dulcis* pips (18c) and *Callistemon citrinus* (18d).

3.2.3. Effects of Specific Surfaces and Initial Total Alkene Concentrations of Raw Materials During Their Esterification with Citric Acid Molecules

As shown on paragraph §3.2.1., these esterification and citric acid polymerization reactions were catalyzed in this case by citric acid's protonic acids H^+ which can move through raw materials' aromatics and polynuclear aromatics alkene functions [21]. So, to evaluate their contributions and activities as citric acid's protonic acids H^+ catalytic-support, the evolutions of citric acid conversions and brown citric acid polymers equivalent (bp-equivalent) concentrations per raw material's specific surfaces and per raw material's initial alkene concentrations were shown in the following table 12 and these figure 19 and figure 20.

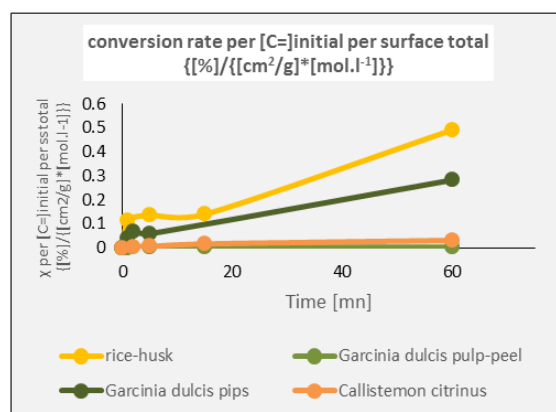


Figure 19. Conversion rate per initial concentration of raw materials' alkenes functions and per surface total of raw materials used evolutions during experimentations.

Table 12. Global results of raw materials characteristics effects on citric acid conversion and on brown citric acid polymers equivalent (bp-equivalent) formation evolutions.

Raw materials	Rice-husk				Garcinia dulcis pulp-peel			
Times [mn]	1	5	15	60	1	5	15	60
Raw materials weight [g]	20.02				25.03	25.03	25.05	27.94
Initial solution volume [ml]	90			101.25	66.5			101.25
Specific surfaces $[cm^2/g]$	43.0677				3079.61			
Total surface $[cm^2]$	862.22				77094		77130	86059
$[C^-]$ initial $[moles.g^{-1}]$	0.000903				0.001034			
Total C^- $[moles]$	0.018078				0.02588			0.02889
$[C^-]$ initial $[mol.l^{-1}]$	0.20087			0.1785	0.38924			0.28538
Total surface* $[C^-]$ initial index	173			154	30007		30036	24559
Conversion per $[C^-]$ initial per surface total $\{[\%]/[cm^2/g]*[mol.l^{-1}]\}$	1.132E-01	1.36E-01	1.39E-01	4.91E-01	8.36E-04	1.274E-03	1.51E-03	2.556E-03
[bp-equivalent] per $[C^-]$ initial per surface total $\{[pm]/[cm^2/g]*[mol.l^{-1}]\}$	2.409E-03	4.016E-03	4.5E-03	5.995E-03	0.905E-05	1.373E-05	1.90E-05	6.89E-05

Table 12. Continue.

Raw materials	<i>Garcinia dulcis</i> pips				<i>Callistemon citrinus</i>			
Times [mn]	1	2	5	60	2	5	15	60
Raw materials weight [g]	13.97	9.18	13.97		13.25			
Initial solution volume [ml]	20	12.9	20	101.25	59			
Specific surfaces [cm ² /g]	106.45				100.79			
Total surface [cm ²]	1488	978	1488		1336			
[C ⁻] initial [moles.g ⁻¹]	0.001567				0.00329			
Total C ⁻ [moles]	0.0219	0.0144	0.021898		0.043599			
[C ⁻] _{initial} [mol.l ⁻¹]	1.0949	1.1157	1.0949	0.2162	0.738967			
Total surface* [C ⁻] _{initial} index	1628	1091	1628	322	987			
Conversion per [C ⁻] _{initial} per surface total {[%]/{[cm ² /g]*[mol.l ⁻¹]}}	3.78E-02	6.75E-02	5.92E-02	2.83E-1	4.43E-03	6.49E-03	1.61E-02	3.10E-02
[bp-equivalent] per [C ⁻] _{initial} per surface total {[pm]/{[cm ² /g]*[mol.l ⁻¹]}}	1.41E-04	2.22E-04	5.84E-04	—	1.31E-04	1.91E-04	3.64E-04	7.38E-04

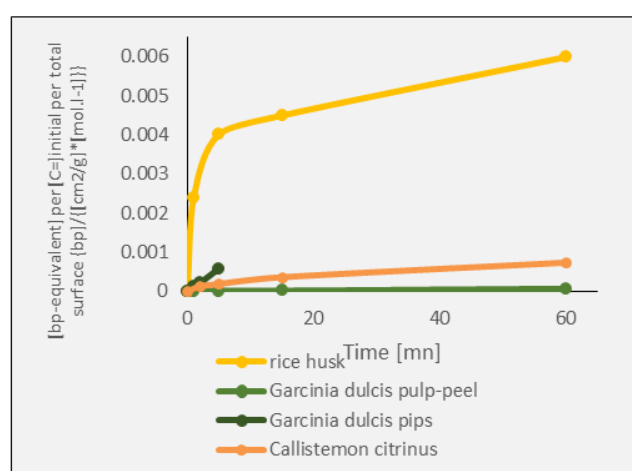


Figure 20. Brown citric acid polymers equivalent per initial concentration of raw materials' alkenes functions and per surface total of raw materials used evolutions during experimentations.

These results showed clearly that initial alkenes concentrations, specific surfaces and total surfaces affected not only the initials conversion and bp-equivalent formation but also their durability along the time. Noticed that more the total surface multiplied by [C⁻]_{initial}-index of raw materials was, less will be the conversion and bp-equivalent ratio results. Noticed also that sometimes even if the time experimentation increased the conversion and bp-equivalent formation per initial alkenes concentration per total surface increased. That allowed to study the effects of citric acid's protonic acid H⁺ and firstly calculate the initial quantities of effective citric acid's protonic acid H⁺ which initially catalyzed reactions was done and to follow their activities and turnovers assuming that these quantities stayed stable during the experimentations seeing that the pH unregistered at 60[mn] were globally slightly higher than the initial pH. So, secondly the dispersion of citric acid's protonic acid on raw materials' aromatics and polynuclear aromatics alkene functions were calculated equals to [H⁺] concentration divided by [C⁻]_{initial} concentration. Finally, the initials and the evolutions of citric acid's protonic acid H⁺ supported on raw materials' aromatics and

polynuclear aromatics alkene functions activities and turnovers were also given as shown in the following table 13.

Noticed that, for lower values of initial {total surface× [C⁻]_{initial}} index, the initial dispersions decreases when {total surface× [C⁻]_{initial}} index increases (Figure 21). But, at a higher value of initial {total surface× [C⁻]_{initial}} index, the initial dispersion value became more important (Figure 21).

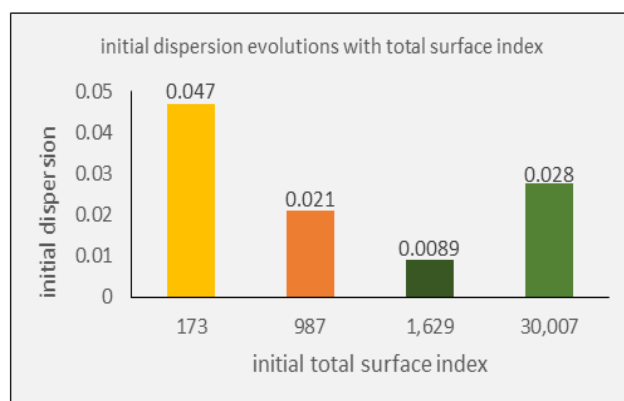


Figure 21. Initial dispersion evolutions according to initial total surface index.

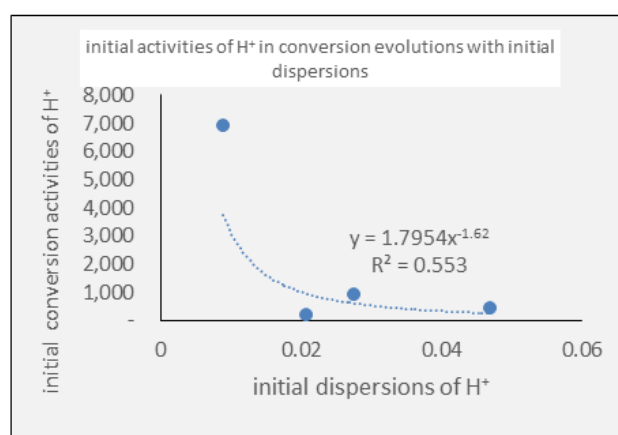


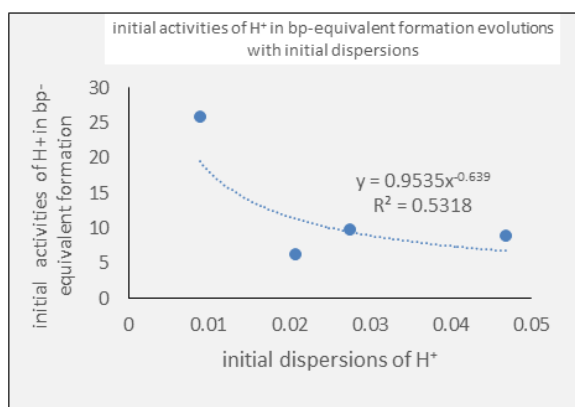
Figure 22. Initial activities of H⁺ in conversion evolutions with initial dispersions.

Table 13. Global results of raw materials' H^+ dispersions, activities and turnovers and activities evolutions.

Raw materials	Rice-husk				Garcinia dulcis pulp-peel			
Times [mn]	1	5	15	60	1	5	15	60
Initial solution volume [ml]	90			101.25	66.5			101.25
Specific surfaces [cm^2/g]	43.0677				3079.61			
Total surface [cm^2]	862.22				77094		77130	86059
$[C^-]$ initial [moles. g^{-1}]	0.000903				0.001034			
Total C^- [moles]	0.018078				0.02588			0.02889
$[C^-]_{initial}$ [mol. l^{-1}]	0.20087			0.1785	0.38924			0.28538
Total surface $\times[C^-]_{initial}$ index	173			154	30007		30036	24559
Citric acid [moles]	0.0044			0.0145	0.0064			0.0097
H^+ [moles]	8.48E-4			2.8E-3	7.16E-4			1.09E-3
$[H^+]$ [moles. l^{-1}]	9.42E-3			2.7E-2	1.08E-2			1.07E-2
H^+ dispersion [mol H^+ per mol C^-]	0.047			0.15	0.028			0.038
X conversion- H^+ activities {[%] \times mol C^- per mol H^+ }	418.02	502.55	516.51	492.15	908.31	1 381.68	1 636.55	1 668.78
[bp]- H^+ activities { [bp] \times mol C^- per mol H^+ }	8.89	14.83	16.61	6.01	9.83	14.89	20.66	44.95
Time intervals	[0;1] _{initiale}	[1;5]	[5;15]	[15;60]	[0;1] _{initiale}	[1;5]	[5;15]	[15;60]
X conversion- H^+ turnovers evolutions per time intervals {[%] \times mol C^- per mol H^+ per hour}	25 081.24	7 538.26	3 099.06	656.20	54 498.44	20 725.22	9 819.28	2 225.04
[bp]- H^+ turnovers evolutions per time intervals { [bp] \times mol C^- per mol H^+ per hour}	533.67	222.44	99.68	8.01	589.95	223.32	123.96	59.93

Table 13. Continue.

Raw materials	Garcinia dulcis pips				Callistemon citrinus			
Times [mn]	1	2	5	60	2	5	15	60
Initial solution volume [ml]	20	12.9	20	101.25	59			
Specific surfaces [cm^2/g]	106.45				100.79			
Total surface [cm^2]	1488	978	1488		1336			
$[C^-]$ initial [moles. g^{-1}]	0.001567				0.00329			
Total C^- [moles]	0.0219	0.0144	0.021898		0.043599			
$[C^-]_{initial}$ [mol. l^{-1}]	1.0949	1.1157	1.0949	0.2162	0.738967			
Total surface $\times[C^-]_{initial}$ index	1628	1091	1628	322	987			
Citric acid [moles]	0.005	0.003	0.005	0.104	0.011			0.029
H^+ [moles]	1.95E-4	1.26E-4	1.97E-4	3.03E-3	9.09E-4			1.6E-3
$[H^+]$ [moles. l^{-1}]	9.76E-3	9.73E-3	9.85E-3	3E-2	1.54E-2			2.7E-2
H^+ dispersion [mol H^+ per mol C^-]	8.9E-3	8.7E-3	9E-3	0.139	0.021			0.04
X conversion- H^+ activities {[%] \times mol C^- per mol H^+ }	6 901.49	8 443.42	10 709.83	654.96	209.62	307.08	764.00	850.73
[bp]- H^+ activities { [bp] \times mol C^- per mol H^+ }	25.71	27.77	105.72	—	6.20	9.02	17.24	20.22
Time intervals	[0;1] _{initiale}	[1;2]	[2;5]	[5;60]	[0;2] _{initiale}	[2;5]	[5;15]	[15;60]
X conversion- H^+ turnovers evolutions per time intervals {[%] \times mol C^- per mol H^+ per hour}	414 089.31	506 604.97	214 196.55	714.51	6 288.47	6 141.51	4 583.99	1 134.31
[bp]- H^+ turnovers evolutions per time intervals { [bp] \times mol C^- per mol H^+ per hour}	1 542.50	1 666.32	2 114.32	—	185.88	180.45	103.42	26.96

**Figure 23.** Initial activities of H^+ in bp-equivalent formation evolutions with initial dispersions.

Noticed that the initial activities and consequently the initial

turnovers of citric acid's protonic acids H^+ for different raw materials decreased when initial dispersion increased as shown in the following figure 22 and figure 23 (Table 13). These exceptionnel results signalized the importance of alkene organic function as parameter and guided to create the "Total surface $\times[C^-]_{initial}$ - index" (Table 13). Also, this index-value obtained by support external total surface multiplied by equivalent alkene organic-function concentration (Table 13) was calculated and it was noticed that at initial time (1') catalyst-citric acid protonic acid- H^+ turnovers and activities increased with this index-value except that at maximum index-value and at 60' their values go down again and confirmed the alkene-support role to improve esterification and polymerization reactions with citric acid molecules; but at 60' the formation of important PN-equivalent polymer could impinge upon catalyst-citric acid protonic acid- H^+ sites and their deactivations (Table 13). That is why, normally the evolution of alkene-equivalent concentration of extracts-esterified

products solution evolution (followed by hydrofluoric acid HF-0.00261N titration) recorded a rise at the expense generally of alkene-equivalent concentration of by-products evolution (followed by hydrofluoric acid HF-0.00261N titration) [17] at the end but as shown in the following table 14, it wasn't all the case. Effectively, the alkene concentrations of extracts-esterified product evolutions recorded a rise with time in all raw materials but in the same time alkene-equivalent concentrations of by-products increased significantly in all raw materials. These results gave notice that there were alkene formation and eventually their transformation which confirmed the synthesis of citric acid monomers and polymers asked and described on paragraph §3.2.1. through all raw materials (Table 14). Noticed that the positive value of total alkene-equivalent formed minus total initial alkene indicates the formation of monomers and its negative values confirmed the hydrogenation (by H₂ formed during

decarboxylation) of alkenes' monomers formed and /or their polymerizations to form respectively D-new monomers (figure 23), (E) (figure 24) with (C) (figure 23) and citric acid polymers as described on paragraph §3.2.1.. That is why generally alkenes formed quantities decreased with time (Table 14). In any case, all these previous results showed that citric acid molecules (with protonic acids H⁺ or not) were initially adsorbed, dispersed and moved on the raw materials surfaces' structure by hydrogen bond. Then a part of citric acid molecules reacted with raw materials organic molecules by esterification to give raw materials citric acid esters and another parts were activated by citric acids' protonic acids H⁺ which were supported and dispersed on alkenes' raw materials surfaces and structure by hydrogen bond to form reactive intermediates necessary to synthesize monomers and citric acid polymers according to the mechanisms described on paragraph §3.2.1..

Table 14. Global results of alkene-equivalent concentrations of extracts-esterified products solution and by-products evolutions.

Raw materials	Rice-husk				Garcinia dulcis pulp-peel			
Times [mn]	1	5	15	60	1	5	15	60
Total C ⁼ [moles]	0.018078				0.02588			
Alkene-equivalent moles of extracts-esterified products evolution [moles]	2.67E-4	1.12E-3	8.74E-4	1.72E-3	3.25E-5	8.90E-5	2.85E-4	8.22E-4
alkene-equivalent moles of by-products evolution [moles]	2.86E-2	2.78E-2	3.98E-2	6.88E-3	7.94E-3	8.24E-3	1.66E-2	4.67E-2
Total alkene-equivalent formed [moles]	2.89E-2	2.89E-2	4.07E-2	8.60E-3	7.97E-3	8.33E-3	1.69E-2	4.75E-2
Total alkene-equivalent formed minus total initial alkene C=[moles]	1.08E-2	1.08E-2	2.26E-2	-9.48E-3	-1.79E-2	-1.76E-2	-9.00E-3	1.86E-2
Alkene-equivalent concentrations of extracts-esterified products solution evolution [mol.l ⁻¹]	5.55E-3	2.57E-2	1.94E-2	3.45E-2	5.20E-4	1.39E-3	4.68E-3	2.08E-2
alkene-equivalent concentrations of by-products evolution [mol.l ⁻¹]	5.94E-1	5.84E-1	8.88E-1	1.38E-1	1.27E-1	1.28E-1	2.72E-1	1.18
Total alkene-equivalent concentration [mol.l ⁻¹]	6.00E-1	6.10E-1	9.07E-1	1.73E-1	1.28E-1	1.29E-1	2.77E-1	1.20

Table 14. Continue.

Raw materials	Garcinia dulcis pips				Callistemon citrinus			
Times [mn]	1	2	5	60	2	5	15	60
Total C ⁼ [moles]	0.0219		0.0144		0.021898		0.043599	
Alkene-equivalent moles of extracts-esterified products evolution [moles]	4.29E-5	1.6E-5	2.68E-5	2.38E-3	5.85E-4	1.00E-3	1.57E-3	6.18E-3
alkene-equivalent moles of by-products evolution [moles]	1.35E-3	8.95E-3	6.36E-3	3.22E-3	2.88E-2	1.55E-2	6.32E-2	2.84E-2
Total alkene-equivalent formed [moles]	1.39E-3	8.97E-3	6.39E-3	5.60E-3	2.94E-2	1.65E-2	6.48E-2	3.46E-2
Total alkene-equivalent formed minus total initial alkene C=[moles]	-2.05E-2	-5.43E-3	-1.55E-2	-1.63E-2	-1.42E-2	-2.71E-2	2.12E-2	-9.02E-3
Alkene-equivalent concentrations of extracts-esterified products solution evolution [mol.l ⁻¹]	3.90E-3	7.80E-4	—	2.50E-2	1.30E-2	2.60E-2	3.72E-2	6.72E-2
alkene-equivalent concentrations of by-products evolution [mol.l ⁻¹]	1.22E-1	4.37E-1	6.36E-3	3.37E-2	6.39E-1	4.02E-1	1.5	0.31E-1
Total alkene-equivalent concentration [mol.l ⁻¹]	1.26E-1	4.38E-1	—	5.87E-2	6.52E-1	4.28E-1	1.54	9.82E-2

That allowed to study and established the partial order versus citric acid concentration to understand the possible adsorption mechanism.

4. Partial Order Versus Citric Acid of Esterification with Citric Acid Molecules Reaction

4.1. Esterification with Citric Acid Molecules Reaction Conditions

The first condition which permit the partial order versus

citric acid of esterification with citric acid molecules reaction calculation was the concentration of citric acid must be negligible in front of raw materials molecules concentration whose verification was done in table 9 paragraph §2.3.1. seeing that reaction was done with constant volume. But to confirm this condition, seeing that there was positive proportionality correlation between initial alkene concentrations deduced by hydrofluoric acid HF-0.00261N-titration and the equivalent raw materials' reactive molecules, the following table 15 showed these initial ratios.

Table 15. Initial alkene and citric acid concentrations ratios.

Raw materials	Rice husk	Garcinia dulcis pulp-peel	Garcinia dulcis pips	Callistemon citrinus
Initial alkene concentration [mol.l ⁻¹]	0.20087	0.38924	1.0949	0.738967
Initial citric acid concentration [mol.l ⁻¹]	0.04889	0.09624	0.2600	0.184851
Initial [Alkene]/[citric acid] ratios	4.10861	4.04447	4.21115	3.99764

Thus, the esterification of raw materials' reactive molecules with citric acid molecules and also citric acid molecules polymerization catalyzed by the own citric acid molecules supported on raw materials' aromatics and polynuclear alkenes global speed was:

$$v = k \times [\text{citric acid}]^a \times [\text{raw materials reactive molecules}]^b$$

Seeing that raw materials' reactive molecules concentration was higher than citric acid concentration (Table 9 – Table 15) the observed speed constant became k_{obs} such as

$$k_{obs} = k \times [\text{raw materials reactive molecules}]^a$$

So, the global esterification and also citric acid molecules polymerization catalyzed by the own citric acids' protonic acid molecules supported on raw materials' aromatics and polynuclear alkenes, which catalyzed all reactions, on raw materials' aromatics and polynuclear alkenes (as Tanin) speed became:

$$v = -\frac{d[\text{citric acid}]}{dt} = k_{obs} \times [\text{citric acid}]^a$$

Studying the citric acid concentrations curve evolution with time conducted to the determination of citric acid partial order.

4.2. Citric Acid Concentrations Evolution in Terms of Time - Partial Order Determination for All Raw Materials

The following table 16 gave the evolution of citric acid concentrations.

Table 16. Citric acid concentrations evolution.

Raw materials	Time [s]	[citric acid]	1/[citric acid]
Rice husk	60	1.12E-2	8.96
	300	1.08E-2	9.30
	900	1.13E-2	8.89
	3600	1.11E-2	9.38
Garcinia dulcis pulp-peel	0	9.62E-2	10.39
	60	1.15E-1	8.70
	300	9.25E-2	10.81
	900	8.63E-2	11.59
Garcinia dulcis pips	0	2.60E-1	3.85
	60	2.75E-1	3.64
	120	6.5E-2	15.38
	120	3.50E-1	2.86
Callistemon citrinus	300	4.00E-1	2.50
	900	3.29E-1	3.04
	3600	3.30E-1	3.03

$$v = -\frac{d[\text{citric acid}]}{dt} = k_{obs} \times [\text{citric acid}]^a$$

Drawing the curve $1/[\text{citric acid}]$ in terms of time, the following figures 16a-16b-16c-16d were obtained for all raw materials. Obtainment of straight curves involved that the

resolution of the equation was possible and compatible with results experimentations only if "a" equals to "2"; in other words the esterification of raw materials' reactive molecules with citric acid molecules was order 2 against to citric acid.

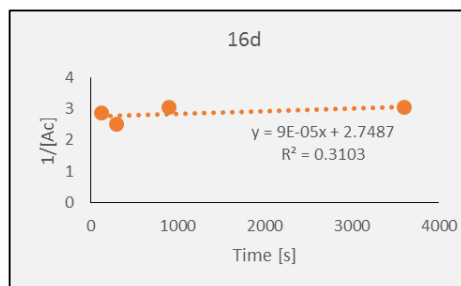
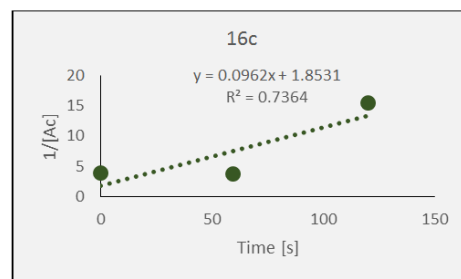
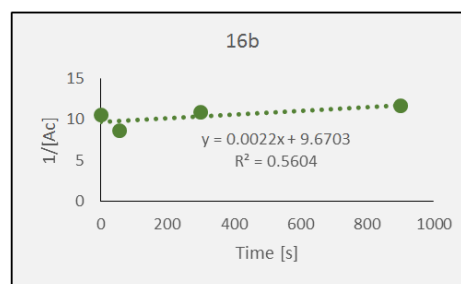
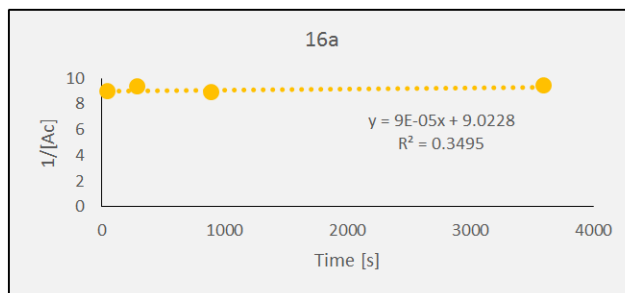


Figure 24. $1/[\text{citric acid}]$ evolution in terms of time for rice-husk (16a)-Garcinia dulcis pulp-peel (16b)- Garcinia dulcis pips (16c) and Callistemon citrinus (16d).

Consequently, from these figure 24 the observed speed constant and then the speed constant can be deduced with taking account of the previous hypothesis-conditions and the initial raw

materials reactive molecules concentration equals to initial total alkene concentration (Table 9-Table 12-Table 13) divided by three assuming that they are all constituted with benzene aromatics and every aromatics there were potential reactive molecules as shown the following table 17. These second order against to citric acid for all raw materials explained and

confirmed not only the important initial conversion (figure 9) of citric acid molecules to reactions products as esters, monomers and polymers of citric acid but also the adsorption, desorption and move of reactants, products and citric acids' protonic acid H⁺ catalysts molecules on raw materials' surfaces/structure aromatics and polynuclear alkenes by hydrogen bond with water.

Table 17. Esterification and polymerization with citric acid speed constant according to the previous hypothesis-conditions.

Raw materials	$k_{obs} [l \times mol^{-1} \times s^{-1}]$	$k [l^2 \times mol^{-2} \times s^{-1}]$	$k_{H^+} [l^3 \times mol^{-3} \times s^{-1}]$
Rice husk	9E-5	1.34E-3	1.43E-1
<i>Garcinia dulcis</i> pulp-peel	2.20E-3	1.70E-2	1.57
<i>Garcinia dulcis</i> pips	9.62E-2	2.64E-1	27.01
<i>Callistemon citrinus</i>	9E-5	3.65E-4	2.37E-2

The experimental pH was all the time less than 3.2, the [OH⁻] could be assumed to be negligible than [H⁺] we can deduced the k_{H^+} (Table 17).

Table 18. Esterification and polymerization with citric acid reactions speed constant-values reported to raw materials total surface.

Raw materials	Rice husk	<i>Garcinia dulcis</i> pulp-peel	<i>Callistemon citrinus</i>
Total surface S [cm ²]	866.22	77094	1336
$([H^+]/S)^2$	1.194E-10	1.963E-14	1.329E-10
$k \times \frac{[H^+]}{S}$	1.469E-08	2.375E-09	4.212E-09
$k1_{H^+}$	48.997		
$k2_{OH^-}$	300 000		

To estimate the general acid constant speed and basic constant speed of the esterification of rice husk's, *Garcinia dulcis* pulp-peels' and *Callistemon citrinus*' reactive molecules with citric acid molecules and also citric acid molecules polymerization catalyzed by the own citric acid molecules supported on rice husk's, *Garcinia dulcis* pulp-peels' and *Callistemon citrinus*' aromatics and polynuclear alkenes using the values of rice husk, *Garcinia dulcis* pulp-peel and *Callistemon citrinus* and seeing that the total surface influenced the values, it was necessary to reported these values per total surface (Table 18).

Drawing the curve $k \times \frac{[H^+]}{S}$ in terms of time, the following figures 25 was obtained for these raw materials. Obtainment of straight curves gave these raw materials global acid constant speed $k1_{H^+}$ and basic constant speed $k2_{OH^-}$ (Table 18).

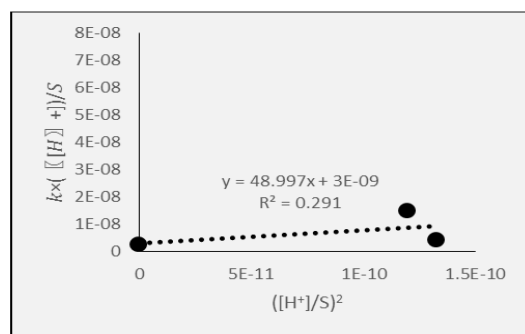


Figure 25. Evaluation of global rice husk's, *Garcinia dulcis* pulp-peels' and *Callistemon citrinus*' esterification and citric acid polymerization reactions acid constant speed $k1_{H^+}$ with basic constant speed $k2_{OH^-}$.

5. Valorizations of by-Products as Catalytic Support–Monomers and Polymers Formation Mechanism Confirmation

According to the previous results and mechanism, it was no doubt that after esterification with citric acids molecules (§3.2.1.), the all raw materials by-products of esterification contained not only aromatics and polynuclear alkenes but also monomers and polymers of citric acid (§3.2.1.). Indeed, the alkene-equivalent moles of by-products compared to initial total alkene-equivalent of raw materials (Table 19) were non negligible.

The aim of this chapter is to show that it was possible to valorize of all these by-products as another catalytic supports for another citric acid polymerizations until dry citric acid monomers; generally white sitting in the center of the glass-reactor; and citric acid polymers, brown and black according to the polymerization duration, were located nearby upside of the glass-reactor. This valorization-experimentation was done with the rice husk by-product and the evolution of these monomers and polymers quantities were followed from dry products (monomers and polymers) formation to confirm their formation-mechanism. The synthesis experimental conditions and procedure were shown in the following paragraph.

Table 19. By-products alkene-equivalent rate compared to initial total raw materials alkene-equivalent.

Raw materials	Rice husk	Garcinia dulcis pulp peel	Garcinia dulcis pips	Callistemon citrinus
Initial raw materials total alkene-equivalent [moles]	1.81E-02	2.89E-02	2.19E-02	4.36E-02
By-products total alkene-equivalent [moles]	6.88E-03	4.67E-02	3.22E-03	2.84E-02
By-products Alkene-equivalent rate compared to initial total raw materials alkene-equivalent rate [%]	38.06	161.65	14.70	65.14

5.1. Citric Acid Polymerization Using Rice Husk by-Products Unsaturated Molecules' Organic Functions as Catalytic Support-Experimental Conditions and Results

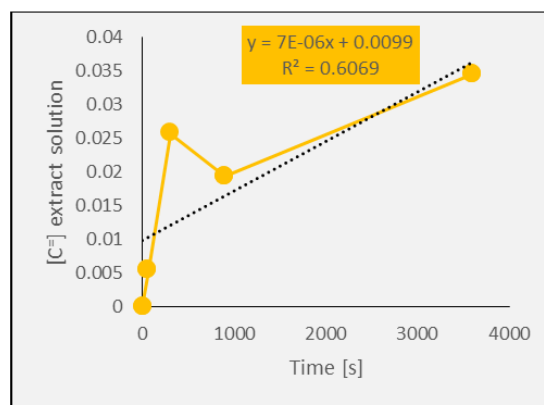
This table 20 contained the experimental conditions such as the initial calculated-pH was as close as possible to the initial calculated-pH during rice-husk esterification and the synthesis was done in a transparent cylinder glass-bottle with a reverse glass-funnel above where gas and vapors could formed during the experimentation could evacuated little by little.

Table 20. Rice husk by-product valorization experimental conditions.

Rice-husk by-products valorization	
Rice husk weight [g]	20
Alkenes by-products rate [molC ⁼ /g]	1.08E-4
Total moles C ⁼ [moles]	2.16E-3
Water volume [ml]	90
Rice husk by-products Total C ⁼ concentration [mol.l ⁻¹]	2.40E-2
Citric acid weight [g]	2.7863
Calculated-pH	2.20
Glass-bottle volume [cm ³]	330
Glass-bottle height [cm]	≈11.5

According to the previous results and mechanism (§3.2.1. - Table 14) the alkene-equivalent concentrations of extracts-esterified products solution generally increased [mol.l⁻¹]. So, the first step duration of oven temperature

program (388.15[°K]) was deduced by the straight trend curve (Figure 26) between time and alkene-equivalent concentrations of extracts-esterified products solution such as the rice husk by-products total C⁼ concentration 2.40E-2 [mol.l⁻¹] became the alkene-equivalent concentrations of extracts-esterified products solution. It's only after the temperature will be increased and stabilized to 523.15 [°K] (Table 21) until the dry citric acid monomers; generally white sitting in the center of the glass-reactor; and citric acid polymers, brown and black according to the polymerization duration were obtained.

**Figure 26.** Extract-solution alkene-equivalent concentration evolution with time.**Table 21.** Rice husk by-products valorization oven program and valorized products states.

Rice-husk by-products valorization – Oven program			
Temperature [°K]	Oven speed [°C/mn]	Total duration [mn]	Valorized Products states
388.15	3	34	-By-products with solution-transparent
523.15	3	60	-By-products-brown Solution-yellow
523.15	3	185	-Dry -Brown citric acid polymers nearby upside -White monomers in the center
523.15	3	207	-Dry -Black poly-polymers -White monomers
523.15	3	222	-Black polymers
523.15	3	231	-Black poly-polymers

To evaluate globally the valorization efficacy, the valorized by-products weight and the equivalent black citric acid polymers (PN-equivalent) titrated by NaOH-0.05N weight were done from the first dry valorized by-products achieved, in this case the samples at total durations 185[mn], 207 [mn] and 222 [mn] as shown the following table 22. Noticed that the valorized by-products weight decreased and their states changed clearly from transparent-solution characteristics of

citric acid monomers (§3.2.1.) to dry monomers, through dry brown citric acid polymers to black poly-polymers equivalent to polymerization of black citric acid polymers. Also, noticed that the previous evaluation of by-products valorization as another catalytic support for another citric acid polymerizations enhance to appreciate the speed transformations of monomers to polymers and poly-polymers which could index the monomers or polymers longevity evolutions.

Table 22. Characteristics results of valorized rice husk by-products.

Rice-husk by-products valorization – Results				
Total duration [mn]	Valorized by-products weight [g]	Total conversion of previous monomers to polymers against previous quantified by-products or valorized by-products [%]	Total black citric acid polymers equivalent weight [g]	Total conversion of previous monomers to PN-equivalent and or poly-polymers against previous quantified by-products or valorized by-products [%]
185	15	65.83	-	-
Speed monomers transformation between [185mn-207mn] [g/mn]		0.36	Speed PN-equivalent formation [185mn-207mn] [g/mn]	0.05
207	7.2 (7)	52	1.1218	14.38
Speed monomers transformation between [207-222] [g/mn]		0.07	Speed PN-equivalent formation [207mn-222mn] [g/mn]	0.021
222	6	14.29	0.3102	31.02
Speed monomers transformation between [222mn-231mn] [g/mn]		0.11	Speed PN-equivalent formation [207-222] [g/mn]	0.007
231	5	16.67		06.46

Now, the aim was to follow and to quantify each citric acid monomers evolution using hexane and dichloromethane solvent.

5.2. Hexane and Dichloromethane Soluble and Insoluble Citric Acid Monomers and Polymers Evolution Control Procedure

The first step was to quantify the total coke soluble in hexane and dichloromethane. Then, seeing that hexane was a non-polar solvent and dichloromethane a polar solvent, normally all molecules insoluble in hexane should be soluble in dichloromethane and vis-versa. However, noticed was done that the total rate of insoluble in hexane was superior to the total rate of soluble in dichloromethane. This difference confirmed the presence of (B)-yellow monomers and (D)-new monomers according to whether respectively two or one of (A)'s carboxylic acid functions were decarboxylized which were more soluble in dichloromethane according its polarity. In the otherwise, this soluble dichloromethane rate gave directly the rate of (B)-yellow monomers and (D)-new monomers with other organic compounds which contains only one alkene-function like (E) or other organic compounds with one alkene potentially soluble in dichloromethane.

Also, noticed that (B)-yellow monomers was only soluble in dichloromethane because of its conjugated-alkene but (D)-new monomers and other organic compounds which contains only one alkene-function like (E) or other organic compounds with only one alkene-function could be soluble in hexane and so constitute the majority of unsaturated molecules soluble in hexane. In that respect, to evaluate the rate of these (D)-new monomers, titration of soluble hexane (D)-new monomers and other organic compounds which contains only one alkene-function like (E) or other organic compounds with only one alkene-function with 0.00261N-HF was carried out with rectification by taking the alkene-amount of initial by-product to be valorized into consideration. Then, we can deduced firstly the rate of (B)-yellow monomers which was the most little probable monomers with two unsaturated seeing that the others conducted immediately to the formation of the most primary product PN-equivalent (Figure 27). Also, we can deduced total weight of molecules without unsaturation which were soluble in hexane. Repeating these

quantifications on each temperature-samples, the evolution of the monomers and saturated citric acid molecules by citric acid polymerization on by-products as another catalytic support will be obtained. These results were shown in the following table 23 and the figure 27.

Table 23. Rice-husk by-products valorization as catalytic support of citric acid molecules polymerization on glass-bottle.

Time [mn]	(B)-Yellow monomers [%]	(D)-new monomers [%]	Saturated products [%]	PN-equivalent [%]
185	-	-	-	-
207	13.51	9.95	0.055	40.26
222	13.7	5.27	2.73	11.13
231	12.34	1.55	9.56	2.32

These results (Table 23, figure 27) confirmed the mechanism described on paragraph §3.2.1 such as:

- (B)-yellow monomers was a primary products which could be not only hydrogenated to give (D)-new monomers but also polymerized to give black citric acid polymers PN [22] and/or PN-equivalent as shown in figure 17.

- (D)-new monomers seemed to be a primary products obtained either by only one of (A)'s carboxylic acid functions decarboxylation, either by (B)-yellow monomers hydrogenation and confirmed its transformation.

- Saturated products which were obtained by hydrogenation of (B)-yellow monomers, (D)-new monomers) and/or (D)-new monomers dismutation products to hydrogenation of (F) - polymer (Figure 28) and confirmed its state as secondary product.

- Finally PN-equivalent molecules constituted not only with black citric acid (PN) formed by radical mechanism [6, 20] but also by similar black citric acid (F)-polymer (Figure 28) formed by ionic mechanism described previously (Figure 17) seemed to be a primary products since 185 [mn] seeing that the hydracids functions were present and titrated by 0.05N-NaOH since the beginning of the citric acid transformation-polymerization. But, noticed that the total PN-equivalent rate decrease from 205 [mn]; so either they were transformed to black poly-polymers by hydracids-decarboxylation followed by polymerization and/or (F)-polymer polymerization (Figure 29), either their quantities

increased but because of the high density of their hydrogen-bond not only on surface but also inside the

rice-husk by-products structure porosity their titration by 0.05N-NaOH became difficult.

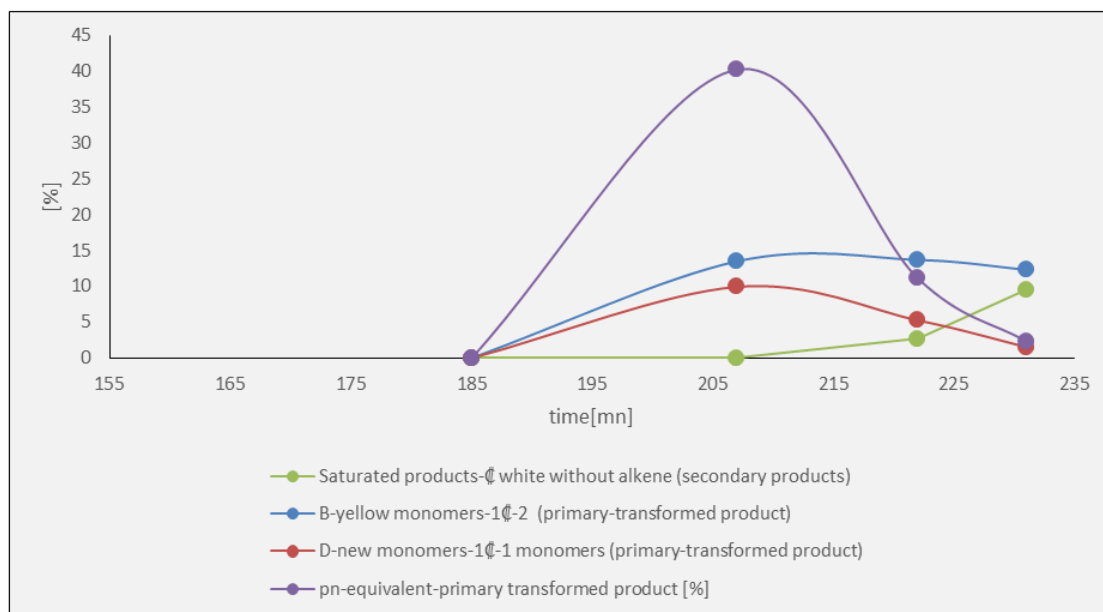


Figure 27. Evolution of citric acid molecules transformation-polymerization on rice-husk by-products as catalytic support using a glass-bottle reactor.

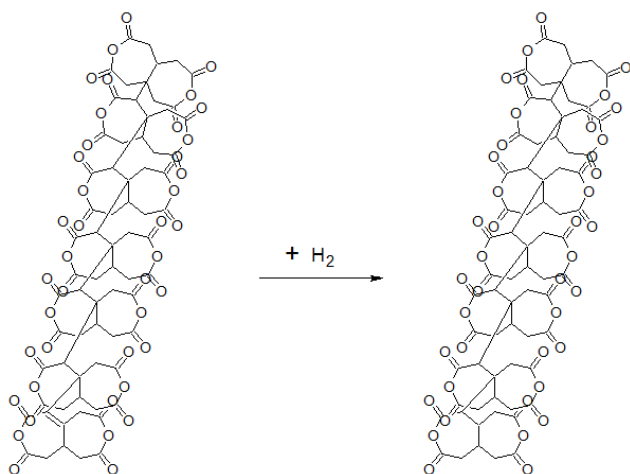


Figure 28. (F)-polymer hydrogenation.

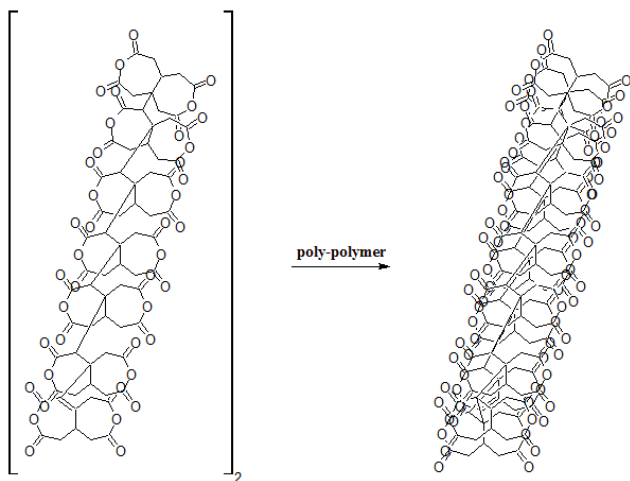


Figure 29. Two molecules of (F) dismutation to form a poly-polymer.

6. Conclusion

The previous results confirmed that raw materials' aromatics molecules and its equivalent fiber structure-porosity characterized by their alkenes organic-function titrated with hydrofluoric acid HF-0.00621N and by their estimated external specific surfaces were efficient support not only for citric acids' protonic acid-H⁺ catalyst but also for the reagents (citric acid and reactive molecules of raw materials Callistemon citrinus, rice husk, Garcinia dulcis pulp-peel, Garcinia dulcis pips) during the esterification with citric acid molecules and their polymerization according to the experimental conditions itemized in the manuscript. Indeed, the conversions (initial conversion at 1'; total conversion at 60') of citric acid molecules and the protonic acid-H⁺ activities [activities], evaluated by the brown citric acid-equivalent formed per catalyst-H⁺ dispersion, for Callistemon citrinus, rice husk, Garcinia dulcis pulp-peel, Garcinia dulcis pips were respectively: {(4.37%; 30.63%) – [6.20]} Callistemon citrinus; {(19.61%; 75.64%) – [8.89]} rice husk; {(25.08%; 62.77%) – [9.83]} Garcinia dulcis pulp-peel and {(61.51%; 90.90%) – [25.71]}. Also, for all raw materials the brown citric acid equivalent concentration increased all the time during esterification with citric acid molecules from 0.13 [mol.l⁻¹] to 1.69 [mol.l⁻¹].

It was also noticed that there was relations between the support raw material characteristics “external specific surfaces” and the catalyst-citric acid protonic acid-H⁺ activities and turnovers. Indeed, when initial dispersion increased, the catalyst-citric acid protonic acid-H⁺ initial activities and turnovers decreased which confirmed that in all the cases citric acid molecules were initially adsorbed, dispersed and moved on aromatics' raw materials

surface-structure porosity then reacted either each over either with raw materials' reactive molecules. But, at 60 minutes the catalyst-citric acid protonic acid- H^+ turnovers and activities values increased with dispersion except that at maximum dispersion these values seemed go down again. These results explained not only the citric acid partial order equals to two but also the necessity of space-support (i.e. low dispersion of the catalyst-citric acid protonic acid- H^+) to favor the citric acid polymerization according to the mechanism established using catalyst-citric acid protonic acid- H^+ . Consequently, an index-value obtained by support external total surface multiplied by equivalent alkene organic-function concentration was calculated on each experiment and it was noticed that at initial time (1') catalyst-citric acid protonic acid- H^+ turnovers and activities increased with this index-value except that at maximum index-value and at 60' their values go down again and confirmed the support role to improve bimolecular catalytic reaction like esterification and polymerization reactions with citric acid molecules catalyzed by citric acid protonic acid- H^+ which could endure deactivations. In this way, new monomers were synthesized with their saturated formed obtained hydrogenations like D-New monomer, C-New product, (E) and its equivalent saturated-hydrogenated form which were generally white and respectively soluble in dichloromethane (unsaturated) and hexane (saturated-hydrogenated). Then their (unsaturated) polymerization conducted to the formation of polymers composed with n-moles of D-New monomers to form PN-equivalent polymer the most primary product during valorization which were generally black and quantified by NaOH-0.05N titration) according to the mechanism established using catalyst-citric acid protonic acid- H^+ . The valorization procedure confirmed that by-products of esterification between raw materials and citric acid molecules could be valorized as support of polymerization like citric acid polymerization which evolution could be appreciated and followed according a procedure.

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