



Research/Technical Note

Synthesis of Glues with Citric Acid and Sulfuric Acid Protonic Acid-H⁺ as Catalysts Using Banana Peel and Kaki as Valorised Raw Materials

Andry Tahina Rabeharitsara*, Ratsimba Marie Hanitriniaina, Rakotomalala Alain Fabrice, Rakotosaona Rijalalaina, Nambinina Richard Randriana

Chemical Process Engineering Department, E. S. P. A (Polytechnics Engineer School of Antananarivo), Antananarivo University, Antananarivo, Madagascar

Email address:

rabeharitsara_andrytahina@yahoo.fr (A. T. Rabeharitsara), ratsimbamarie@yahoo.fr (R. M. Hanitriniaina),

rakotomalalaalainfabrice@gmail.com (R. A. Fabrice), rijalalaina.rakoto@gmail.com (R. Rijalalaina),

richardrandriana@gmail.com (N. R. Randriana)

*Corresponding author

To cite this article:

Andry Tahina Rabeharitsara, Ratsimba Marie Hanitriniaina, Rakotomalala Alain Fabrice, Rakotosaona Rijalalaina, Nambinina Richard Randriana. Synthesis of Glues with Citric Acid and Sulfuric Acid Protonic Acid-H⁺ as Catalysts Using Banana Peel and Kaki as Valorised Raw Materials. *Advances in Materials*. Vol. 9, No. 1, 2021, pp. 21-35. doi: 10.11648/j.ajac.20210901.14

Received: January 14, 2021; **Accepted:** January 22, 2021; **Published:** January 28, 2021

Abstract: Seeing that banana peel or banana skin composed 35% to 40% of banana fruit and also seeing that kaki were widely cultivated at Madagascar since the XIXth century with non-negligible quantities of valorisable waste during their collection; a study of their valorization as raw materials to synthesize glues was undertaken in this manuscript. Synthesized glues were classified into two categories: the ecological glues with citric acid protonic acid H⁺ catalyst and the sulfuric acid glues-Sglues with sulfuric acid protonic acid H⁺ catalyst. All glues were composed with two main compounds firstly the pH-raiser-support and secondly the crushed banana peel citric acid esters EAcBa. These pH-raiser-supports was composed not only with citric acid protonic acid H⁺ catalyst (E-pH-Natural for the ecological glues) and/or sulfuric acid protonic acid H⁺ catalyst (E-pHS-sulfuric acid for the Sglues) but also pure ethanol and kaki composed with alkenes organic functional group from its betacarotenes molecules; they increased the pH of the glues and catalysts were dispersed and moved on. All synthesized glues were tested such as: the ecological glues were tested to glue the school notebook paper and the Sglues were tested to glue the packing carton paper. So, to study the effects of these gluing components, the effects of the test papers dry matter, the effects of tested papers nature-components, and the effects of the test papers porosities; the total weight diminution of the glue-reagents which indicated the formation of covalent links between glues and paper responsible of its best gluing results were followed with time. In terms, the activities of each glues' initial protonic acid H⁺ were calculated and confirmed their roles as very active catalysts for dehydration reactions particularly the sulfuric acid protonic acid H⁺ catalysts, for addition reactions principally esterification, additions with alkenes-C⁼ and etherification for all synthesized glues especially with the stronger-smallest sulfuric acid protonic acid H⁺ which were responsible of their capacities to stick with very good quality.

Keywords: Banana Peel, Kaki, Glue, Paper, Citric Acid, Sulfuric Acid, Protonic Acid H⁺, Catalyst, Ethanol

1. Introduction

First of all, bibliographies and characterizations of raw materials banana peel, kaki and citric acid, sulfuric acid

protonic acid H⁺ were carried out. Then, the compositions and the procedure to synthesize the ecological-natural glues and

sulfuric acid glues were described after seeing the procedure and the experimental conditions to synthesize the two main compounds such as: the pH-raiser-support and the crushed banana peel citric acid esters EAcBa. To test all ecological-natural and sulfuric acid synthesized glues, they were used to glue respectively school notebook paper and packing carton paper whose bibliographies and characterizations were described on paragraph-§4. Thus, a gluing test procedure were laid out and characteristics of school notebook paper and packing carton samples used to test the synthesized glues were given seeing that the total weight diminution of glue-reagents values used to glue these samples papers were followed up with time and permit to characterize and to describe the gluing mechanism, the protonic acid H⁺ activities according to the used catalysts and the tested samples papers characteristics. All tested samples were weighed with KERN-AJP 10-4 precision balance.

2. Raw Materials Used to Synthesize Glues with Citric Acid and Sulfuric Acid Protonic Acid H⁺ Catalysts

2.1. Banana Peel

Banana peel or banana skin is the outer covering of the banana fruit which is composed with 35% to 40% of skin [1]. Banana peel are used as food animals, in water purification, for manufacturing of several biochemical products [2-5] and current baseline projections call for annual growth in world banana production of 1.5% to reach 132.6 million tons in 2029 [6]. In this study, banana peel was recycled as raw material to synthesize glues seeing that it is composed of not only water estimated around 20% [7] but also organic chemical compounds potential sources of chemical bonding reactions and polymerizations such as latex [8], cellulose 9 [wt.%], hemicellulose 8 [wt.%], glucose 2 [wt.%], starch 3 [wt.%] and lignin 9 [wt.%] [7]. Also, equivalent alkene content evaluated by HF-0.0026 [mol.l⁻¹] [9-10] and dry matter* of the banana peel used during the experiences were carried out and showed in the following table 1. * Noticed that dry matter was determined by dispersing 1.4934[g] of banana peel in a beaker 250 [ml]. Then, put it into a forced ventilation oven set at 75°C during 4 hours after this the dry banana peel product which began to turn completely black was weighted. This procedure was inspired by the following bibliography [11]. This dry matter or dry weight gave indicatives and confirmed the presence of carbohydrates (cellulose, hemicellulose, glucose, starch and lignin), fats, proteins, vitamins, minerals and antioxidants in plant and animal materials [12].

Table 1. Banana peel used during experiences equivalent alkene content and dry matter*.

Characteristics of banana peel used during glues synthesis	
Equivalent alkene content [mol.g ⁻¹]	15.3789E-4
Dry matter [%]*	11.14
Relative humidity [%]	88.86

2.2. Kaki

Kaki is a fruit from the far east and introduced in Madagascar in the XIXth century. The most widely cultivated of these is the Asian or Japanese persimmon, *Diospyros kaki* [13]. It contains not only water such as water content was estimated around 75.5 [%] [14] but also carbohydrates 18.59% like sugars 12.53% and dietary fiber 3.6%; fat (0.19%); proteins (0.58%); vitamins and minerals [15]. The *Diospyros kaki* used during these experiences of glues synthesis was from Ambano – AntsirabeII 19° 48' 00" sud, 47° 02' 00" est – Antanananrivo Madagascar [16]. Also, equivalent alkene content evaluated by HF-0.0026 [mol.l⁻¹] [9-10] and dry matter* of the *Diospyros kaki* used during the experiences were carried out and showed in the following table 2. Also, equivalent alkene content evaluated by HF-0.0026 [mol.l⁻¹] [9-10] and dry matter* of the banana peel used during the experiences were carried out and showed in the following table 1. * Noticed that dry matter was determined by dispersing 1.8019[g] of *Diospyros kaki* in a beaker 250 [ml]. Then, put it into a forced ventilation oven set at 75°C during 4 hours after this the dry banana peel product which began to turn completely black was weighted. This procedure was inspired by the following bibliography [11] and the obtained *Diospyros kaki* dry matter (25.83% - Table 2) was not far from those given by the literature 20% and 19.86% respectively for *Yémon* and *Voatabia Diospyros kaki* determined according to the NF V 03-903 procedure [16]. This dry matter or dry weight gave indicatives and confirmed the presence of carbohydrates (cellulose, hemicellulose, glucose, starch and lignin), fats, proteins, vitamins, minerals and antioxidants in plant and animal materials [12].

Table 2. *Diospyros kaki* used during glues synthesis equivalent alkene content and dry matter.

Characteristics of <i>Diospyros kaki</i> used during glues synthesis	
Equivalent alkene content [mol.g ⁻¹]	9.94334E-05
Dry matter [%]*	25.83
Relative humidity [%]	74.17

2.3. Citric Acid

Citric acid C₆H₈O₇ is a tricarboxylic acid α- hydrolyzed. It contains three acids with pKa such as pKa₁ = 3.14, pKa₂ = 4.77 and pKa₃ = 6.39 and a α-alcohol function with pKa = 14.4 [17-19] “Figure 1”.

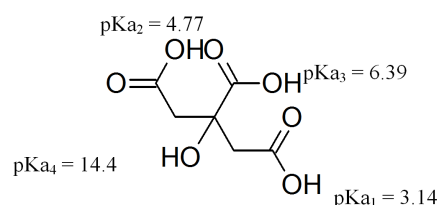


Figure 1. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid).

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 [20-21]. 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 [22]. 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 dominates and if $pK_a (AH) \leq pH \leq [pK_a (AH) + 2]$ the basic form A- dominates [22]. Consequently, for the citric acid we noted in the following Table 3 the acids and basics forms according to the pK_a and pH :

Table 3. 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

Thus, citric acid molecules were used to extract organic molecules because of its capacity to react with those molecules with valorization of eventual by-product by esterification with formations of esters, amides and other molecules with alkene organic functions [23-25]. These reactions were catalyzed by protonic acids H^+ from citric acid molecules [25-26] or from sulfuric acid molecules [26-27] and noticed that these reactions were at least potentially involved in the creation of covalent bonds responsible for the bonding

phenomenon using synthesized glues described in this manuscript.

2.4. Sulfuric Acid

The following table 4 give the acids and basics forms according to the pK_a and pH and the table 5 give Physicals and chemicals characteristics of used sulfuric acid and the one drop sulfuric acid nH^+ moles [27-29].

Table 4. Dominant forms of "sulfuric acid" according to the pH.

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
$pH \leq -9$	H_2SO_4/HSO_4^-	≈ -9	$H_2SO_4 \rightleftharpoons HSO_4^- + H^+$	H_2SO_4	Sulfuric acid
$-9 \leq pH \leq 1.9$	H_2SO_4/HSO_4^-	≈ -9	$H_2SO_4 \rightleftharpoons HSO_4^- + H^+$	$HSO_4^- (H^+)$	Hydrogenosulfate ion
$1.9 \leq pH$	HSO_4^-/SO_4^{2-}	1.9	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$SO_4^{2-} (H^+)$	Sulfate ion

Table 5. Physicals and chemicals characteristics of used sulfuric acid and the one drop sulfuric acid nH^+ moles.

PHYSICALS AND CHEMICALS CHARACTERISTICS	H_2SO_4
Density $[g \cdot ml^{-1}]$	1.8357
Molar Mass $[g \cdot mol^{-1}]$	98.07
Purity [%]	98
Volume	1 [drop] 0,1 [ml]
Mass [g]	0.1799
H_2SO_4 (n) moles quantity [moles]	1.8344×10^{-3}
H^+ moles quantity at $pH=2$ [moles H^+]	$\approx 2.7516 \times 10^{-3}$
Molecular diameter $[\text{\AA}]$	4.87
Maximum size of a sulphuric acid molecule (Internuclear distance of the most distant oxygen atom and hydrogen atom)	$3.289 \text{\AA} \times 3.293 \text{\AA}$

3. The Glues Components and the Synthesized Glues Compositions

3.1. Crushed Banana Peel Citric Acid Esters – the First Glues Components Synthesis

To extract and synthesize the active molecules, crushed and esterified the banana peel with citric acid molecules according to the procedure described in literature until a sticky yellow solution was obtained composed with esters, amides and other molecules with alkene organic functions [23-25]. Three experimental conditions were used to synthesize three citric acid esters of banana peel including EAcBa1 (citric acid quantities were less) and EAcBa2 and EAcBa3 where citric acid quantities were significant as shown the following table 6.

Table 6. Experimental conditions for crushed banana peel citric acid esters – the first glues components synthesis EAcBa.

Raw materials used	Crushed banana peel citric acid esters – the first glues components synthesis		
	EAcBa1	EAcBa2	EAcBa3
Banana peel weight [g]	62.1367	3.8466	1.3497
Citric acid weight [g]	1	1	1
Water weight [g]	20	20	20
Raw materials weight [g]	83.1367	24.8466	22.3497
Citric acid [wt.%]	1.20	4.02	4.47
Citric acid/banana peel [wt.%]	1.58	20.63	42.56
Alkenes [moles]	$9.56E-2$	$5.92E-3$	$2.08E-3$
Alkenes concentration $[mol \cdot l^{-1}]$	4.78	$2.96E-1$	$1.04E-1$
Alkene/Citric acid $[mol/mol]$	18.37	1.14	0.40
pH - calculated	2.1	2.1	2.1
pH – pH meter	3.3	2.23	2.12

3.2. Natural and with Sulfuric Acid pH-raiser and Support – the Second Glues Component Synthesis E-pH

It was noticed that not only the alkene functions but also the experimental pH influenced the protonic acid H^+ catalysts activities [25, 27]. So, a natural pH-raiser and support composed with kaki source of alkene functions, pure ethanol and citric acid was synthesized to form the second glues component as shown the following table 7.

Table 7. Natural and with sulfuric acid pH-raiser and support – the second glues component E-pH.

Raw materials used	E-pH-raiser and support – the second glues component synthesis	
	E-pH - Natural	E-pHS-sulfuric acid
Kaki weight [g]	300	300
Pure ethanol [ml]	600	600
Pure ethanol weight [g]	473.67	473.67
Citric acid weight [g]	0.1	0.1
Sulfuric acid one drop [ml]	-	0.1
Sulfuric acid weight [g]	-	0.1799
Citric acid [wt.%]	0.0129	0.0129
Sulfuric acid [moles]	-	1.8344E-3
Alkenes [moles]	2.98E-2	2.98E-2
Alkenes concentration [mol.l ⁻¹]	4.97E-2	4.97E-2
Alkene/Citric acid [mol/mol]	57.25	57.25
Alkene/sulfuric acid [mol/mol]	-	16.2451
Alkene/(sulfuric acid+citric acid) [mol/mol]	-	12.6545
pH – calculated	3.33	-3.09
pH – pH meter	4.71	-

Take and crushed the kaki with its peel using a blender. Then, add pure ethanol, citric acid and mixed the obtained mixture carefully with a glass spatula until having a homogeneous mixture of E-pH-Natural. Finally, for the E-pH with sulfuric acid, add one drop – 0.1 [ml] of sulfuric acid and mixed carefully with a glass spatula until having a new homogeneous mixture of E-pH with sulfuric acid E-pHS-sulfuric acid.

3.3. Synthesized Glues Procedure

The synthesized glues were obtained by mixing carefully with a glass spatula, until having a homogeneous mixture, the crushed banana peel citric acid esters – the first glues components and the E-pH-Natural or E-pHS-sulfuric acid/pH-raiser and support - the second glues components.

3.3.1. Ecological Glues with Citric Acid Protonic Acid H^+ Catalysts Compositions

To synthesize the ecological glues to be tested, take $[X] = 2[\text{ml}]$ of the E-pH-Natural/pH-raiser and support (This quantity was taken because it was sufficient to realize the gluing between the materials-surface [§-4] used to test the synthesized glues) and add different quantities of EAcBa1 or EAcBa2 or EAcBa3. Then, mixed the obtained mixture carefully with a glass spatula until having different homogeneous mixtures equivalent to the different ecological glues with citric acid protonic acid H^+ catalysts as shown the following figure 2.

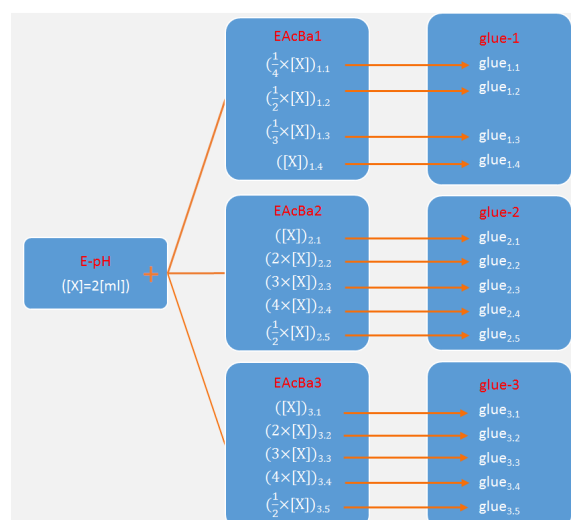


Figure 2. Tested ecological glues with citric acid protonic acid H^+ catalysts.

3.3.2. Glues with Sulfuric Acid Protonic Acid H^+ Catalysts Sglues Compositions

To synthesize the ecological glues to be tested, take $[X] = 2[\text{ml}]$ of the E-pHS-sulfuric acid/pH-raiser and support (This quantity was taken because it was sufficient to realize the gluing between the materials-surface [§-4] used to test the synthesized glues) and add different quantities of EAcBa1 or EAcBa2 or EAcBa3. Then, mixed the obtained mixture carefully with a glass spatula until having different homogeneous mixtures equivalent to the different Sglues – glues with sulfuric acid protonic acid H^+ catalysts as shown the following figure 3.

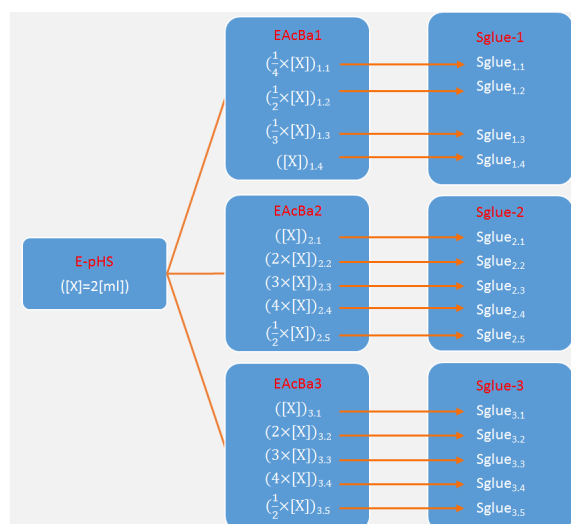


Figure 3. Tested glues with sulfuric acid protonic acid H^+ catalysts – Sglues.

4. Characteristics of Materials Used to Test the Synthesized Glues

4.1. Papers Fabrication Generalities

Paper and packing cartons used to test the synthesized glues were made from paper pulp, the main component usually up to

70% and various additives usually up to 30% [30]. The paper pulp was made from wood (usually pinewood) and composed with α -cellulose (~43%), hemicellulose (~30%), lignin (~25%), extractives (~1%) and Minerals with other inorganic materials (~1%) [31]. The additives are used to improve the paper surfaces and porosities in order to give them certain properties. These additives could be subdivided into two categories: organic additives and inorganic additives [31]. Organic additives are mainly used as adhesives such as firstly rosin (colophony) for internal bonding to prevent liquid penetration; 90% composed of diterpenes organic acids mixture called rosin acids ($C_{19}H_{29}COOH$) having two organics functional groups-carboxylic acids and alkenes, secondly latex to strengthen, to fix additives, to fill the porous and to prevent liquid penetration to the paper; it could be natural from hevea polyisoprene high molecular weight made of 1,500 to 150,000 isoprene units or synthetic like polybutadiene BR (Butadiene Rubber) [32-34] and SBR (Styrene Butadiene Rubber) having principally one organic functional groups-alkenes [32, 35-37]; latex never exceeds 15% of additives [38] and thirdly co-binder as starch, CMC (carboxymethyl cellulose), polyvinyl alcohol, soy protein for surface gluing to prevent liquid penetration, to increase strength, to limit peeling, to improve pulp fibers and additives fixations-adherences [31, 38]. In addition, inorganic additives are mainly used to prevent tar deposition and accumulation ($Talc-CaCO_3$); coating to make the paper glossier, softer, more opaque ($Talc-CaCO_3$ – Kaolin - Titan dioxide- TiO_2); pigment to lighten paper and to improve printing (Titan dioxide- TiO_2); to accelerate the rosin and additives adherences to the fibers ($Alun-Al_2(SO_4)_3$) [31]. In general, the average concentration of all additives, also named coating sauce, is 55-60% of dry matter and coating weight is about 7-9 $[g/m^2]$ [38]. Noticed that functional groups (carboxylic acids, alcohol, amines, and alkenes) of all paper's additives also named paper's coating sauce were able to react and/or to link with synthesized glues molecules (carboxylic acids, alcohol, amines, epoxydes and alkenes) catalyzed by glues' citric acid or sulfuric acid protonic acid H^+ (§3.3.) to form covalent links [21, 23-25, 27,39-43] and/or hydrogen-bridge bonds responsible of papers gluing during gluing tests (§5.). Tests were carried out on materials (School notebook paper and packing carton) used to test the synthesized glues to evaluate their porosities and their dry matter content; two characteristics which confirmed the presence of carbohydrates (cellulose, hemicellulose, glucose, starch and lignin), fats, proteins, vitamins, minerals and antioxidants [12] and could correspond to their concentrations with the average concentration of all additives also named coating sauce [38].

4.2. Characteristics of School Notebook Paper and Packing Carton Used to Test the Synthesized Glues

Firstly, dry matter was determined by putting 0.2067[g] and 0.3325[g] of respectively the school notebook paper and the packing carton in a beaker 250 [ml]. Then, put it into a forced ventilation oven set at 75°C during 4 hours after this the school notebook paper and the packing carton were weighted. This procedure was inspired by the following bibliography [11]. This dry matter or dry weight gave indicatives and confirmed the

presence of carbohydrates (cellulose, hemicellulose, glucose, starch and lignin), fats, proteins, vitamins, minerals and antioxidants in plant and animal materials [12] and could correspond to their concentrations with the average concentration of all additives also named coating sauce [38].

Secondly, the porosity was evaluated by putting 4[g] and 5[g] of respectively the school notebook paper and the packing carton. Put water in flat containers and leave them to soak for 9 hours. Then, remove and leave the school notebook paper and the packing carton in the open air for respectively 3hours and 1hour to remove water molecules adsorbed by hydrogen bridge links on the paper surface. Finally, take the sample papers weights and deduce the water mass equivalent in percentage to the porosities on these school notebook paper and packing carton. This procedure was inspired by the following bibliography [44]. The school notebook paper and the packing carton used to test the synthesized glues characteristics were shown in the following table 8.

Table 8. Porosity and dry matter content of school notebook paper and packing carton used to test the synthesized glues.

characteristics	school notebook paper	packing carton
Sample length [cm]	32.9	23.9
Sample width [cm]	21.2	14.4
Thickness [mm]	~0.375	~0.25 – thickness of adhering surface ^[*] (initially flute 1.5[mm]≤E ≤2[mm])
Sample weight [g]	4	5
Evaluated volume [cm ³]	26.1555	8.6040
Evaluated density [g/cm ³]	0.1529	0.5811
Dry matter [%]	95.90	93.96 (less additives)
Porosity [%]	50	60
Evaluated porosity volume [cm ³]	13.0778	5.1624
Evaluated porosity concentration per the total sample weight [cm ³ /g]	3.2695	1.0325
Evaluated porosity concentration per dry matter weight [cm ³ /g]	3.4092	1.0989
Evaluated dry matter weight per porosity [g/cm ³]	0.2933	0.9100

[*] Thickness of adhering surface was the thickness of the packing carton (flute 1.5[mm]≤E ≤2[mm]) face that will be coated with glue during gluing tests.

Noticed that the dry matter for packing carton was less than for school notebook paper which indicated and confirmed the presence of more additives on the school notebook papers to improve its quality such as its surfaces and its porosities in order to give them certain properties like high initial impermeability [31] and consequently the presence of more paper pulp on the packing carton leading to higher permeability. Indeed, it was said that the pore volume or porosity of paper consists of all the space outside the solid materials included in the paper and can be roughly divided into two categories: the interfibre volume that consists of the space between the fibres, and the intrafibre volume that consists of the pore volume within the fibre which are considerably smaller than the typical fibre dimensions. Due to that, the permeability of the fibre network is assumed to be

chiefly governed by the properties of interfibre volume, even in a highly compressed state [45]. Also, for a freeze-dried material with minimal bonding, nitrogen adsorption surface area per mass was found to be as high as 20 m²/g for fines of chemical pulp, while it was 8 m²/g for mechanical fines. A typical value for fibres is 1 m²/g [46] and some of factors affecting the interfibre pore size are closely related to fibre properties and pulp treatment; For decreasing basis weight from 176 g/m² to 52 g/m², the average interfibre pore size was found to increase in water permeation measurements from 17 µm to 25 µm with standard deviation doubled [47].

5. Gluing Tests

5.1. Gluing Test Procedure

Globally, the gluing tests procedure consisted of gluing two

school notebook for the natural-ecological glues with citric acid protonic acid H⁺ catalysts and gluing two packing carton sample for the Sglues-glues with sulfuric acid protonic acid H⁺ catalysts. Then, each glues samples weights were followed-up with time.

5.1.1. School Notebook and Packing Carton Samples to Be Glued Dimensions and Characteristics

To have an ideal and practice gluing tests of all synthesized glues composed with [X]=2[ml] of pH-raiser and support (natural E-pH or E-pHS-sulfuric acid) (figure 2 – figure 3) and crushed banana peel citric acid esters (EAcBa) quantities between $\frac{1}{4} \times \{[X] = 2[ml]\}$ and $4 \times \{[X] = 2[ml]\}$, a constant size of school notebook and packing carton samples tests 5[cm] × 10[cm] were glued during the gluing tests. The following table 9 showed the characteristics of these school notebook and packing carton samples tests.

Table 9. Characteristics of school notebook paper and packing carton samples used to test the synthesized glues.

characteristics	school notebook paper	packing carton
Sample length [cm]	10	10
Sample width [cm]	5	5
Thickness [mm]	~0.375	~0.25 – thickness of adhering surface (initially flute 1.5[mm] ≤ E ≤ 2[mm])
Sample weight [g]	0.5522	7.12 [*]
Evaluated adhering volume [cm ³]	(1.875×2)=3.75	~ (1.25×3)×2 = 7.5[*]
Dry matter [%]	95.90	93.96 (less additives)
Porosity [%]	50	60
Evaluated adhering porosity volume [cm ³]	1.875	~ (0.75×3)×2 = 4.5[*]
Evaluated porosity concentration per the total sample weight [cm ³ /g]	3.3955	0.6320
Dry matter weight [g]	0.5296	6.68995
Evaluated porosity concentration per dry matter weight [cm ³ /g]	3.5404	0.6727
Evaluated dry matter weight per porosity [g/cm ³]	0.2825	1.4867
Additives [g] / (30% of paper) (§4.1.)	0.16566	2.136
Latex [g] / (<15% of additives) (§4.1.)	<0.024849	<0.3204
Medium number average molar mass [Kg/mol] [48]	118.75 ^[48]	
Medium weight average molar mass [Kg/mol] [48]	725.25 ^[48]	
Moles latex by number average molar mass [moles]	<2.09E-7	<2.6981E-6

Table 9. Continue.

characteristics	school notebook paper	packing carton
Moles latex by weight average molar mass [moles]	<3.43E-8	<4.4178E-7
Minimum ratio (Minimum C ⁻ moles of all synthesized natural and sulfuric glues/Moles latex by number average molar mass-Table 10-11)	>765.55	>59.26
Minimum ratio (Minimum C ⁻ moles of all synthesized natural and sulfuric glues/Moles latex by weight average molar mass-Table 10-11)	>4,664.72	>362.17

[*] These weight, evaluated adhering volume and evaluated adhering porosity volume corresponded to the total two packing carton samples (flute E) to be glued because during test after gluing and during the tests these samples were slightly compressed under a charge that enabled glues diffusions.

Noticed that not only, as said previously (§4.2), the packing carton samples tests contained less additives but also its evaluated adhering porosity volume and evaluated dry matter weight per porosity were more important even if its evaluated porosity concentration per the total sample weight was few (Table 9). These results influenced evidently the gluing quality on these supports samples particularly the gluing quality on the school notebook paper.

Also, noticed that normally the synthesis of this packing carton didn't use latex additives but if it was considered that it still contained the maximum value (Table 9) so the latex moles

quantities was all the time very negligible compared to the alkenes organic functional group-C⁻ of all synthesized glues (Table 9).

5.1.2. Glued Samples Weights Followed-up

Once glued, samples were compressed slightly and weighed. This first weight was taken as the weight of the glued sample after the first minute of gluing. Then, samples were all the time slightly compressed under a charge and every five minutes the glued samples were weighed. From the previous datas were deduced the initial total weight of each test glued sample equal to the weight of glued papers sample plus the

weight of the glue-reagents used. Let's recall that the weight of the used glued-reagent for each glue tested was equal to the weight of the EAcBa which changed according to the glue composition plus the weight of the pH-raiser and support (natural E-pH or E-PHS-sulfuric acid) (figure 2 – figure 3) which was constant. Then, the glue-reagents weight for each time was equal to the record glued sample for each time minus the school notebook or the packing carton weight. Noticed that all the time the glue-reagents weight decreased with time and the total weight diminution of glue-reagents at each time was equal to the initial total weight of glue-reagents minus the glue-reagents weight for each time calculated previously.

This total weight diminution of glue-reagents value could be assimilated to the weight of by-products like water molecules formed not only by esterification between the glue-reagents active molecules (citric acid molecules – alcohol and amine organic functions from banana (§2.1.)) and the school notebook or the packing carton active molecules (alcohol organic functions and carboxylic acid organic functions from additives (§4.2.)) but also by dehydration of all alcohol organic functions which were all catalyzed only by protonic acid H^+ from citric acid molecules for the natural glues and with sulfuric acid molecules for the Sglue-sulfuric acid glues. Noticed that other by-products could be formed like carbon dioxide and hydrogen by decarboxylation-mechanism of molecules with carboxylic acid functional groups [25] with formation of alkenes and eventually their hydrogenation [25].

In other words, this total weight diminution of glue-reagents value was a good indicator and should be proportional for covalent links formed by reactions between functional groups (carboxylic acids, alcohol, amines, and alkenes) of all paper's active molecules and additives also named paper's coating sauce with synthesized glues molecules (carboxylic acids, alcohol, amines and alkenes) catalyzed by glues' citric acid or sulfuric acid protonic acid H^+ (§3.3.) [21, 23-25, 27, 39-43] and hydrogen-bridge bonds responsible of papers gluing quality during gluing tests (§5.). Consequently, also the covalent linked formed between two consecutive times was evaluated with weight diminution of glue-reagents between two consecutive times and gave an idea of the protonic acid H^+ catalysts activities. However, this total weight diminution of glue-reagents value was slightly overestimated because of possible over water molecules and carbonic dioxide formed during reactions of glue-reagents with pulp structure could be retained by hydrogen bridge links-adsorption in its intrafibre or interfibre volume even if for all evaluations of this covalent links formed by the total weight diminution of glue-reagents value, all water molecules and ethanol quantities from kaki, banana peel, citric acid monohydrated were taken into consideration and removed.

5.2. Gluing Test Results and Discussions

5.2.1. Weight of Glued-reagent Samples Followed-up Results

The following figure 4 to figure 7 showed the total weight

diminution of glue-reagents and weight diminution of glue-reagents between two consecutive times taking into consideration, removing all waters for the natural glues like “glue-1” (figure 2) made with natural E-pH and EAcBa1 and for the sulfuric acid glues like “Sglue-1” (figure 3) made with E-PHS and EAcBa1.

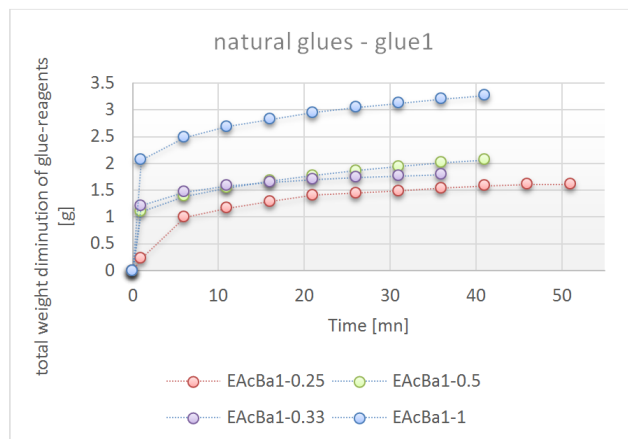


Figure 4. Total weight diminution of glue-reagents for natural glues – glue1.

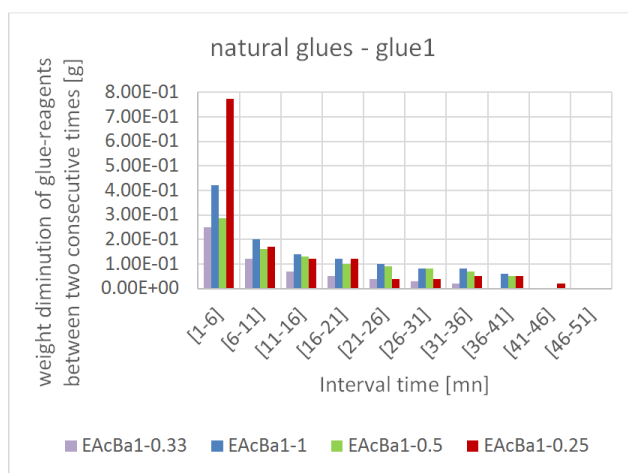


Figure 5. Weight diminution of glue-reagents between two consecutive times for natural glues – glue1.

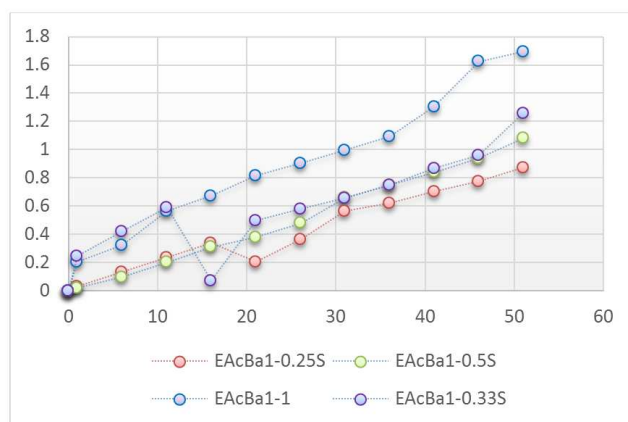


Figure 6. Total weight diminution of glue-reagents for sulfuric Sglues – Sglue1.

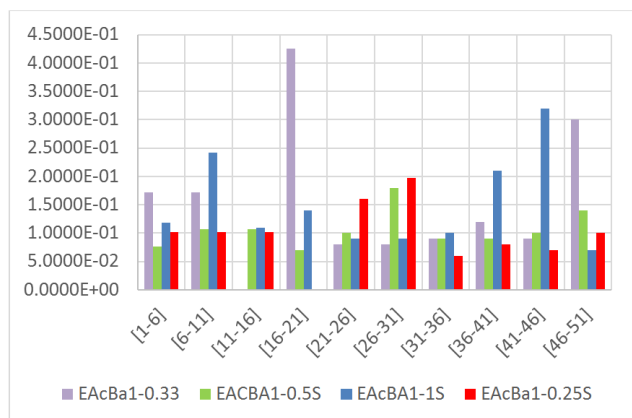


Figure 7. Weight diminution of glue-reagents between two consecutive times for sulfuric acid Sglues – Sglue1.

The total weight diminution of glue-reagents for natural glues – glue1 were initially very important (figure 4) because there was initially formation of water molecules; not only by esterification reactions between additives active molecules with natural glue-reagents but also by dehydration reactions of alcohol functions; which were immediately vaporized with the solvent ethanol molecules seeing that the water and ethanol rate ratio in each synthesized natural glue were respectively on average of 46% and 54%. These reactions increased with the EAcBa certainly due to the increase of citric acid's protonic acid H⁺ catalyst concentration in the synthesized natural glues whose effects will be seen later. However, these reactions tend to decrease drastically overtime especially for natural glues synthesized with low EAcBa (EAcBa1-0.25 and EAcBa1-0.33) (figure 5) certainly due to the presence of non-insignificant additives on the school notebook paper gluing sample which prevent

liquid-glue-reagents-catalyst H⁺ penetrations in the initial time. For natural glues synthesized with higher EAcBa (EAcBa1-0.5 and EAcBa1-1), these reactions between additives active molecules and glue-reagents persist over time (figure 5) and certainly responsible of the best quality of the gluing tested samples (§5.2.2.) particularly in this case (natural glues gluing tests) because of the progressive dismantling of the additives barrier by their participation in these gluing reactions accompanied in long term with glues-reagents and catalysts accessibility-activities into the paper pulp porosities which were more important for the school notebook paper (natural glues tests) in the order of 3.3955 [cm³/g] even if the molar volume of the citric acid protonic acid H⁺ catalyst was large equal to 109.7±3.0 [cm³] and its estimated dimension was (7.81Å×3.091Å×6.155Å) [28]. Among these reactions were firstly esterification reactions between natural glues-carboxylic acids functional group with paper pulp-hydroxyls functional group (figure 8) and/or esterification reactions between natural glues-alcohols functional group with paper pulp-carboxylic acids (rosin) (figure 9); secondly etherification between natural glues-carboxylic acids functional group with school notebook paper-pulp-alkenes functional groups formed during pulp-dehydration and school notebook additives(latex)-alkenes functional groups (figure 10); and finally addition reactions between natural glues-alkenes functional groups (banana peel latex and alkenes by alcohol dehydration) with school notebook paper-pulp-alkenes functional groups on additives (latex or rosin) and formed during pulp-dehydration (figure 11). All these reactions were catalyzed by citric acid protonic acid H⁺.

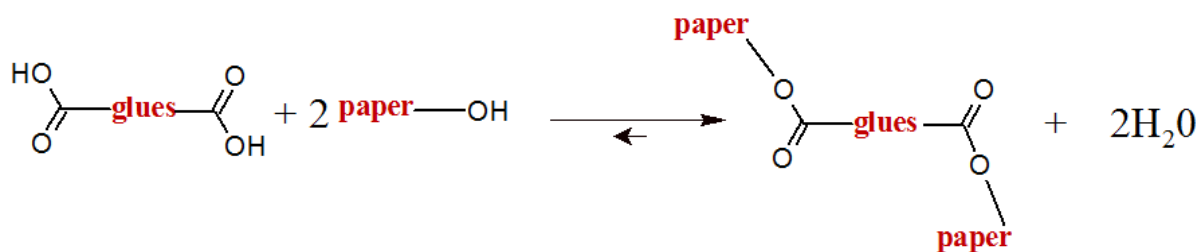


Figure 8. Gluing covalent linked formed by esterification.

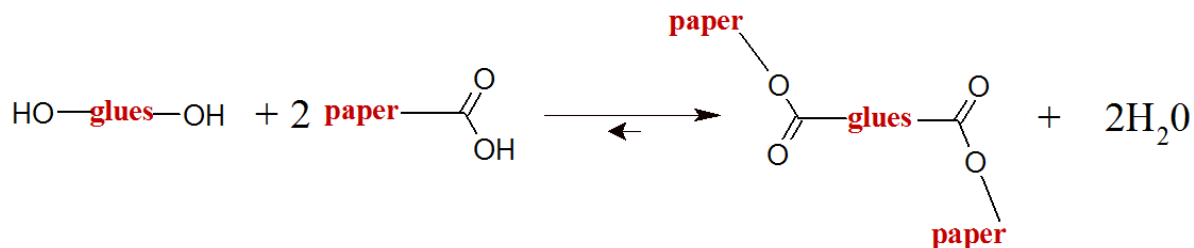


Figure 9. Second possibility of gluing covalent linked formed by esterification.

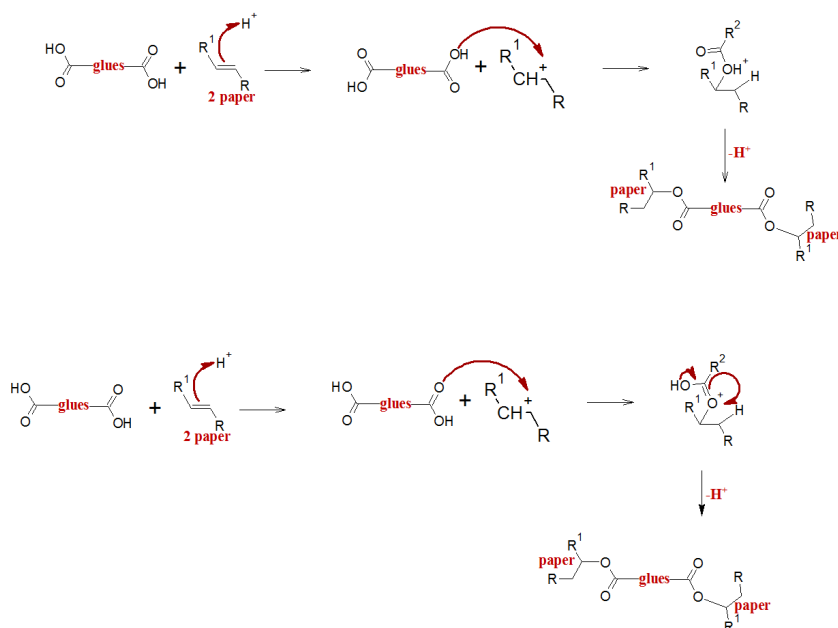


Figure 10. Gluing covalent linked formed by etherification.

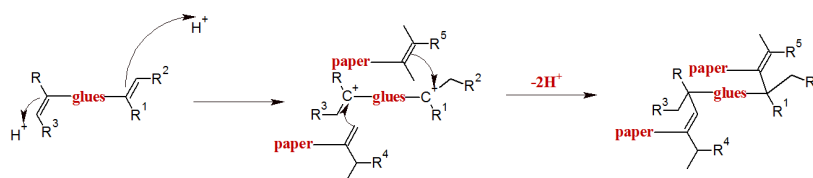


Figure 11. Gluing covalent linked formed by alkene addition catalyzed by protonic acid H^+ .

For the sulfuric acid Sglues like “Sglue-1”, the initial total weight diminution of glue-reagents appeared less important than for the natural glues like “glue-1” (figure 4 – figure 6) due certainly to its compositions marked by less additives (dry matter-93.96% - Table 9) for the benefit of pulp (Dry matter weight [g]=6.68995 - Evaluated dry matter weight per porosity [g/cm³]= 1.4867 – Table 9) and high porosity size (§4.2. [46-47]) (porosity [%]=60 – Table 9). These conditions were favorable for the gluing-reactions described previously in the case of the natural glue tests except that in this case with packing carton not only a significant water molecules formed could be retained in the pulp interfibre/intrafibre porosities but also and especially dehydration reactions (easily catalyzed by sulfuric acid protonic acid H^+ [27]) with alkenes functional group formation quickly followed by the addition reactions (figure 10 – figure 11) between the EAcBa glue-reagents [25] and those of packing carton were very important. In addition, the molar volume of sulfuric acid protonic acid H^+ catalyst was small equal to 44.5±3.0 [cm³] and its estimated dimension was (3.29Å×2.709Å×2.342Å) [28] against those of citric acid protonic acid H^+ catalyst. Thus, they move durably and catalyzed in depth on E-pHS all gluing reactions listed below (like figure 8 to figure 11) that's why the total weight diminution of glue-reagents for sulfuric acid Sglues like Sglue1 increased constantly with time (figure 6) and all gluing reactions persisted in time for all Sglues (figure 7). Consequently, for sulfuric acid Sglues like Sglue1, the most likely in depth principal active catalyst were sulfuric acid

protonic acid H^+ and responsible of the best quality of the gluing tested samples (§5.2.2.) particularly in this case of Sglues (sulfuric acid glues gluing tests). Indeed, noticed that for tested Sglue1 with small amount of EAcBa (EAcBa1-0.25S and EAcBa1-0.33S – figure 6) after a few minutes of gluing tests, the weight diminution of glue-reagents decreased which indicated that the amount of retained water molecules and addition reactions increased as explained previously included the possible participation of citric acid molecules and their derivatives [25] into these addition reactions (figure 8 to figure 11).

5.2.2. Effects of pH-raiser Supports (Natural E-pH – E-pHS) and Protonic Acids H^+ on Natural Glue and on Sulfuric Acid Glues Sglues

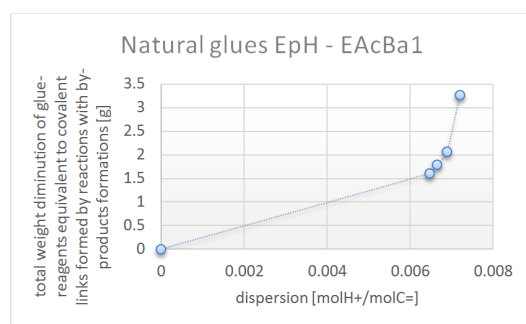
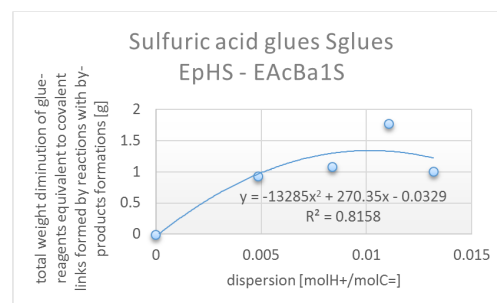
The following table 10 and table 11 showed the alkenes functional group quantities which not only support the sulfuric acid and citric acid protonic acids H^+ catalyst [27] but also raise the global pH of the glues enabled to calculate the initial quantities of H^+ and their concentrations for respectively natural glues-glue1 and sulfuric acid glues-Sglue1. Thus, the initial dispersion of the protonic acids H^+ on the alkenes functional group for each synthesized glues was calculated by dividing the initial quantities of H^+ with initial alkenes functional group quantities. Also, the initial quantities of citric acid and their concentrations were calculated seeing that the citric acid conversion during the slimy EAcBa1s synthesis were evaluated at 95%.

Table 10. Characteristics of the synthesized natural glues – glue1.

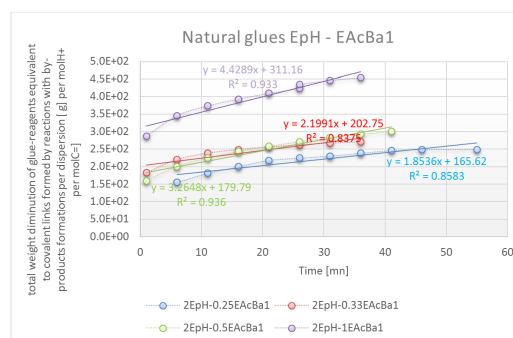
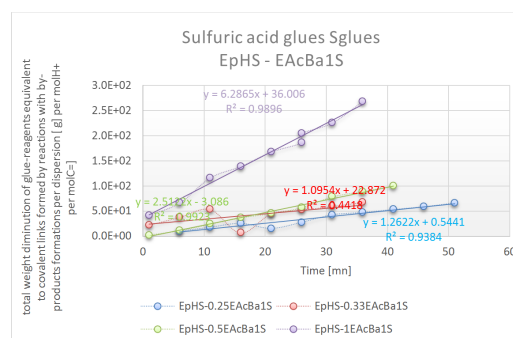
Natural glues – glue1	EAcBa1-0.25	EAcBa1-0.33	EAcBa1-0.5	EAcBa1-1
nH^+ initial [moles] such as EAcBa1 at 95% of conversion	1.0352E-06	1.2692E-06	1.7373E-06	3.1417E-06
$[H^+]_{initial}$ [mol.l ⁻¹]	4.1407E-04	4.7596E-04	5.7911E-04	7.8541E-04
citric acid [moles] initial such as EAcBa1 at 95% of conversion	3.69704E-06	4.5329E-06	6.2048E-06	1.1220E-05
[citric acid] initial [mol.l ⁻¹]	1.48E-03	1.70E-03	2.07E-03	2.81E-03
Initial moles total C^- [moles]	1.60E-04	1.91E-04	2.52E-04	4.36E-04
Initial dispersion	6.4602E-03	6.6476E-03	6.8856E-03	7.1979E-03

Table 11. Characteristics of the synthesized sulfuric acid glues – Sglue1.

Sulfuric acid glues – Sglue1	EAcBa1S-0.25	EAcBa1S-0.33	EAcBa1S-0.5	EAcBa1S-1
nH^+ initial [moles] such as EAcBa1 at 95% of conversion	2.1210E-06	2.1210E-06	2.1210E-06	2.1210E-06
$[H^+]_{initial}$ [mol.l ⁻¹]	8.4841E-04	7.9538E-04	7.0701E-04	5.3025E-04
citric acid [moles] initial such as EAcBa1 at 95% of conversion	3.7114E-06	4.5329E-06	6.2191E-06	1.1235E-05
[citric acid] initial [mol.l ⁻¹]	1.48E-03	1.70E-03	2.07E-03	2.81E-03
Initial moles total C^- [moles]	1.60E-04	1.91E-04	2.52E-04	4.37E-04
Initial dispersion	1.3169E-02	1.1061E-02	8.3788E-03	4.8503E-03

**Figure 12.** Total weight diminution of glue-reagents in terms of protonic acid H^+ dispersions for the natural glues EpH-EAcBa1.**Figure 13.** Total weight diminution of glue-reagents in terms of protonic acid H^+ dispersions for the sulfuric acid glues EpHS-EAcBa1S.

These figure 12 and figure 13 showed that the total weight diminution of glue-reagents during the tests generally increased with the initial dispersion. Firstly, it indicated that the covalent links basis of good gluing (§5.2.3) involve higher dispersion and secondly it confirmed that the alkenes functional group not only performed its support role where catalysts molecules interspersed efficiently but also they performed its pH-raiser role by moving with the catalysts protonic acids H^+ through the school notebook paper/packing carton samples interfibre/intrafibre porosities and explained the constant increasing of their activities with times (figure 14 – figure 15) especially for the sulfuric acid glues – Sglue1 tested on the packing carton as explained previously (§5.1.2). Noticed that, particularly the molar volume of betacarotene molecule was equal to 570.1 ± 3.0 [cm³] but its estimated dimension was $(30.75\text{\AA} \times 4.219\text{\AA} \times 6.499\text{\AA})$ [28]. Indeed, the molar volume of sulfuric acid protonic acid H^+ catalyst was small equal to 44.5 ± 3.0 [cm³] and its estimated dimension was $(3.29\text{\AA} \times 2.709\text{\AA} \times 2.342\text{\AA})$ [28] against those of citric acid protonic acid H^+ catalyst. Noticed that for tested Sglue1, the weight diminution of glue-reagents decreased at higher value of dispersion (figure 13) which indicated and confirmed that the amount of retained water molecules and addition reactions increased as explained previously included the possible participation of citric acid molecules and their derivatives [25] into these addition reactions (figure 8 to figure 11).

**Figure 14.** Total weight diminution of glue-reagents from 1mn to 55mn in terms of time for the natural glues EpH – EAcBa1.**Figure 15.** Total weight diminution of glue-reagents from 1mn to 55mn in terms of time for the sulfuric acid glues EpHS – EAcBa1S.

Deduced from these figure 14 and figure 15 were the following table 12 – table 13 which showed the medium activities and the initial activities from 1mn to 55mn of

protonic acids H^+ for respectively the natural glues EpH – EacBa1 and the sulfuric acid glues EpHS – EacBa1S.

Table 12. Activities of citric acid protonic acids H^+ for the natural glues EpH – EAcBa1.

natural glues EPh – EAcBa1	T.A.	I.A.	T.A.A.V.	T.A.D.M.	T.A.A.P.V.	I.A.A.V.	I.A.D.M.	I.A.A.P.V.	T.A.P.C.S.	T.A.P.C.D	I.A.P.C.S	I.A.P.C.D.
2EpH-0.25EAcBa1	3.35	63.38	0.895	6.34	1.79	16.91	119.76	33.83	0.55	0.52	10.315	9.89
2EpH-0.33EAcBa1	3.98	331.40	1.06	7.52	2.12	88.32	625.38	176.64	0.65	0.62	53.86	51.66
2EpH-0.5EAcBa1	5.90	289.57	1.58	11.16	3.15	77.24	546.94	154.49	0.96	0.92	47.11	45.18
2EpH-1EAcBa1	8.02	521.19	2.14	15.14	4.28	138.98	984.12	277.97	1.30	1.25	84.76	81.29

Table 13. Activities of sulfuric acid protonic acid H^+ for the sulfuric acid glues EpHS – EAcBa1S.

Sulfuric acid glues EpHS – EAcBa1S	T.A.	I.A.	T.A.A.V.	T.A.D.M.	T.A.A.P.V.	I.A.A.V.	I.A.D.M.	I.A.A.P.V.	T.A.P.C.S.	T.A.P.C.D	I.A.P.C.S	I.A.P.C.D.
2EpHS-0.25EAcBa1S	0.18	0.23	0.024	0.0265	0.0394	0.0304	0.0340	0.3603	1.20	1.88	2.57	2.41
2EpHS-0.33EAcBa1S	0.15	0.69	0.146	0.0230	0.0342	0.0919	0.1030	1.0901	1.73	1.63	7.76	7.29
2EpHS-0.5EAcBa1S	0.35	0.31	0.335	0.0527	0.0784	0.0413	0.0464	0.4906	3.98	3.73	3.49	3.28
2EpHS-1EAcBa1S	0.88	0.98	0.838	0.1319	0.1962	0.1313	0.1472	1.5585	9.95	9.35	11.10	10.43

- T.A.: Trend Activities of initial H^+ were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per [g] between 1[mn] and 55[mn]
- I.A.: Initial Activities of initial H^+ were the initial weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per [g] between 0[mn] and 1[mn]
- T.A.A.V.: Trend Activities of initial H^+ per Adhering Volume were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per adhering volume (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per cm^3 per [g] between 1[mn] and 55[mn]
- T.A.D.M.: Trend Activities of initial H^+ per initial Dry Matter were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per initial dry matter quantities (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per g of dry matter per [g] between 1[mn] and 55[mn]
- T.A.A.P.V.: Trend Activities of initial H^+ per Adhering Porosity Volume were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per adhering porosity volume (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per cm^3 per [g] between 1[mn] and 55[mn]
- I.A.A.V.: Initial Activities of initial H^+ per Adhering Volume were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per adhering volume (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per cm^3 per [g] between 0[mn] and 1[mn]
- I.A.D.M.: Initial Activities of initial H^+ per initial Dry Matter were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per initial dry matter quantities (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per [g] between 0[mn] and 1[mn]
- I.A.A.P.V.: Initial Activities of initial H^+ per Adhering Porosity Volume were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per adhering porosity volume (Table 9) per gram of sample test paper; [g] per mn per $molH^+$ per $molC^=$ per cm^3 per [g] between 0[mn] and 1[mn]
- T.A.P.C.S.: Trend Activities of initial H^+ per evaluated Porosity Concentration per the total Sample weight were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per porosity concentration per the total sample weight (Table 9); [g] per mn per $molH^+$ per $molC^=$ per cm^3 per $[cm^3/g]$
- T.A.P.C.D.: Trend Activities of initial H^+ per evaluated Porosity Concentration per Dry matter weight $[cm^3/g]$ were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per porosity concentration per dry matter weight (Table 9); [g] per mn per $molH^+$ per $molC^=$ per cm^3 per $[cm^3/g]$
- I.A.P.C.S.: Initial Activities of initial H^+ per evaluated Porosity Concentration per the total Sample weight were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per porosity concentration per the total sample weight (Table 9); [g] per mn per $molH^+$ per $molC^=$ per cm^3 per $[cm^3/g]$
- I.A.P.C.D.: Initial Activities of initial H^+ per evaluated Porosity Concentration per Dry matter weight $[cm^3/g]$ were the total weight diminution of glue-reagents equivalent to covalent links formed by reactions with by- products formations per minute per dispersion per porosity concentration per dry matter weight (Table 9); [g] per mn per $molH^+$ per $molC^=$ per cm^3 per $[cm^3/g]$

Firstly, the initial activities per weight of sample paper test (I.A.) of citric acid protonic acids H^+ for the natural glues (Table 13) were very important than for the sulfuric acid protonic acids H^+ . These results confirmed and indicated that not only the kaki's alkenes functional group but also the pure ethanol and all additives of the school notebook paper performed its support role where catalysts molecules interspersed efficiently. Also they performed the kaki's alkenes and pure ethanol functional pH-raiser role by moving with the citric acid catalysts protonic acids H^+ through the

school notebook paper. Noticed that, particularly the molar volume of betacarotene, ethanol and water molecules was respectively equal to $570.1 \pm 3.0 [cm^3]$, $59 \pm 3.0 [cm^3]$, $3.67 \pm 3.0 [cm^3]$ but their estimated dimension was respectively $(30.75 \text{Å} \times 4.219 \text{Å} \times 6.499 \text{Å})$, $(2.27 \text{Å} \times 3.856 \text{Å} \times 1.18 \text{Å})$ and $(1.6 \text{Å} \times 1.012 \text{Å})$ [28]. That's why the I.A.D.M. of the citric acid protonic acids H^+ increased with the EAcBa (Table 12). Thus, there was initially formation of water molecules; not only by esterification reactions between additives and paper active molecules with natural glue-reagents (figure 8 to figure 11)

but also by dehydration reactions of all alcohol functions; which were immediately vaporized with the solvent ethanol molecules seeing that the water and ethanol rate ratio in each synthesized natural glue were respectively on average of 46% and 54%.

Secondly, in addition, the growth rate of T.A.D.M. from 0.25EAcBaS to 1EAcBaS for the sulfuric acid glues EpHS – EAcBa1S were more important than for the natural glues EpH-EAcBa1 respectively 397.74% and 138.80% which indicated and confirmed that generally the porosity-accessibility of the paper tests in particular school note book paper-packing carton paper and the catalysts sizes and the catalysts' protonic acid H^+ quantities influenced positively their activities and the continuity of their activities. Thus, the growth rate of (T.A.A.V. - T.A.A.P.V.) from 0.25EAcBaS to 1EAcBaS for the sulfuric acid glues EpHS – EAcBa1S were very important than for the natural glues EpH-EAcBa1 respectively (3,391.66% -139.11%) and (397.97% - 139.11%); and also, the T.A.P.C.S. and the T.A.P.C.D. of the sulfuric acid glues EpHS – EAcBa1S were all the time very important.

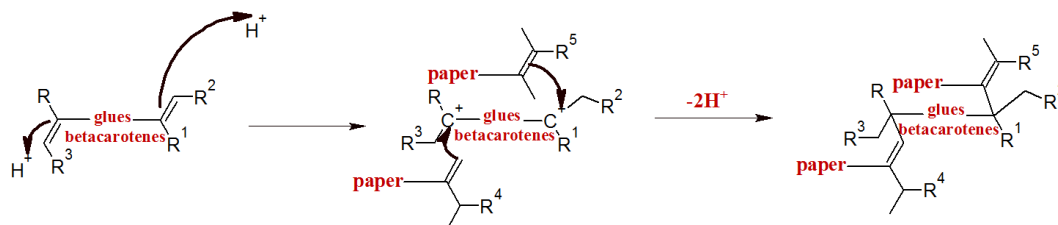


Figure 16. Gluing covalent linked formed by betacarotenes' alkene addition catalyzed by sulfuric acid's protonic acid H^+ .

Indeed, it was explained that a significant water molecules, formed by dehydration reactions (easily catalyzed by sulfuric acid protonic acid H^+ [27]) with alkenes functional group formation, could be retained in the pulp interfibre/intrafibre porosities (§5.2.1.). These water molecules hydrolyzed the proteins molecules to generate amino-acids molecules containing two organic functional groups: carboxylic acids and amines [49] and noticed that these proteins hydrolysis

could not take place without the activity of the sulfuric acid protonic acid H^+ catalyst with probably a low hydrolysis rate (HD) in the short time, since total hydrolysis requires fairly severe conditions [50]. Thus, once formed, peptides' carboxylic acids and amines quickly suffered the addition reactions respectively like on figure 9, like on figure 17 amines from papers-additives (§4.1.) and like on figure 18 amines from glues (figure 18) reacted with alkene of papers.

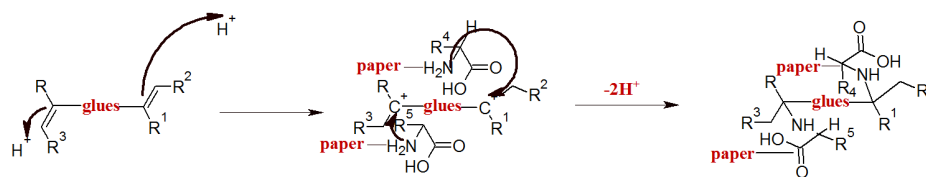


Figure 17. Gluing covalent linked formed by betacarotenes' alkene and/or over glues' alkene additions with amine organic functional group catalyzed by sulfuric acid's protonic acid H^+ .

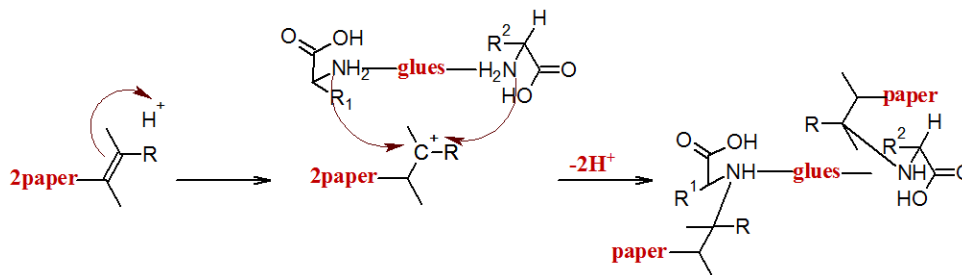


Figure 18. Gluing covalent linked formed by papers' alkene additions with glues' amine organic functional group catalyzed by sulfuric acid's protonic acid H^+ .

5.2.3. Global Results of All Synthesized Glues Capacities to Stick

The following table 14 showed the global results of all synthesized glues to stick such as the percentages were equivalent to the surface really glued at the end of the test in comparison to the total surface to be glued (5cm×10cm).

Table 14. Global results of all synthesized glues capacities to stick.

Synthesized glues	Gluing tests results			
	Percentage of surface really glued at the end of each test in comparison to the total surface to be glued (5cm×10cm) highlighted in red			
Gluing tests on school notebook paper samples				
glue _{1,1}	<25%]25% – 50%[]50% – 75%[>75%
glue _{1,2}	<25%]25% – 50%[]50% – 75%[>75%
glue _{1,3}	<25%]25% – 50%[]50% – 75%[>75%
glue _{1,4}	<25%]25% – 50%[]50% – 75%[>75%
glue _{2,1}	<25%]25% – 50%[]50% – 75%[>75%
glue _{2,2}	<25%]25% – 50%[]50% – 75%[>75%
glue _{2,3}	<25%]25% – 50%[]50% – 75%[>75%
glue _{2,4}	<25%]25% – 50%[]50% – 75%[>75%
glue _{3,1}	<25%]25% – 50%[]50% – 75%[>75%
glue _{3,2}	<25%]25% – 50%[]50% – 75%[>75%
glue _{3,3}	<25%]25% – 50%[]50% – 75%[>75%
glue _{3,4}	<25%]25% – 50%[]50% – 75%[>75%
Gluing tests on packing carton samples				
Sglue _{1,1}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{1,2}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{1,3}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{1,4}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{2,1}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{2,2}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{2,3}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{2,4}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{3,1}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{3,2}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{3,3}	<25%]25% – 50%[]50% – 75%[>75%
Sglue _{3,4}	<25%]25% – 50%[]50% – 75%[>75%
Gluing tests on packing carton samples				
SNglue _{1,1}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{1,2}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{1,3}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{1,4}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{2,1}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{2,2}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{2,3}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{2,4}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{3,1}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{3,2}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{3,3}	<25%]25% – 50%[]50% – 75%[>75%
SNglue _{3,4}	<25%]25% – 50%[]50% – 75%[>75%

6. Conclusion

Two categories of glues were synthesized by valorizing banana skin and kaki which were widely cultivated at Madagascar. The ecological glues with citric acid protonic acid H⁺ catalyst and the sulfuric acid glues Sglues with sulfuric acid protonic acid H⁺ catalyst. It was noticed that the pH-raiser-support (The first main compound of glues) composed with kaki, especially their betacarotenes molecules and pure ethanol performed not only their pH-raiser role by increasing the global glues' pH higher than the EAcBa1 (Citric

acid esters of banana peel molecules – The second main compound of glues), but also their support role on which catalysts molecules interspersed efficiently and could move through the test-papers' porosities. That's why, the protonic acid H⁺ activities were important and persisted over time. Thus, the trend activities of initial protonic acid H⁺ between 1mn and 55mn of all glues were between 0.88 and 8.02. Especially, the activity of the sulfuric acid H⁺ increased sufficiently with time through the packing carton because of its smallest size and its strength which consequently promoted firstly dehydration reactions to form alkenes functional group followed by addition reactions between tested paper-cartons' molecules and glues-reagent molecules like etherification, alkenes additions, addition reactions between amine and alkene and eventually esterification reactions. It wasn't the case for the natural-ecological glues tested with paper containing additives and less porosities which tend to decrease without blocking the citric acid protonic acid H⁺ activity favoring directly addition reactions like etherification between tested papers additives' alkene and glues' carboxylic acid functional group. In the end, these addition reactions between glues' reagents molecules and tested paper-cartons' molecules generated covalent links with each other and gave the glues capacity to stick efficiently.

Acknowledgements

Sincere thanks to the E. S. P. A Polytechnics' President and the I.E.S.A.V. Institute's President. Also, sincere gratitude to Chemical Process Engineering Chief Department (E. S. P. A) as well as Chemical Engineering Laboratory staff.

References

- [1] N. Amnuaysin, K. Seraypheap & M. Kidyoo, «Anatomical Changes in Peel Structure of 'Hom Thong' Banana during Fruit Development and Ripening», Tropical Natural History, vol. 12, no 2, octobre 2012, p. 129.
- [2] Oliveira L, Freire CS, Silvestre AJ, Cordeiro N, «Lipophilic extracts from banana fruit residues: a source of valuable phytochemicals», J Agric Food Chem., vol. 56, no 20, 22 octobre 2008, p. 9520-9524 (DOI 10.1021/jf801709t).
- [3] Debra Rose Wilson, Ph.D., MSN, R. N., IBCLC, AHN-BC, CHT — Written by Scott Frothingham on August 29, 2019 «23 Uses of Banana Peels for Skin Care, Hair Health, First Aid and More»
- [4] Kapadia SP, et al. (2015). «Detection of antimicrobial activity of banana peel (Musa paradisiaca L.) on Porphyromonas gingivalis and Aggregatibacter actinomycetemcomitans: An in vitro study». DOI:10.4103/0976-237X.169864
- [5] Sundaram S, et al. (2011) «Antioxidant activity and protective effect of banana peel against oxidative hemolysis of human erythrocyte at different stages of ripening». ncbi.nlm.nih.gov/pubmed/21369778
- [6] Organisation des Nations Unies pour l'alimentation et l'agriculture «examen du marché de la banane» <http://www.fao.org/3/ca9212fr/ca9212fr.pdf>

- [7] Alula Gebregergs Halefom, Mebrahtom Gebresemati, Omprakash Sahu «Industrial ethanol from banana peels for developing country: Response surface methodology» - Biofuels from lignocellulosic biomass. Addis Abeba and Mekelle University. DOI: 10.1016/j.psra.2016.06.002. July 2016.
- [8] Yusriha Binti Mohd Yusoff «Effect of banana skin on biodegradable natural rubber latex» Faculty of Industrial Sciences and Technology. Universiti Malaysia Pahang. January 2012.
- [9] Rabeharitsara Andry Tahina – Rabearimihaja Phandry Nomena Ndjiva (2016) «Betacarotenes Dosage by Hydrofluoric Acid Solution and Validation of This New Process by SPC» - Chemical Process Engineering Department (E.S.P.A), Antananarivo University – Madagascar - American Journal of Applied Chemistry in Vol. 4. May 2016 DOI: 10.11648/j.ajac.20160403.14
- [10] Rabearimihaja Phandry Nomena Ndjiva «Valorisation du bêta-carotène extrait de l'huile de palme brute par de l'acide acétique pour la détermination des teneurs en eau de produits pétroliers (Gaz oil-Fuel oil) et dosage des teneurs en bêta-carotène par de l'acide fluorhydrique. Mémoire de fin d'étude en vue de l'obtention du diplôme d'Ingénieur en génie des procédés chimiques et industriels (Mai 2016).
- [11] Nathalie Fatianoff et Ph. Gouet «Relation Permettant De Corriger Rapidement et Avec Précision La Matière Sèche des Ensilages Séchés A l'étuve» Laboratoire de Recherches sur la Conservation et l'Efficacité des Aliments, 16, rue Claude Bernard, 75 - Paris (5e) Institut national de la Recherche agronomique. *Ann. Zootech.*, 1969, 18 (4), 407-418.
- [12] Carbohydrates, Proteins, and Fats. The Merck Manual.
- [13] Morton JF (1987). "Japanese persimmon". NewCROP, New Crops Resource Online Program, Purdue University Center for New Crops and Plant Products; from Morton, J. 1987. Japanese Persimmon. p. 411–416. In: Fruits of warm climates.
- [14] DTU-Valeur nutritive pour 100 [g] - DTU [archive]
- [15] US. Department of agriculture – Agricultural Research Service. USDA Nutrient Database
- [16] RAJOMALAZA Rima Leterakotonobosoa – «Contribution à la valorisation des deux variétés de Diospyros kaki: yémou et voatabia dans la commune rurale d'Ambano, sous-préfecture d'Antsirabe II» Mémoire de fin d'étude en vue de l'obtention du diplôme d'Ingénieur Agronome Option industries Agricoles et Alimentaires. ESSA – Université d'Antananarivo. 2005. http://madadoc.irenala.edu.mg/documents/10931_Rajomalaza%20Rima.pdf
- [17] M. Laffitte, F. Rouquerol La réaction chimique Tome 2. Aspects thermodynamiques (suite) et cinétiques, 1991, Eds. Masson p. 22.
- [18] Silva AM, Kong X, Hider RC, Pharmaceutical Sciences Research Division, King's College London, London, UK «Determination of the pKa of the hydroxyl group in the alpha-hydroxycarboxylates citrate, malate and lactate by ¹³C NMR: implications for metal coordination in biological systems».
- [19] Citric acid/C₆H₈O₇ - PubChem
- [20] Gougerot-Schwartz A. "Cosmétologie et dermatologie esthétique" Encyclopédie Méd. Chir. (2000) 7p.
- [21] Sammy Eric ANDRIAMBOLA «Valorisation de l'acide citrique en polymères et en sels de mono- di- et tri-ammonium». Mémoire de fin d'étude en vue de l'obtention du diplôme d'Ingénieur en Génie Chimique. E. S. P. A. Université d'Antananarivo. 2013.
- [22] M. Laffitte, F. Rouquerol La réaction chimique Tome 2. Aspects thermodynamiques (suite) et cinétiques, 1991, Eds. Masson p. 30.
- [23] Raharilaza Paulin Merix «Esterification entre les molécules d'acide citrique et les molécules organiques des graines de courges –hydrolyse et valorisations des esters comme additifs des hydrocarbures», Mémoire en vue de l'obtention du diplôme de licence en Génie des Procédés Chimiques et Industriels. ESPA – Université d'Antananarivo. 2018.
- [24] Rabeharitsara Andry Tahina, Raharilaza Paulin Merix, Randriana Richard Nambinina – Chemical Process Engineering Department (E.S.P.A), Antananarivo University – Madagascar – "Esterification Between Citric Acid and Pumpkin Pips' Organic Molecules – Esters Hydrolysis and Esters Used as Hydrocarbons Additives" - American Journal of Applied Chemistry in Vol. 6, Issue Number 3, June 2018.
- [25] Rabeharitsara Andry Tahina, Sedraniaina Domoina Marie Esperance, Ny Idealy Elite Randriamanantena, Raïssa Faneva Mampitefa, Nambinina Richard Randriana Esterification Between Citric Acid and Callistemon citrinus, Rice-Husk, Garcinia dulcis Catalysed by Citric Acid's-H⁺- Monomers and Polymers Formation Mechanism. American Journal of Applied Chemistry. Volume 8, Issue 2, April 2020, Pages: 31-54. Received: Mar. 25, 2020; Accepted: Apr. 10, 2020; Published: Apr. 28, 2020.
- [26] Rabeharitsara Andry Tahina, Jaochim Raherimandimby, Nambinina Richard Randriana, Trans-"Esterification Between Citric Acid and Peanut Oil at Low pH and Ambient Temperature Catalyzed by Citric Acid and Sulfuric Acid Protonic Acid-H⁺" American Journal of Applied Chemistry - Volume 8, Issue 4, August 2020, Pages: 100-116 Received: Jul. 12, 2020; Accepted: Jul. 25, 2020; Published: Aug. 13, 2020
- [27] Andry Tahina R., Behevitra R., Nambinina R. R. F., (2017), Pine Wood Powder Treatment to Obtain B_xH⁺ Homogeneous Catalyst (H⁺/H₂SO₄) Supported On Its Aromatics and Polynuclear Aromatics Alkenes – Application in Citric Acid Polymerization to Black Polymers (PN), American Journal of Polymer Science and Technology. Vol. 4, No. 1.
- [28] Advanced Chemistry Development ACD/Chem Sketch.
- [29] Sulfuric acid safety data sheet". Arkema-inc.com. Archived from the original on 17 June 2012. "Clear to turbid oily odorless liquid, colorless to slightly yellow." https://en.wikipedia.org/wiki/Sulfuric_acid#cite_note-ds-5
- [30] <http://lepapier.e-monsite.com/pages/la-composition-du-papier.html> (25.12.2020).
- [31] Anya Keefe et Kay Teschke «Les Principaux Secteurs Et Procédés Les Sources De Fibres Servant À La Fabrication De Pâte Et De Papier» <http://www.ilocis.org/fr/documents/ilo072.htm>
- [32] ISO 1629:2013(fr) Caoutchouc et latex — Nomenclature [archive].
- [33] Morton, Maurice (1987), Rubber Technology (3 ed.), Springer, ISBN 978-0-412-53950-3.

- [34] Vernadsky, George (January 1969), "Rise of Science in Russia 1700-1917", *The Russian Review*, 28 (1): 37–52, doi:10.2307/126984, JSTOR 126984.
- [35] Werner Obrecht, Jean-Pierre Lambert, Michael Happ, Christiane Oppenheimer-Stix, John Dunn, Ralf Krüger (2012). "Rubber, 4. Emulsion Rubber". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH. doi: 10.1002/14356007.o23_o01.
- [36] International Institute of Synthetic rubber Producers, Inc. (IISRP) article on S-SBR (retrieved 2011-12-02).
- [37] <https://lewebpedagogique.com/classesbilingueslpb/files/2018/06/Le%C3%A7on32.pdf> (24.12.2020)
- [38] Laura Dos Santos, Fleur Rol «Latex de PLA, une solution pour l'enduction des papiers?» - <http://cerig.pagora.grenoble-inp.fr/memoire/2015/latex-pla-papier.htm>
- [39] Gatien Géraud Essoua Essoua: «Développement d'une stratégie de modification du bois afin de limiter les variations dimensionnelles du produit lambris dans un contexte éco-responsable». Thèse en vue de l'obtention du Doctorat en sciences du bois, Philosophiae doctor (Ph.D.) – Université de Laval, Québec – Canada, 2016, 156p.
- [40] Jeremy Damay: «Développement de nouveaux traitements du bois basés sur le procédé d'imprégnation axiale». Thèse CIFRE portée par Initialité, Ingénierie et Territoire soutenue publiquement le 27 Novembre 2014 pour l'obtention du Doctorat de l'Université de Lorraine Ecole doctorale RP2E, spécialité Sciences du bois et des fibres, 317p.
- [41] M. Olivier Pignolet: «Optimisation de la durabilité de bois d'œuvre (classe d'emploi 4) à l'aide d'anhydrides alkényles succiniques d'origine végétale». Thèse en vue de l'obtention du Doctorat de l'Université de Toulouse, délivré par l'Institut National Polytechnique de Toulouse, discipline ou spécialité: Sciences des Agro-ressources.
- [42] Mohamed Jebrane: «Fonctionnalisation chimique du bois par Trans-estérification des esters d'énol». Thèse présentée à l'Université de Bordeaux I Ecole Doctorale des Sciences Chimiques, spécialité: chimie organique, 2009, 141p.
- [43] Raveloson Eddy Francis: «Modifications physico-chimiques du bois de pin par traitements avec les polymères d'acide citrique». Mémoire de fin d'études en vue de l'obtention du diplôme d'Ingénieur en Génie des Procédés Chimiques et Industriels. ESPA – Université d'Antananarivo.
- [44] Marcel Roubault, H. de la Roche, Alain Godard, P. Marchal: «Une méthode simple d'étude de la porosité des roches cristallines». *Revue Géographique de l'Est*. Année 1961/1-3/ pp. 223-233.
- [45] Marko Rasi: «Permeability properties of paper materials». Academic Dissertation for the Degree of Doctor of Philosophy. University of Jyväskylä. December 17, 2013.
- [46] Niskanen K. (Ed.), "Paper Physics", Papermaking Science and Technology, Book 16, Finnish Paper Engineers Association and TAPPI, Helsinki, Finland, 1998.
- [47] Dodson C. J. T. and Sampson W. W., "The Effect of Paper Formation and Grammage on its Pore Size Distribution", *Journal of Pulp and Paper Science*, 22 (5): 165, 1996.
- [48] WISUNTHORN PANSOOK Suwaluk «Etude De L'elaboration Par Sechage Controle Et Des Proprietes Fonctionnelles De Films A Base De Latex Naturel D'*Hevea brasiliensis*». Thèse de Doctorat. Université de Montpellier II. 20 Avril 2006.
- [49] Catherine Sarazin « Structure Des Protides: Acides A-Amines, Peptides, Protéines »
- [50] Michail A. Alterman; Peter Hunziker (2 December 2011). *Amino Acid Analysis: Methods and Protocols*. Humana Press. ISBN 978-1-61779-444-5.