

Research/Technical Note

Trans-Esterification Between Citric Acid and Peanut Oil at Low pH and Ambient Temperature Catalyzed by Citric Acid and Sulfuric Acid Protonic Acid-H⁺

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Abstract: The reason of this manuscript was to study the trans-esterification between the peanut oil and alcohol of citric acid molecules at ambient temperature with low pH and peanut oil was in excess in comparison with citric acid using two types of protonic acid-H⁺ catalyst such as the unattached protonic acid-H⁺ of reagent citric acid molecules at pH=1.66 with citric acid catalyst-unattached protonic acid-H⁺/peanut oil-fatty acids ratio [mol./mol.%]=1.21% and the unattached protonic acid-H⁺ of sulfuric acid molecules at pH=-3.76 with sulfuric acid catalyst-unattached protonic acid-H⁺/peanut oil-fatty acids ratio [mol./mol.%]=1.05%. Thus, biodiesel has been synthesized and basically characterized. Also, citric acid conversions evolutions with reaction-time and evaluation of reacted and unreacted peanut oil fatty-acids evolutions with reaction-time has been done following a protocol which allowed the quantification of the unreacted citric acid molecules. In the same time, the used protonic acid-H⁺ catalysts were characterized by their activities and turnovers evolutions. All these results helped the comprehension of the very probable mechanisms of this trans-esterification catalyzed by these protonic acids-H⁺. Particularly, it was noticed that the initial catalysts' activities and turnovers were all the time very important but decreased in a sizeable way from 1mn reaction-time until obtaining generally a yellow biodiesel after 60mn reaction-time. These results allowed to consider that at these previous experimental conditions, molecules steric size influenced the catalysts' activities and turnovers; and the first step was composed not only by the trans-esterification reaction between citric acid's alcohol organic function and peanut oil but also the dehydration of citric acid molecules to form the white citric acid monomer, it could be transformed to another great molecules like yellow citric acid monomer or to another more great molecules composed with new alkene-unsaturated organic function which concentration increased and/or decreased with reaction-time according to the protonic acid-H⁺ nature as molecules and influenced the color of biodiesel in this case yellow or imperial yellow. Indeed, it was noticed that even if all catalysts activities and turnovers decreased globally, the citric acid protonic acid-H⁺ catalyst became clearly more active than the sulfuric acid protonic acid-H⁺ catalyst with time certainly because of the decrease of its alkene -unsaturated organic function concentration with time and still confirmed the alkene-unsaturated organic function effects as efficient support for protonic acid-H⁺ catalyst mobility.

Keywords: Trans-Esterification, Peanut Oil, Catalyst, Citric Acid, Sulfuric Acid, Protonic Acid H⁺, Alkene, Biodiesel

1. Introduction

Firstly, characterizations of the peanut oil, the used protonic

acid-H⁺ catalysts and the experimental conditions were done. Then, the trans-esterification reactions between citric acid's alcohol organic function and peanut-oil at ambient temperature was followed with time such as two protocols were established

to quantify the unreacted citric acid molecules, a protocol for experimentations using sulfuric acid protonic acid-H⁺ catalyst and another protocol for experimentations using the unattached protonic acid-H⁺ of reagent citric acid molecules at low pH as catalyst. A clear layer of biodiesel was obtained above and not much samples were held delicately to be characterized basically. Then, citric acid concentration evolutions according to reaction-time was followed to determine the citric acid partial order, the global observed speed constants and global acid speed constants at pH=1.66 (for unattached citric acid protonic acid-H⁺ catalyst) and pH=3.76 (for sulfuric acid protonic acid-H⁺ catalyst). Also, to confirm the white monomer formation freely soluble in water and/or their transformations according to the protonic acid-H⁺ catalysts nature; the biodiesel molecules volume soluble in the distilled water used during the previous protocols were recorded, followed and studied. Finally, results interpretations allowed to suggest a very probably global mechanisms during trans-esterification between citric acid's alcohol organic function and peanut oil catalyzed by these two types of protonic acid-H⁺.

2. Trans-Esterification Between Alcohol Organic Functions of Citric Acid Molecules and Peanut Oil Catalyzed by Protonic Acid-H⁺

2.1. Citric Acid Generalities

Citric acid C₆H₈O₇ is a tricarboxylic acid α- hydrolyzed. It

contains three acids with pKa such as pKa₁ = 3.1 pKa₂ = 4.77 and pKa₃ = 6.39 and a α-alcohol function with pKa = 14.4 [1-3] "Figure 1". By its reactivity, the citric acid and its derivate like black citric acid polymer (PN) were the objects of several studies and was used in several fields like the cosmetics, the food one, the chemistry [4-9] and others like valorization of by-products after esterification with citric acid [9]. Noticed that the acid form is AH with pKa (AH). It was shown that if the pH ≤ [pKa (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 ≥ [pKa (AH) + 2], the quantity of acid AH associated to the acid/base couple AH/A⁻ is negligible in comparison with the A⁻ quantity [10]. For [pKa (AH) - 2] ≤ pH ≤ [pKa (AH) + 2], the basic A⁻ and the acid AH forms coexist but if [pKa (AH) - 2] ≤ pH ≤ pKa (AH) the acid form AH dominate and if pKa (AH) ≤ pH ≤ [pKa (AH) + 2] the basic form A⁻ dominate [6]. Consequently, for the citric acid we noted in the following Table 1 the acids and basics forms according to the pKa and pH:

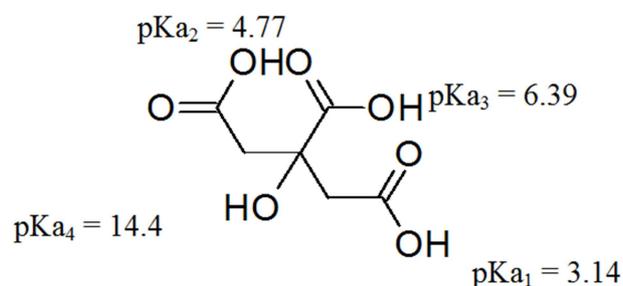


Figure 1. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid).

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 ≤ 3.14	AH ₃ /AH ₂ ⁻	3.14	AH ₃ ⇌ AH ₂ ⁻ + H ⁺	AH ₃	Citric Acid
3.14 ≤ pH ≤ 4.77	AH ₂ ⁻ /AH ²⁻	4.77	AH ₂ ⁻ ⇌ AH ²⁻ + H ⁺	AH ₂ ⁻	Di-Hydrogenocitrate
4.77 ≤ pH ≤ 6.39	AH ²⁻ /A ³⁻	6.39	AH ²⁻ ⇌ A ³⁻ + H ⁺	AH ²⁻	Mono-Hydrogenocitrate
6.39 ≤ pH	AH ²⁻ /A ³⁻	6.39	AH ²⁻ ⇌ A ³⁻ + H ⁺	A ³⁻	Citrate

During all experimentations, monohydrated citric acid solid with monoclinic as crystal structure, white, odorless and excessively sour flavor was used (Table 2) [3]. Indeed, citric acid exists in hydrates forms, the monohydrate melts towards 343.15°K and the anhydrous state melting point is 426.15°K.

Citric acid is soluble in alcohol, either, ethyl acetate and DMSO and insoluble in C₆H₆, CHCl₃, CS₂, and toluene. Its solubility in ethanol at 298.15°K is 62g/100g. Citric acid is very soluble in water and its solubility increases with the temperature as shown the following table (Table 3) [11].

Table 2. Citric acid physicochemical properties.

Physicochemical Properties	CITRIC ACID - C ₆ H ₈ O ₇
Appearance	Crystalline white solid
Crystal structure	Monoclinic
Molar mass	192.12 [g.mol ⁻¹]
Density	1.665 [g.cm ⁻³] anhydrous - 1.542 [g.cm ⁻³] monohydrate at 291.15°K
Melting point	426.15°K anhydrous - 343.15°K monohydrate
Boiling point	448.15°K
Solubility in ethanol	62g/100g
Solubility in water	59.20% at 293.15°K (Table 3)
Refractive Index	1.493–1.509 (20 °C) 1.46 (150 °C)

Table 3. Evolution of the citric acid solubility in water (w/w) following to the temperature (°K).

T°K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
Solubility (% g/100mg)	54.0	59.2	64.3	68.6	70.9	73.5	76.2	78.8	81.4	84.0

Noticed that citric acid molecules could be subjected to some transformations to form another products [5, 9, 12] like citraconic acid which refractive index was slightly fewer 1.4502 [13].

2.2. Peanut Oil Generalities

2.2.1. Peanut Oil Characteristics and Compositions

Generally, peanut oil, also called arachis oil or groundnut oil was oil extracted by peanut seeds using either mechanical pressing unit which may be conducted in hydraulic presses driven by fluid pressure [14, 15] or in screw presses [14, 16, 17] either chemical methods such as solvent extraction [14], extraction using enzymes [18] or extraction using esterification reaction with citric acid molecules [8] even if actually other methods can be used such as steam distillation [19] and supercritical fluid extraction (SFE) [16, 20]. Peanut oil was used in cuisine, used to make soap by process of saponification, used as massage oil but also it could be used as a source of fuel for the diesel engine generally by trans-esterification with alcohol [21]. The peanut oil major component fatty acids are oleic acid (46.80% as olein), linoleic acid (33.40% as linolein) and palmitic acid (10.00% as palmitin). It also contains stearic acid, arachidic acid, behenic acid, lignoceric acid and other fatty acids [22]. All oils or fats could be characterized by their own smoke point also referred to their burning point which is the temperature they began to produce a continuous bluish smoke that becomes clearly visible dependent upon specific and defined conditions [23] such as the volume of oil utilized, the size of the container, the presence of air currents, the type and source of light and/or heat as well as the quality of the oil and its acidity content, otherwise known as free fatty acid (FFA) content [24]. The more the FFA and oil contains, the quicker it will break down and start smoking [24, 25]. In otherwise, the lower in FFA, the higher the smoke point [26]. It's important to consider, however, that the FFA only represents typically less than 1% of the total oil and consequently renders smoke point a poor indicator of the capacity of fat or oil to withstand heat [26-28]. Other oils and fats characteristics are also fire points, flash points [23], refractive index. Indeed, it was established a correlation between peanuts refractive index, peanuts oleic acid rate and peanuts linoleic acid rate such as increasing concentrations of oleic acid and corresponding of decreases in

linoleic acid were associated with decreasing oil density, decreasing refractive index, and increasing viscosity [29].

2.2.2. Malagasy Peanuts Oil Characteristics and Compositions

The following table 4 showed the Malagasy peanuts compositions. These peanuts was cultivated at the district of Mandritsara (SOFIA region) located at the north-west of Madagascar and belongs to *Arachis hypogaea* species. Its local name and variety is "voanjo-tsinefo" or "petit espagnol". Their oil used during transesterification reactions experimentations described on this manuscript was extracted by a mechanical pressing unit. The components of this peanuts-oil were characterized at LCP^[*] laboratory (*Laboratoire de Contrôle des Pesticides*) located at Nanisana-Antananarivo using a gas chromatography instrument (CPG) according to the norm *NF ISO 3961 (1996)*.

Table 4. Malagasy peanuts oil fatty acid components,

Fatty acid components	wt/wt (%) ^[*]	Mol/mol (%)
Palmitic acid (saturated)	12.12	13.20
Stearic acid (saturated)	03.59	03.53
Arachidic acid (saturated)	01.40	01.25
Behenic acid (saturated)	00.46	00.38
Erucastic acid (mono-unsaturated) C20:1 w-9	01.30	01.17
Oleic acid (mono-unsaturated) 18:1 w-9 (cis)	58.80	58.15
Palmitoleic acid (mono-unsaturated) w-7	00.74	00.81
Linoleic acid (poly-unsaturated) C18:2 w-6	21.44	21.36
Alpha-linoleic acid ALA (poly-unsaturated) C18:3 w-3	00.15	00.15
Oleic/Linoleic ratios	2.74	2.72

Also, some characteristics of the used peanuts oil were represented in the following table 5. The smoke point and the auto-inflammation point representative of the fire point and viscosity of peanut oil given by bibliographies were shown in the following table 5 [30-33]. According to these characteristics (Table 5), this is a high quality peanut oil slightly oxidized [29].

Table 5. Malagasy peanuts oil characteristics,

Characteristics	Values	Bibliographic values [min, max]
Density [g/ml]	0.9114	[0.917-0.921]
Saponification index	191.50	[188-195]
Molar mass [g/mol]	292.43	Oleic acid molar mass-282.47 Linoleic acid molar mass-280.4472
Refractive index [20°C]	1.4732*/1.4743	[1.4700-1.4717-1.4800] [29]
Smoke point [°K]		[433.15*]*unrefined [500.37-502.59] *refined
Auto-inflammation point [°K]		[615.15-636.15-644.15]
Viscosity [Pa.s]		0.06 ≈ 0.1 à 22.5°C

*Refractive index at 22.5°C / refractive index at 20°C.

2.3. Trans-Esterification Between Alcohol Organic Function of Citric Acid Molecules and Malagasy Peanut Oil Catalyzed by Protonic Acid- H^+

2.3.1. General Mechanism of Trans-esterification Catalyzed by Protonic Acid- H^+ Homogeneous Catalysts

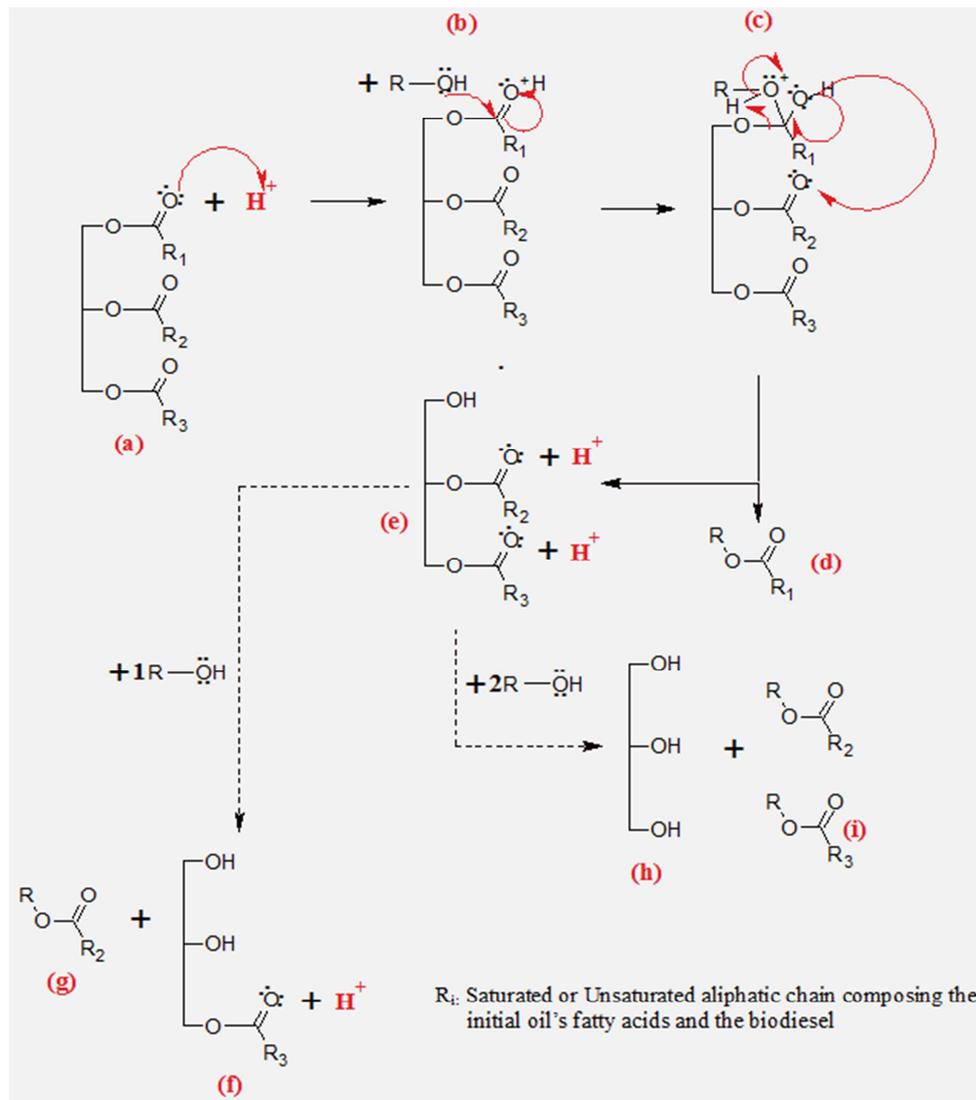


Figure 2. General mechanism of trans-esterification catalyzed by protonic acid- H^+ homogeneous catalysts.

Firstly, the catalyst's protonic acid H^+ was attracted by the electron pair of oil's oxygen [34, 35], localized at its end of chain (figure 2(a)), to form an instable intermediary ions product (figure 2(b)) which conducted to a stable tertiary carbocation (figure 2(c)). Then, this stable tertiary carbocation could be attracted by the electron pair of the alcohol's oxygen to form another second instable intermediary ions product (figure 2(c)) which incurred rearrangement to form the first product composed with oil such as its end of chain became alcohol function (figure 2(e)) and an ester formed with an acid's oil and an alcohol's alkyl function composing the bio-ester solution (figure 2(d)) with catalyst's protonic acid H^+ regeneration. Secondly, either this same regenerated protonic acid H^+ , or another catalyst's protonic acid H^+ activated the second electron pair of oil's oxygen localized at its end of chain (figure 2(e)) and following the same mechanism as the

first electron pair oil's oxygen to form the second product composed with oil such as its two ends of chain became alcohol functions (figure 2(f)) and another second ester formed with the second acid's oil and one another alcohol's alkyl function composing the bio-ester solution (figure 2(g)) with catalyst's protonic acid H^+ regeneration. Finally and the third, either these same regenerated protonic acid H^+ , or another catalyst's protonic acid H^+ activated the third electron pair of oil's oxygen localized at its end of chain (figure 2(f)) and following the same mechanism as the first and second electron pair oil's oxygen to form the third product composed with glycerol (figure 2(h)) and another third ester formed with the third acid's oil and one alcohol's alkyl function composing the bio-ester solution (figure 2(i)) with catalyst's protonic acid H^+ regeneration.

2.3.2. Trans-esterification Between Citric Acid's alcohol and Peanut Oil Experimental Conditions Catalyzed by Citric Acid and Sulfuric Acid Protonic Acid-H⁺

As said previously, the aim of the experimentations on this manuscript was to use the citric acid's alcohol function in trans-esterification reaction seeing that citric acid and its derivatives such as citric acid's esters [8, 37-39] and black citric acid polymers-pn [7] were showed to be used as additives in different domains especially for diesel and fueloil [7, 37-38].

Also, it was established that during esterification with raw materials citric acid was not only a reactant but also a catalyst using its citric acid protonic-H⁺ supported on alkene functions of grinded raw materials [9], like H⁺/H₂SO₄ supported on pinewood's alkene function [12]. [8] It was important to notice that initial C= moles ([8] - table 6) corresponded to the initial total peanut-oil's fatty-acid alkene-unsaturated moles quantities.

Table 6. Experimental conditions for each used catalysts,

Experimental Conditions	Used catalysts	
	Citric acid protonic acid-H ⁺	Sulfuric acid protonic acid-H ⁺
Temperature [°K]	Ambient ~ 22.5 [°K]	Ambient ~ 22.5 [°K]
Catalyst weight [g]	9.754	0.1799
Peanut-oil volume [ml]	28	28
Peanut-oil weight [g]	25.5192	25.5192
Catalyst and-or reagent/Peanut-oil [wt./wt.%]	38.22	0.7050
Peanut-oil fatty-acids [moles]	0.08727	0.08727
Citric acid weight- source of -OH function for trans-esterification reaction [g]	9.7540	9.7540
Citric acid moles - source of -OH function for trans-esterification reaction [moles]	0.0508	0.0508
fatty acid/citric acid (Moles ratio)	1.7188486	1.7188486
Calculated pH - [35]	1.66	-3.76
H ⁺ - amounts [Moles]	0.0010583	0.0009172
Catalyst-H ⁺ /fatty acid [mol./mol.%]	1.21	1.05
Initial C ⁻ moles [Moles] [8]	0.09015	0.09015
[H ⁺] [Mol.l ⁻¹] - [9]	0.037796	0.032756291
[C ⁻] [Mol.l ⁻¹] - [9]	3.2195	3.2195
Dispersion [%]- [9]	0.0117 - 1.17%	0.0102 - 1.02%

2.3.3. Trans-esterification Between Alcohol Organic Function of Citric Acid Molecules and Peanut Oil Procedure Until Conversion Determination

Two different catalysts were used during experimentations so there were two different procedures to conduct the trans-esterification reactions until conversion determination such as procedure with citric acid-H⁺ catalyst and another procedure with sulfuric acid catalyst.

(i) Trans-esterification Between Citric Acid's Alcohol and Peanut Oil Catalyzed by Citric Acid-H⁺ Procedure Until Unreacted Citric Acid Titration

Take the peanut-oil volume used to the trans-esterification reaction in a beaker-250 [ml] where a clean stirring rod was putted and all assembly was placed on a magnetic stirrer such as its rotation was adjusted at 4-position, maximally 5. Then, weigh the used equivalent citric acid according to the experimental conditions of trans-esterification reactions catalyzed by citric acid protonic acid-H⁺ (Table 6). Put on the magnetic stirrer and when the stirring rod rotation was constant, add instantly the used citric acid and the beginning of the trans-esterification reaction was recorded with a chronometer. When the programmed reaction-time was completed, stop the magnetic stirrer, take the beaker-250 [ml] out of it to be putted on a container with a few ice cubes to lock the trans-esterification reaction and decantation. Indeed, a clear layer of biodiesel was obtained above and not much samples were hold delicately to be characterized basically, then add firstly an amount of cold distilled water in the beaker-250 [ml] to dissolve inter alia glycerol and the remains

of unreacted-citric acid molecules and transfer the content of the beaker-250 [ml] into a separating funnel. Generally, during these trans-esterification experimental conditions, 35 [ml] of cold distilled water were totally used on average. So, the second amount of this cold distilled water were used to wash out maximally the beaker in such a way that its content were totally transferred into the separating funnel. Thereafter, add into the separating funnel a cold hexane obtained by putting it into a refrigerator to lock reactions. Basically, the cold hexane volume amount was chosen in such a way that the hexane-molecules moles were five times more superior than the estimated fatty-acids moles and the cold distilled water moles were eleven times more superior than the citric acid molecules moles. However, sometimes the hexane amount was divided by two and the water amount was slightly added for efficiency's sake. Decant the obtained heterogeneous solution in the separating funnel during fifteen-15 minutes minimum and three-3 hours maximum. Indeed, experimentations showed that fifteen-15 minutes settling duration was as efficient as three-3 hours settling duration to recover the same amount of unreacted citric acid molecules by following the procedure described previously. At the end of the decantation, two heterogeneous phases were obtained, an organic phase above including inter alia biodiesel with eventually a few non-transformed intermediate products as glycerol derivatives (e) and/or (f) (figure 2) whose volume was recorded, an aqueous phase below including inter alia glycerol, unreacted citric acid molecules with eventually a few non-transformed intermediate products as glycerol derivatives (e)-certainly very few and probably (f) (figure 2). Recover the

aqueous phase below with taking care to register its total volume. Finally, proceed to its unreacted citric acid molecules titration according to the same procedure described on bibliography [12-§8.2.] with taking care to the first variation of to be titrated solution color.

(ii) *Trans-esterification Between Citric Acid's Alcohol and Peanut Oil Catalyzed by Sulfuric Acid-H⁺ Procedure Until Unreacted Citric Acid Titration*

Take the peanut-oil volume used to the trans-esterification reaction in a beaker-250 [ml] where a clean stirring rod was putted and all assembly was placed on a magnetic stirrer such as its rotation was adjusted at 4-position, maximally 5. Then, weigh the used equivalent citric acid according to the experimental conditions of trans-esterification reactions catalyzed by supported or non-supported sulfuric acid protonic acid-H⁺ (Table 6). Put on the magnetic stirrer and when the stirring rod rotation was constant, add instantly firstly the sulfuric acid drop (according to the experimental conditions-table 6) and secondly the used citric acid, in the same time the beginning of the trans-esterification reaction was recorded with a chronometer. When the programmed reaction-time was completed, stop the magnetic stirrer, take the beaker-250 [ml] out of it to be putted on a container with a few ice cubes to lock the trans-esterification reaction and decantation. Indeed, a clear layer of biodiesel was obtained above and not much samples were hold delicately to be characterized basically, then add firstly an amount of cold distilled water in the beaker-250 [ml] to dissolve inter alia glycerol, the remains of unreacted-citric acid molecules and supported or non-supported sulfuric acid catalyst, then transfer the content of the beaker-250 [ml] into a separating funnel. Generally, during these trans-esterification experimental conditions, 35 [ml] of cold distilled water were totally used on average. So, the second amount of this cold distilled water were used to wash out maximally the beaker in such a way that its content were totally transferred into the separating funnel. Thereafter, add into the separating funnel a cold hexane obtained by putting it into a refrigerator to lock reactions. Basically, the cold hexane volume amount was chosen in such a way that the hexane-molecules moles were five times more superior than the estimated fatty-acids moles and the cold distilled water moles were eleven times more superior than the citric acid molecules moles. Decant the

obtained heterogeneous solution in the separating funnel during fifteen-15 minutes minimum and three-3 hours maximum. Indeed, experimentations showed that fifteen-15 minutes settling duration was as efficient as three-3 hours settling duration to recover the same amount of unreacted citric acid molecules and also supported or non-supported sulfuric acid catalyst by following the procedure described previously. At the end of the decantation, two heterogeneous phases were obtained, an organic phase above including inter alia biodiesel with eventually a few non-transformed intermediate products as glycerol derivatives (e) and/or (f) (figure 2) whose volume was recorded, an aqueous phase below including inter alia glycerol, supported or non-supported sulfuric acid catalyst, unreacted citric acid molecules with eventually a few non-transformed intermediate products as glycerol derivatives (e)-certainly very few and probably (f) (figure 2). Recover the aqueous phase below with registering eventually its total volume and transfer it again to a separating funnel with adding dichloromethane such as dichloromethane volume amount was chosen in such a way that the dichloromethane moles were five-5 times and minimally 2.5-times more superior than the initial citric acid moles. Decant the heterogeneous solution during fifteen-15 minutes until obtaining two phases, an organic phase below containing dichloromethane and unreacted citric acid molecules, an aqueous phase above containing supported or non-supported sulfuric acid catalyst. Recover the organic phase with taking care to record its total volume. Finally, proceed to its unreacted citric acid molecules titration according to the same procedure described on bibliography [12-§8.3.] with taking care to the first variation of to be titrated solution color.

3. Catalyzed Trans-Esterification Between Citric Acid's Alcohol And Peanut Oil Global Results

3.1. Citric Acid Conversions Evolution in Terms of Time

These following tables table 7, table 8 and table 9 continue showed all global results of citric acid conversions evolution in terms of time, biodiesel characteristics like viscosities-densities-refractive index-colors which conducted to elaborate and confirmed the trans-esterification mechanism for each experimental conditions.

Table 7. Global results of peanut-oil trans-esterification with citric acid's alcohol function

Used catalysts	Global results of peanut-oil trans-esterification with citric acid's alcohol function				
	Time [mn]	Citric acid conversion [%]	Biodiesel density [g/ml]	Biodiesel refractive index	Colors
Citric acid	1	27.80	-	1.4565	Imperial yellow
protonic acid-H ⁺	5	31.42	0.90625	1.4565	Imperial yellow
	60	36.87	0.90625	1.4550	Imperial yellow
Sulfuric acid	1	35.42	0.8068	1.4550	light yellow
protonic acid-H ⁺	5	37.26	0.8503	1.4550	light yellow
	60	39.98	0.8460	1.4550	light yellow

Bibliographies indicated that the kinematic viscosity of biodiesel at 313 °K (39.85°C) were generally between 3.5 [cS] to 5.5 [cS] [40]; between 1.9 [cS] to 6 [cS]-D445/EN ISO

3104 [41, 42]. The maximum kinematic viscosity value 6 [cS] is equivalent to 5.28E-3 [kg/(m.s)] i.e 5.28E-3 [Pa.s] dynamic viscosity. Noticed that the obtained biodiesel dynamic

viscosities were certainly largely superior to the acceptable maximum value of general-standard biodiesel viscosity and 1.6 [cS] to 5.9 [cS] for diesel [40] because of the synthesized biodiesel using citric acid protonic acid- H^+ catalyst viscosity determined by simple laboratory experimentation was 0.30603 [Pa.s]. These results confirmed that the trans-esterification reaction between citric acid's alcohol functions and peanuts oil fatty acids, leading to the citric acid-biodiesel, occurred according to the mechanism described on paragraph §2.3.1. – figure 2 with formations of great esters molecules, composed minimally of basic-citric acid molecule with aliphatic's peanuts oil fatty acids (figure 3/[a-i]), than the general-standard trans-esterification reaction using oil fatty acids and methanol as reagents seeing that eventually citric acid auto-esterification [43] (figure 2) accompanied eventually by decarboxylation according to mechanism showed on bibliography [9] (figure 5) and eventually citric acid auto-polymerization catalyzed by protonic acid- H^+ could occur beside on alkene function (figure 5-b) formed by decarboxylation [9, 12]. In the figure 3-a, noticed that the product (a) was obtained by esterification between two citric acid molecules such as the most and probable carbonic acid $-COOH$ activated by protonic acid- H^+

of catalyst was its which had the high pKa than the others (figure 3-a'); then a relative stability was established between these two citric acid molecules by hydrogen bond ($=O$; $HOOC-$) (figure 3-e) because there could be a dehydration conducting to the product (h) (figure 3-h) following the mechanism described on the figure 3-e. The stability of these products (g)-(h)-(i) was given on the figure 4. Thereafter, decarboxylation could occur on the red carboxylic acids of figure 3-g, figure 3-h and figure 3-i following a mechanism described on bibliography [9-p11-§3.2.1.-figure 13] with formation of hydrogen and formation of alkene function on the α -position of each red carboxylic acids (figure 3) as shown on the figure 5-a. The stability of these alkene products was given on the figure 5-b. In all cases, bibliography said that the dynamic viscosity of biodiesel potentials and lubricating properties of *Citrus sinensis* Seed Oil range was between 0.46546 [Pa.s] to 0.34702 [Pa.s] [44] which were slightly superior than these citric acid-biodiesel (table 7) synthesized by peanut-oil trans-esterification with citric acid's alcohol function biodiesel viscosities and confirmed the formation of great esters molecules (figure 3) and their derivatives (figure 4 - figure 5).

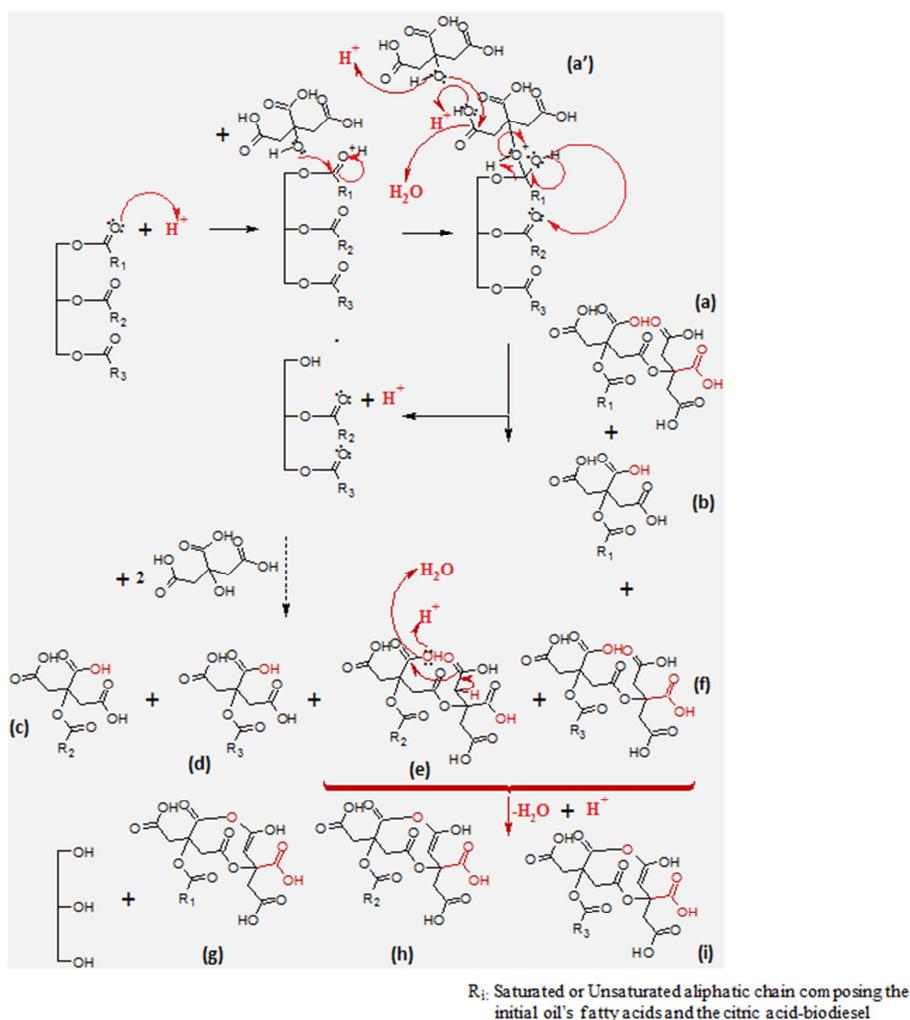


Figure 3. General mechanism of trans-esterification between fatty acids and citric acid's alcohol organic function accompanied by citric acid auto-esterification catalyzed by protonic acid- H^+ homogeneous catalysts.

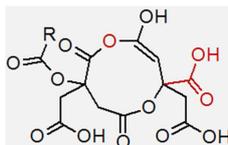


Figure 4. Stability of the products (g), (h) and (i) given by the structure drawing software for academic ACD/ChemSketch.

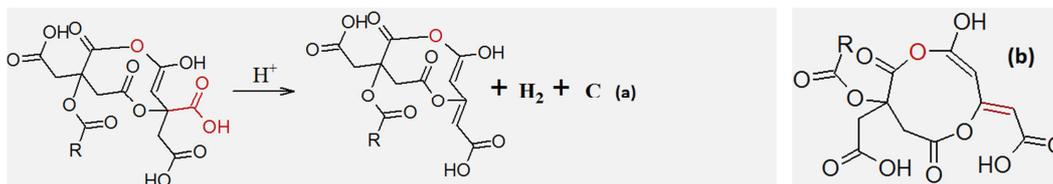


Figure 5. Decarboxylation of the first trans-esterification products between citric acid molecules and oils' fatty-acids (figure 3).

Finally, noticed that polymerization could occurred on each alkene functions formed (figure 5-b) and other alkene functions formed during trans-esterification reactions [5, 12]. But, the aim and experimental conditions of this publication stay to biodiesel synthesis by trans-esterification between oils like peanut oil and alcohol's citric acid molecules and it will be another project.

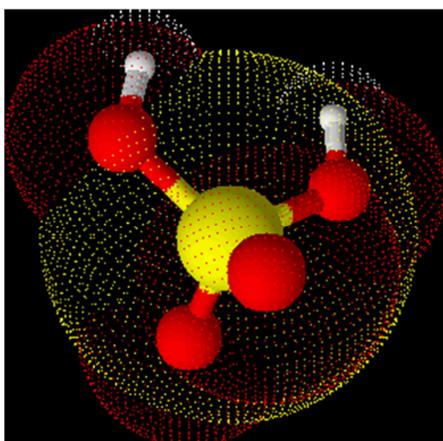


Figure 6. Sulfuric acid molecule structure given by the structure drawing software for academic ACD/ChemSketch.

Then, noticed that generally the total conversion of initial citric acid molecules after one hour of reaction didn't exceed 50% (table 7). These results allowed to confirm that there was another reactions parallel of trans-esterification reaction which transformed the initial citric acid molecules to a product freely soluble in water and titrated with the unreacted citric acid molecules residues. This product was without a doubt the (2Z)-but-ene-1,2,4-tricarboxylic acid which was obtained by citric acid dehydration catalyzed by protonic acid-H⁺ [12] and induced the diminution of the citric acid-biodiesel from 1.4732 (Table 5-Malagasy peanuts oil) to 1.4556 probably the refractive index of the (2Z)-but-ene-1,2,4-tricarboxylic acid not far from of the citraconic acid's refractive index equals to 1.4502. In addition to that, the obtained results of citric acid-biodiesel (table 7) such as decreasing refractive index, decreasing oil density and increasing viscosity compared to the initial peanut oil raw material characteristics confirmed its high quality with increasing concentrations of oleic acid

corresponding of decreases in linoleic [29] and the presence of high oxygenated great molecules as described on the previous paragraphs and figures (figure 3 to figure 5) which contribute to improve the auto-inflammation temperature [6, 7] of the citric acid-biodiesel synthesized. In otherwise, it can be deduced that the first steps of citric acid trans-esterification with oils were composed generally of the trans-esterification reaction between citric acid's alcohol function and oils' fatty-acids reaction in parallel with dehydration of citric acid molecules reaction to form the (2Z)-but-ene-1,2,4-tricarboxylic acid freely soluble in water. Thus, in all cases this second reaction (dehydration of citric acid molecules reaction to form the (2Z)-but-ene-1,2,4-tricarboxylic acid) was followed by the (2Z)-but-ene-1,2,4-tricarboxylic acid dismutation catalyzed by protonic acid H⁺, as described on bibliography during citric acid molecules polymerization [5, 12], to form the yellow monomers molecules [5, 12] responsible and form the basis of yellow color of citric acid-biodiesel (table 7). But, noticed that there was a slight difference according to used catalyst such as the citric acid-biodiesel catalyzed by citric acid's protonic acid-H⁺ had slightly dark yellow color like imperial yellow when the citric acid-biodiesel catalyzed by sulfuric acid's protonic acid-H⁺ had slightly light yellow color (table 7). Indeed, the sulfuric acid sizes [molar volume=44.5±3cm³-maximum Internuclear distance (H6-O1)= 3.293Å] and its structure (figure 6) allowed to high mobility on alkene functions and increase their activities [9, 12] to the realization of the first steps reactions, trans-esterification and citric acid dehydration with low density 0.8068 [g/ml] lightly yellow color of citric acid-biodiesel oil, to the detriment of decarboxylation and polymerization during the first 60 minutes at ambient temperature. While, the citric acid sizes [molar volume =109.7±3cm³-maximum Internuclear distance (H16-H21) =7.81Å] which were respectively 2.5 times and 2.4 times higher and its structure sterically bulky (figure 7) promoted not only the first steps reactions, trans-esterification and citric acid dehydration, but also decarboxylation [9-p11-§3.2.1.-figure 13] and eventually alkene-polymerization (§3.1.-figure5 -new project) during the first 60 minutes at ambient temperature with high density

0.90625 [g/ml] imperial yellow coloration of citric acid-biodiesel oil as described on figure 3 to figure 5.

Table 8. Global results of peanut-oil trans-esterification with citric acid's alcohol using

Global results of peanut-oil trans-esterification with citric acid's alcohol function								
Used catalysts	Time [mn]	Evaluated unreacted Fatty-acids [moles] (a)	Evaluated Fatty acids difference between initial and at instant i (b)	Evaluated reacted fatty acid in each interval time (c)	Evaluated biodiesel total weight [g] (d)	Evaluated biodiesel total volume [ml]=f (densité) (e)	Evaluated reacted fatty-acid concentration evolution in biodiesel synthesized for each interval time [mol.l ⁻¹] (f)	Cumulated reacted fatty acid concentration [mol.l ⁻¹]
Citric acid	1	0.07315	0.01411	0.01411	6.58435	7.26549	1.94245	1.94245
protonic acid-H ⁺	5	0.07131	0.01595	1.8394E-3	7.44257	8.21249	0.22399	3.66091
	60	0.06855	0.01872	2.7649E-3	8.73253	9.63589	0.28694	5.06258
Sulfuric acid	1	0.06929	0.01798	0.01798	8.38906	10.39794	1.72929	1.72929
protonic acid-H ⁺	5	0.06835	0.01892	9.375E-4	8.82649	10.38044	0.09031	3.55472
	60	0.06696	0.02030	1.3853E-3	9.47292	10.88808	0.12373	5.10869

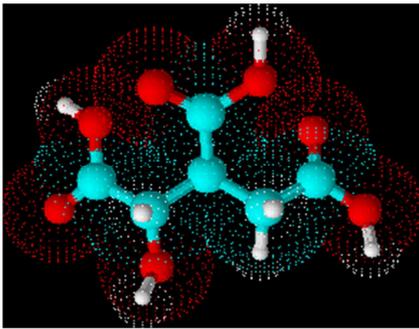


Figure 7. Citric acid molecule structure given by the structure drawing software for academic ACD/ChemSketch.

Evaluated unreacted fatty-acids (a) was the moles quantities of equivalent fatty-acids which didn't reacted and deduced by the rest of citric acid assuming that first the used oil was a pure triglyceride, assuming also that each mole of fatty-acid could react with one mole of citric acid and assuming finally that the citric acid dismutation was negligible. Thus, the initial total moles of equivalent pure fatty-acids was estimated by the weight of the used oil divided to the equivalent molar mass of its equivalent pure fatty-acid assuming that the used oil was composed with equivalent pure triglyceride such as its equivalent fatty-acids molar mass was deduced by its saponification index using the theoretical formula:

$$M (\text{equivalent pure fatty}_{\text{acid}} \text{ of used } - \text{oil molar mass}) = \left(\frac{56}{\text{used-oil saponification index}} \right) \times 1000 = 292.43$$

Indeed, noticed that

$$M_{\text{equivalent pure triglyceride}} \left[\frac{\text{g}}{\text{mol}} \right] = (3 \times (M_{\text{equivalent pure fatty-acid}} - 1)) + (3 \times M_{\text{Carbone}}) + (5 \times M_{\text{Hydrogen}})$$

And,

$$n_{\text{equivalent pure triglyceride}} [\text{moles}] = \frac{m_{\text{used-oil}}}{M_{\text{equivalent pure triglyceride}}}$$

And

$$n_{\text{equivalent pure fatty-acid}} [\text{moles}] = 3 \times n_{\text{equivalent pure trygliceride}} = \frac{3 \times m_{\text{used-oil}}}{M_{\text{equivalent pure trygliceride}}}$$

Now, noticed that in all the cases,

$$(3 \times M_{\text{equivalent pure fatty-acid}}) \gg (3 \times M_{\text{Carbone}}) + (5 \times M_{\text{Hydrogen}}) - 3$$

Finally,

$$n_{\text{equivalent pure fatty-acid}} [\text{moles}] = \frac{3 \times m_{\text{used-oil}}}{3 \times M_{\text{equivalent pure trygliceride}}} = \frac{m_{\text{used-oil}}}{M_{\text{equivalent pure trygliceride}}}$$

as said previously

So,

$$(a - \text{Table } 8b) = (\text{initial moles of equivalent fattyacids} - \left(\begin{array}{l} \text{initial moles of citric acid} \\ \text{-corrigned unreacted citric acid*} \end{array} \right))$$

*This value was deduced by NaOH-0.05N titration [8]

Noticed that for all catalysts, the unreacted fatty-acids

values decreased with reaction time and initially between 0 minute and 1 minute this diminution was very important (from

0,0872666 to around 0.07 that was ten twice more important than between 1 minute to 5 minutes reaction duration).

But for the sulfuric acid protonic acid-H⁺ catalyst the initial reacted fatty-acids value was 1.27 twice more important than for the citric acid protonic acid-H⁺ catalyst. Between 1 minute to 5 minutes this tendency reversed ((b)-Table 8), for the citric acid protonic acid-H⁺ catalyst, the evaluated reacted fatty-acids value became 1.96 twice more important than for the sulfuric acid protonic acid-H⁺ catalyst ((c) 1.8394E-3 > 2.7649E-4 - table 8) and these tendencies were confirmed by the evaluated reacted fatty-acid concentration evolution in biodiesel synthesized for each interval time such as between 1 minute and 5 minutes this concentration value for the citric acid protonic acid-H⁺ catalyst was 2.48 twice more important than for the sulfuric acid protonic acid-H⁺ catalyst ((f) 0,22399 > 0.09031 - table 8). These results confirmed the influence of citric acid-reagent structure, the influence of catalysts structures as molecules, the influence of the equivalent dispersion of each catalyst's protonic-acid H⁺ on alkene functions (§3.3.) and consequently the different mechanisms described previously. Indeed, bibliographies [9, 12] showed that catalysts activities increased with their dispersions on alkene organic functions present during reactions seeing that citric acid protonic acid-H⁺ catalyst's dispersion was 1.17 slightly superior than sulfuric acid protonic acid-H⁺ dispersion equals to 1.02 (table 6).

Thus, the evaluated reacted fatty-acid concentration evolution in biodiesel synthesized for each interval increased constantly from 0.22 [mol.l⁻¹]-5minutes to 0.29 [mol.l⁻¹]-60minutes for the citric acid protonic acid-H⁺

catalyst that is to say the trans-esterification reactions continued and increased in activity even if the fatty-acids in solution decreased. It was certainly caused by the formation of other alkene functions like (a)-figure 5 which supported the citric acid protonic acid's-H⁺ catalyst dispersion during first products of trans-esterification by citric acids transformations (figure 3 – figure 4 – figure 5) described previously. That wasn't the case for the trans-esterification catalyzed by the sulfuric acid protonic acid-H⁺ such as the evaluated reacted fatty-acid concentration evolution in biodiesel synthesized for each interval time increased very slowly from 0.09 [mol.l⁻¹]-5minutes to 0.12 [mol.l⁻¹] - 60minutes and confirmed the mechanism of the trans-esterification catalyzed by the sulfuric acid protonic acid-H⁺ catalyst where citric acid dehydration was the first important reaction step in parallel with the trans-esterification.

Also, these previous results confirmed the formation of citric acid derivatives molecules obtained by dehydration and/or decarboxylation as described previously with alkene organic functions (figure 3 to figure 5) and eventually their equivalent hydrogenated forms these products on figure 8 – figure 9 – figure 10 with citric acid protonic acid-H⁺ catalyst [9-p11-§3.2.1.-figure 13] allowing to an increase of the alkene-unsaturated moles-concentration in reaction-solution in comparison to its initial total peanut-oil's fatty-acid alkene-unsaturated moles quantities (^[*] - table 6) with time and eventually the general diminution of biodiesel refractive index to a value in the neighbor of citraconic acid refractive index at 60minutes reaction-time as said previously.

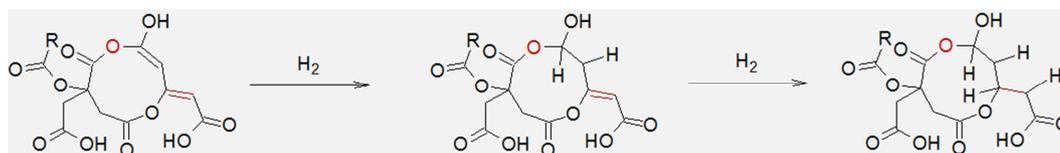


Figure 8. figure 5.b products hydrogenation.

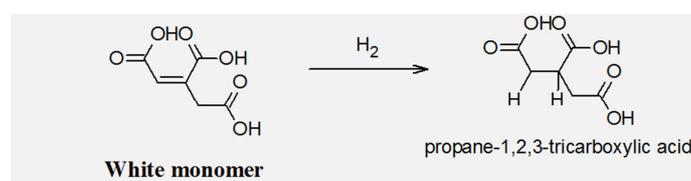


Figure 9. White monomer hydrogenation.

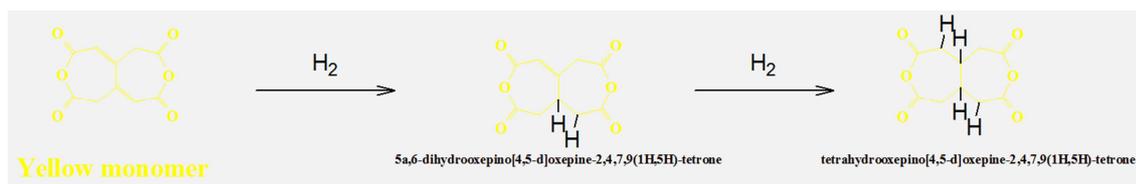


Figure 10. Yellow monomer hydrogenation.

To confirm the citric acid dehydration to prop-1-ene-1, 2, 3-tricarboxylic acid – White monomer and eventually the formation of other products [12], the following table 9 was established for the sulfuric acid protonic acid-H⁺ catalyst.

Indeed, this table 9 confirmed that the first step of trans-esterification with citric acid's alcohol function catalyzed by sulfuric acid H⁺ contains two parallel reactions such as citric acid dehydration and trans-esterification which

apparently predominate initially with solubility of biodiesel's molecules solution in hexane to the detriment of biodiesel's molecules solution soluble in the distilled water. But, from 1 minute to 60 minutes of reactions, there was an increase of solubility of biodiesel's molecules solution in the distilled water to the detriment of biodiesel's molecules solution soluble in hexane confirming the constant formation of the prop-1-ene-1, 2, 3-tricarboxylic acid – White monomer by

citric acid dehydration as dominant first step during trans-esterification with citric acid's alcohol function catalyzed by sulfuric acid H^+ . Their dismutation conducted to the formation of yellow monomers (2, 4, 7, 9-tetraoxooctahydrooxepino [4, 5-d] oxepine-5a, 10a-dicarboxylic acid-[12]) responsible of the constant light yellow color of synthesized biodiesel (table 7).

Table 9. Biodiesel's molecules solubility in distilled water and in hexane using.

Global results of peanut-oil trans-esterification with citric acid's alcohol function						
Used catalysts	Time [mn]	Used distilled water volume [ml] (a)	Aqueous phase volume [ml] (b)	Biodiesel's molecules solution volume soluble in the distilled water [ml] (c)=(b)-(a)-(total rest of citric acid volume)	Biodiesel's molecules solution volume soluble in hexane [ml] (d)=(a)-(b)-(total rest of citric acid volume)	Evaluated biodiesel volume [ml]
Sulfuric acid protonic acid- H^+	1	35	33	-	-	10.3979
	5	35	41	2.31	-	10.3804
	60	35	42	3.47	-	11.1973
Citric acid protonic acid- H^+	1	35	37.5	1.74	-	7.2655
	5	35	40	0.97	-	8.2125
	60	35	38	-	-	9.6359

In contradiction to the previous trans-esterification mechanism first step catalyzed by sulfuric acid protonic acid- H^+ , the low and constant diminution values of biodiesel's molecules solution volume soluble in the distilled water using citric acid protonic acid- H^+ catalyst (table 9) indicated that the citric acid dehydration occurred a little in benefit of trans-esterification

reaction followed by citric acids esterification and decarboxylation followed eventually by polymerization [9] (new project) as described on figure 3 to figure 5 (§.3) to form high oxygenated great molecules responsible of the high density of biodiesel obtained using citric acid protonic acid- H^+ catalyst and its imperial color (table 7).

3.2. Partial Orders Versus Citric Acid of Peanut Oil Trans-esterification with Citric Acid's Alcohol Function

3.2.1. Citric acid Concentrations Evolution in Terms of Time

Table 10. Global results of citric acid concentrations evolution in terms of time.

Used catalysts	Global results of citric acid concentrations evolution in terms of time			
	Time [mn]	Citric acid conversion [%]	Citric acid concentration [citric acid] [mol.l ⁻¹]	$\frac{1}{[citric acid]}$ [l.mol ⁻¹]
Citric acid protonic acid- H^+ pH=1.66	0	0	1.81323	0.55150
	1	27.80	0.97753	1.02298
	5	31.42	0.87032	1.14900
	60	36.87	0.84352	1.18551
	0	0	1.81323	0.55150
Sulfuric acid protonic acid- H^+ pH=-3.76	1	35.42	0.99330	1.00674
	5	37.26	0.81671	1.22442
	60	39.98	0.72527	1.37880

Noticed that all the time citric acid concentration decrease with time and initially, between 0minute to 1minute, it was recorded approximately 50% of citric acid concentration diminution (table 10).

3.2.2. Citric Acid Partial Order Determination – Trans-esterification's Speed Constants Determination

The first condition which permit the partial order versus citric acid of trans-esterification between oil and citric acid's alcohol calculation was the initial concentration of citric acid must be negligible in front of the initial concentration of oil. In this experimental condition, the global speed of this trans-esterification catalyzed by protonic acid H^+ was:

$$v = k_{acide} \times [citric acid]^a \times [oil]^b \times [H^+] \quad (1)$$

Seeing that [oil] is in excess, so

$$v = k_{acide} \times [citric acid]^a \times [oil] \times [H^+]$$

Seeing that the principal experimental condition choice in this study was low pH less than the lowest citric acid's pK_{a1} (3.14) (table 6), so the initial evaluated ratio:

$$\left(\times \frac{\frac{oil \text{ moles}}{citric \text{ acid moles}}}{oil \text{ stoichiometric coefficient}} \right) = 1.7188$$

for all used catalysts and these ratios increased more than two until 60 minutes of reaction assuming that this trans-esterification reaction occurred with constant volume.

According to these conditions and after studying the evolution of citric acid concentrations (table 10) curve with time, the following straight line tendency curve (figure 11, figure 12) were obtained with correlation R² higher than 0.60. These results showed that, not only the initial experimental conditions were compatible with initial concentration of citric acid negligible in front of the initial concentration of oil (in excess), but also it could be deduced that the against citric acid partial order for catalysts citric protonic acid-H⁺ and sulfuric

acid protonic acid-H⁺ must be two-2 in solution to the differential equation deduced by the previous equation (1)-§3.2.2. assuming the previous hypothesis such as the observed speed constant k_{obs} was $k_{obs} = k_{acide} \times [oil] \times [H^+]$ And the differential equation is

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

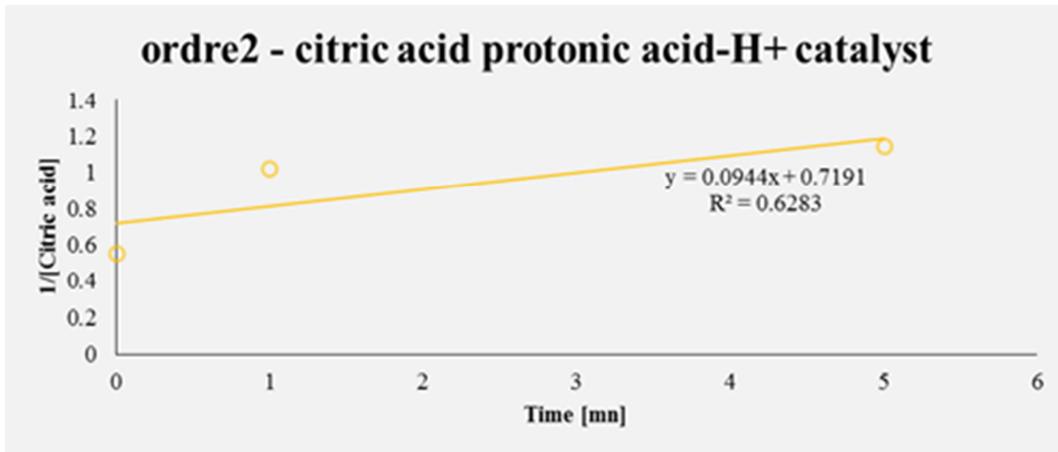


Figure 11. 1/[citric acid] evolution with time for trans-esterification reactions catalyzed by citric acid protonic acid-H⁺.

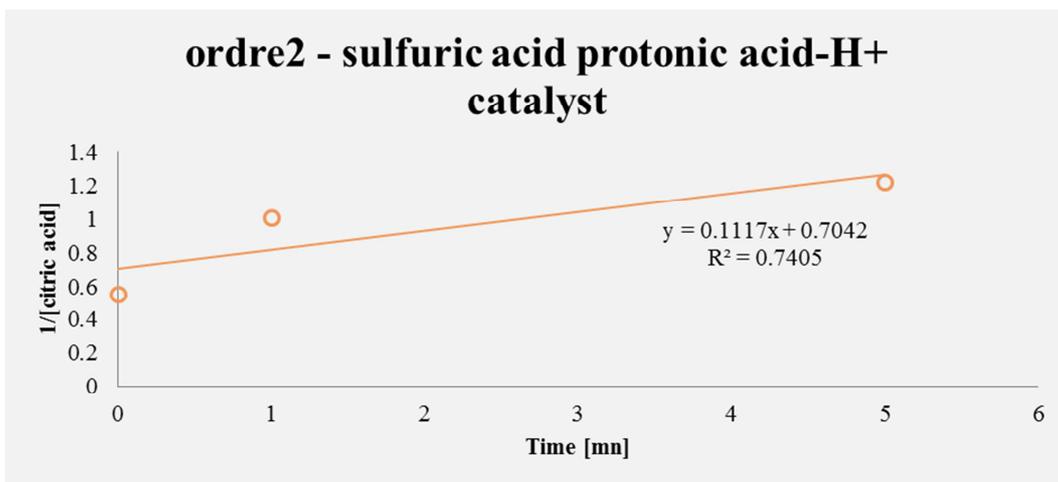


Figure 12. 1/[citric acid] evolution with time for trans-esterification reactions catalyzed by sulfuric acid protonic acid-H⁺.

Table 11. Global results of trans-esterification's with citric acid's alcohol function speed constants.

Used catalysts	Global results of trans-esterification's speed constants			
	Observed speed constant - $k_{observed}$ [L×mol ⁻¹ ×mn ⁻¹]	Initial oil concentration [mol.l ⁻¹]	Initial Real speed constant - k_{acide} [L ³ ×mol ⁻³ ×mn ⁻¹]	Initial Real speed constant - k_{acide} [L ³ ×mol ⁻³ ×s ⁻¹]
Citric acid protonic acid-H ⁺ pH=1.66	0.0944	1.0389	2.4041	0.0401
Sulfuric acid protonic acid-H ⁺ pH=-3.76	0.1117	1.0389	3.2823	0.0547

This table 11 showed the Global results of trans-esterification's with citric acid's alcohol function speed constants which were very important because they could be used to evaluate and control in advance the citric acid molecules evolutions used in the vicinity of the present experimental conditions (table 6) and another else in reactor design.

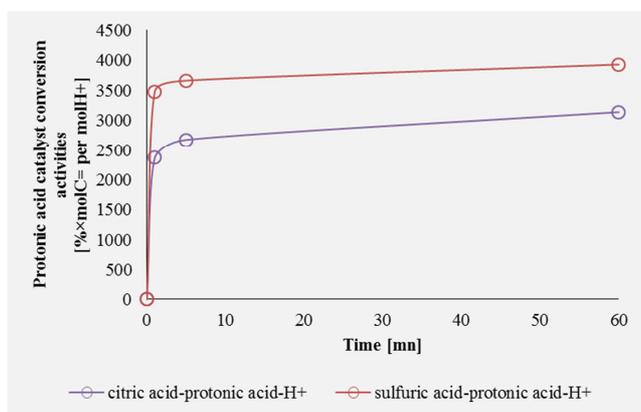
3.3. Alkene's Support Effects During Trans-esterification

The following table 12 showed the activities and turnovers of these H⁺-catalysts.

Table 12. Global results of catalysts characteristics.

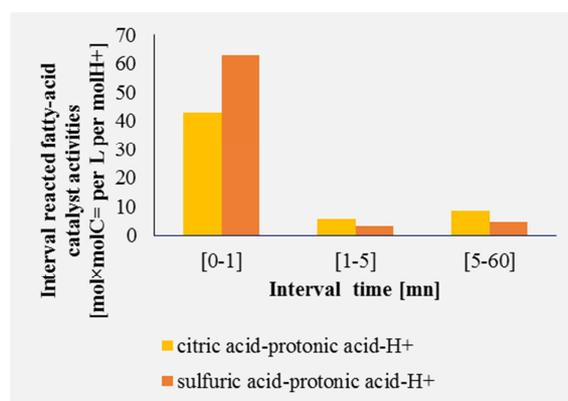
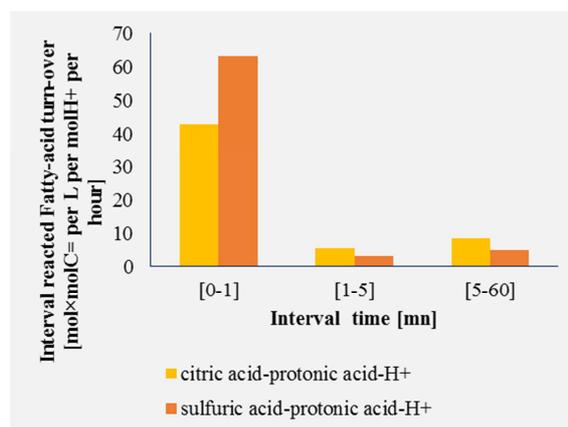
Used catalysts	Global results of catalysts activities and turn-overs				
	Time [mn]	Conversion-activities [%×molC ⁼ per molH ⁺]	Interval reacted fatty-acid activities [mol×molC ⁼ per L per molH ⁺]	Conversion-turn-over [%×molC ⁼ per molH ⁺ per hour]	Interval reacted fatty-acid turn-over [mol×molC ⁼ per L per molH ⁺ per hour]
Citric acid protonic acid-H ⁺	0	0	-	-	-
	1	2 367.80	42.93	142 068.01	2 576.02
	5	2 676.70	5.60	40 150.47	83.94
	60	3 140.27	8.41	3 425.75	9.18
Sulfuric acid protonic acid-H ⁺	0	0	-	-	-
	1	3 481.69	63.12	208 901.45	3 787.08
	5	3 662.47	3.29	54 937.01	49.36
	60	3 931.07	4.86	4 288.45	5.31

As seen previously in paragraph §2.3.2-table 6, the H₂SO₄-protonic acid-H⁺ catalyst dispersion was slightly inferior than the one of the citric acid protonic acid-H⁺, in otherwise initially the H⁺- concentration per peanut oil's alkene-unsaturated organic function concentration used with H₂SO₄-protonic acid-H⁺ catalyst was more than the one used with citric acid protonic acid-H⁺ catalyst. So, noticed that consequently the initial [0minute to 1minute] conversion activity of H₂SO₄-protonic acid-H⁺ catalyst was slightly superior than for citric acid protonic acid-H⁺ catalyst (figure 13) and the initial [0minute to 1minute] interval reacted fatty-acid activities was clearly superior with H₂SO₄-protonic acid-H⁺ catalyst than with citric acid protonic acid-H⁺ catalyst (figure 14 - table 12 - 63.12 [mol×molC⁼ per L per molH⁺] > 42.93 [mol×molC⁼ per L per molH⁺]). These first results confirmed the non-negligible role of peanut oil's alkene-unsaturated organic function as efficient support for protonic acid-H⁺ catalyst support showed in bibliographies [9, 12].

Figure 13. Protonic acid-H⁺ catalysts conversions activities.

Thus, all protonic acid-H⁺ catalysts interval reacted fatty-acid activities decreased considerably from 1minute which could be due to the steric congestion of reagent citric acid molecules (figure 7), the steric congestion between reagent and intermediary product molecules (figure 3-a; figure 3-a') and essentially the steric congestion of product molecules for the citric acid protonic acid-H⁺ catalyst (figure 3-figure 5). That was why initially ([0-1]) the citric acid protonic acid-H⁺ catalyst's interval reacted fatty-acid activities was less important than the one of the sulfuric acid protonic acid-H⁺ catalyst which size was not only less bulky but also the most

intermediate molecules obtained by the first step parallel reaction (citric acid dehydration) as white monomers (figure 9) and their derivatives were also less bulky than the one of the citric acid protonic acid-H⁺ catalyst (figure 3 – figure 5).

Figure 14. Protonic acid-H⁺ catalysts interval reacted fatty-acid activities.Figure 15. Protonic acid-H⁺ catalysts interval reacted fatty-acid turn-over.

But noticed that, between [1-5] and [5-60] minutes interval time the citric acid protonic acid-H⁺ catalyst's interval reacted fatty-acid activities became more important than the one of the sulfuric acid protonic acid-H⁺ catalyst (figure 14). These results were certainly due to the formation of not only high oxygenated molecules but also another alkene organic functions (figure 5) which, increased their concentrations in experimental solution more than the initial total peanut-oil's fatty-acid alkene-unsaturated moles-concentration quantities (^[*] - table 6) with time; decreased the dispersion of the remainder citric acid

molecules thereafter increased the citric acid protonic acid-H⁺ catalyst's mobility and consequently interval reacted fatty-acid activities and the citric acid protonic acid-H⁺ catalyst's interval reacted fatty-acid turn-over (figure 15).

Therefore, for all protonic acid-H⁺ catalysts, between interval times [1-5] to [5-60] the interval reacted fatty-acid activities and turn-over increased 47.22% (sulfuric acid protonic acid-H⁺ catalyst) 50% (citric acid protonic acid-H⁺ catalyst). These results confirmed that, as said previously, during the first step of trans-esterification with citric acid's alcohol function there were two parallel reactions such as the trans-esterification and the citric acid dehydration which was

dominant with the sulfuric acid protonic acid-H⁺ catalyst but the noticed constant diminution of its reacted fatty-acid activities and turnover from 1 minute allowed to affirm that once formed these citric acid's alkenes functions were transformed to another products; by reactions like etherification with citric acid's alcohol function (figure 16) or hydrogenation with hydrogen formed by decarboxylation during yellow monomers formation (figure 9) according to bibliography mechanism [9-p11-§3.2.1.-figure 13] (figure 17); which certainly decrease the alkene concentration as well as its activities especially for the sulfuric acid protonic acid-H⁺ catalyst.

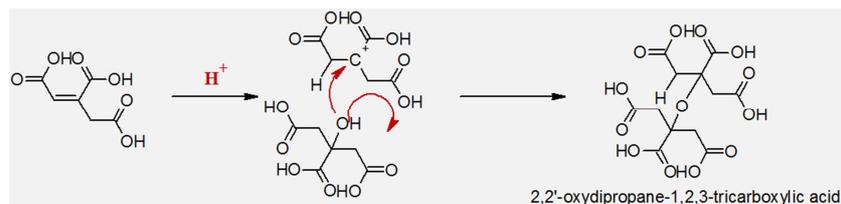


Figure 16. White monomer etherification catalyzed by protonic acid-H⁺ catalyst.

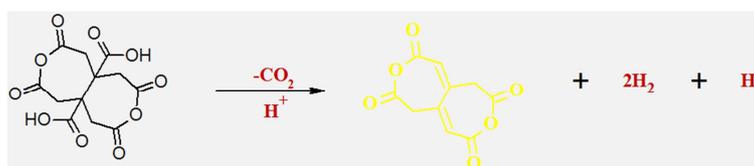


Figure 17. Yellow monomer formation catalyzed by protonic acid-H⁺ catalyst according to mechanism [9-p11-§3.2.1.-figure 13].

Noticed that the 2,2'-oxydipropene-1,2,3-tricarboxylic acid (figure 16) could be transformed to 3,5,9,11-tetraoxo - 4,10,13-trioxabicyclo [5.5.1] tridecane-1,7-dicarboxylic acid by dehydration which could be decarboxylated to form (1Z)-4,10,13-trioxabicyclo [5.5.1]trideca-1,7-diene-3,5,9,11-tetrone (figure 18).

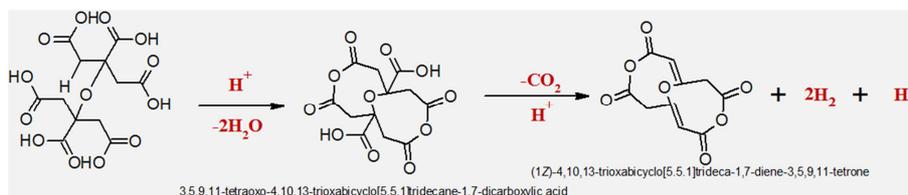


Figure 18. 2,2'-oxydipropene-1,2,3-tricarboxylic acid transformations.

Probably, the (1Z)-4,10,13-trioxabicyclo [5.5.1] trideca-1,7-diene-3,5,9,11-tetrone was hydrogenated to form 4,10,13-trioxabicyclo [5.5.1] tridecane-3,5,9,11-tetrone and/or (1Z)-4,10,13-trioxabicyclo [5.5.1] tridec-1-ene-3,5,9,11-tetrone (figure 19).

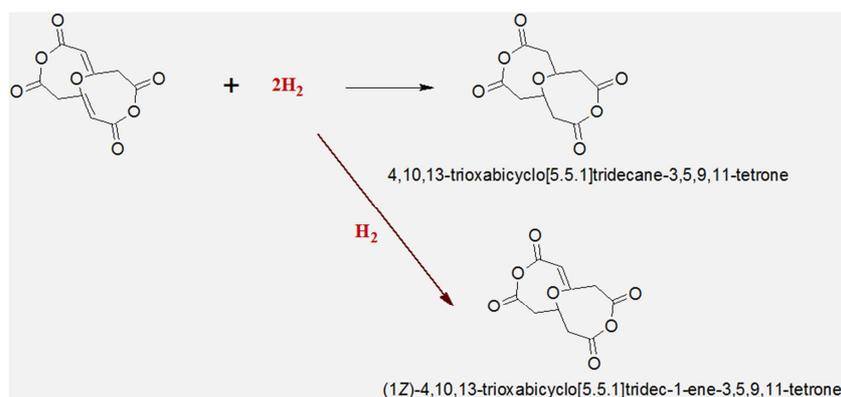


Figure 19. (1Z)-4,10,13-trioxabicyclo [5.5.1]trideca-1,7-diene-3,5,9,11-tetrone hydrogenations.

4. Conclusion

With sulfuric acid protonic acid-H⁺ catalyst at pH=−3.76, the first step was composed of trans-esterification, between citric acid's alcohol organic function and peanut oil, and citric acid dehydration to form the white citric acid monomer which could either suffered dismutation, decarboxylation and/or hydrogenation or other etherification, decarboxylation and/or hydrogenation all the time catalyzed by protonic acid-H⁺ to form yellow citric acid monomers and/or their derivatives produced by hydrogenation. But with unattached protonic acid-H⁺ of reagent citric acid molecules at pH=1.66, the first step was composed also of trans-esterification, between citric acid's alcohol organic function and peanut oil, and citric acid dehydration to form the white citric acid monomer; however, because of reagent, catalyst citric acid protonic acid-H⁺ and intermediate products sizes steric, the citric acid molecules dehydration followed by decarboxylation and/or hydrogenation to form yellow monomers were very probably accompanied by citric acid molecules reactions with intermediate products catalyze by citric acid protonic acid-H⁺ to form higher oxygenated and new unsaturated molecules with eventually their hydrogenated derivatives to form a yellow imperial biodiesel. Even if, all protonic acid-H⁺ catalysts' activities-turnovers decreased notably from 1minute reaction-time, it was noticed that with sulfuric acid protonic acid-H⁺ the activities-turnovers decreased constantly with reaction-time in comparison to the unattached citric acid protonic acid-H⁺ activities which increased with reaction-time certainly due to its mobility on alkene-unsaturated organic function concentration which increased during reaction even if there could be the hydrogenation of these unsaturated organic functions with reaction-time. In short, the trans-esterification between citric acid's alcohol organic function and peanut oil catalyzed by unattached citric acid protonic acid-H⁺ and sulfuric acid protonic acid-H⁺ at low pH and at ambient temperature afforded to synthesize an excellent oxygenated and unsaturated biodiesel setting above and experimental results could helped to realize an efficient reactor.

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