

# Valorization of Glycerin from Biodiesel by Acetylation over Acid Treated Montmorillonite catalyst

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## Abstract

To ensure the viability of conventional biodiesel production, new ways to value by-products are mandatory. Fuel oxygenate additives manufactured from glycerin are envisaged as a relevant usage of the glycerin glut arising from a growing biodiesel industry.

Acetins obtained through glycerin esterification with acetic acid over acid solid catalysts, intended on achieving the maximum triacetin yield. Commercial K10, K30, and KSF montmorillonite were employed as catalysts, with both pure (99.9%) and crude (80%) glycerin being used as feedstock, the latter having a slight negative effect on the catalysts performances. In order to improve the catalytic activity of commercial K10 clay, acid treatments were performed using inorganic (hydrochloric, sulfuric and phosphoric) and organic (propionic, acetic, lactic, citric, tartaric and oxalic) acids.

Several analytical methods were employed in order to assess the solids surface morphology and chemical composition (SEM-EDS) of fresh and post-reaction catalysts, crystallographic changes promoted by acid treatment or during reaction (XRD), and the surface acidity of acid treated clay materials (skeletal isomerization of 1-butene).

Solvent-free acetylation catalytic tests were carried out at reflux temperature using 10% (W/W) of catalyst and an acetic acid:glycerin molar ratio around 9.6. Sulfuric acid was the most effective overall catalyst, showing a triacetin selectivity of 33.0% after 2h of reaction. Citric and oxalic acids performed the best among the used organic acids, leading to 27.2% and 25.6 % of TAG selectivity.

**Keywords:** Glycerin valorization, acetylation, clay catalysts, acetins, triacetin, oxygenate additives

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## 1. Introduction

Glycerin is the main by-product of the biodiesel production by transesterification of oil, at a rate of 10% wt. production, creating an important glut in the European market. This compound's biggest markets are personal care industry, as a moisturizer, or the chemical and pharmaceutical industries as a feedstock. [1] Glycerol acetates, named acetins, produced through acetylation of glycerin, present many different uses, with the most relevant being as fuel additives for diesel and biodiesel engines. [2]

Acetylation reactions are conventionally carried out homogeneously using inorganic strong acids as catalysts, which have shown problems regarding waste treatment and environmental effects.

Solid acid catalysts have lately been heavily referenced in literature as viable, more selective, alternatives that do not face the same disposal issues. Among these, acid exchange resins [3] [4] [5], montmorillonite [6][7], activated carbons [8][9][10], mesoporous and modified silica [11][12], Zeolites HZSM-5 and H- $\beta$  [7], metal oxides and heteropolyacids [13] [14] [10].

Montmorillonite is natural cheap and abundant clay, known for being a lamellar mineral with unique characteristics, such as an expanding lattice, large surface area as well as a sizable pore volume, making it suitable for a wide range of catalytic reactions [15]. The work presented will focus on the evaluation of clays K10, K30 and KSF as acid catalysts and as acetylation promoters.

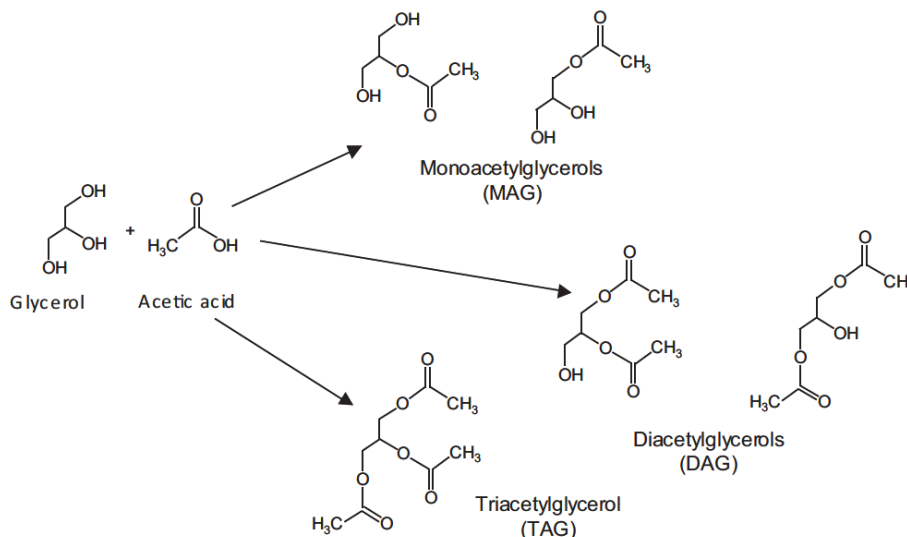


Figure 1 –Acetylation of glycerin with acid acetic (adapted from [16]).

## 2. Experimental

### 2.1 Raw materials

The glycerin acetylation was carried out using glacial acetic acid (Carlo Erba, 99.8 %) and crude glycerin from a local biodiesel industry. The reported glycerin composition (weight basis) was glycerin  $\leq 82$  %, 10% of water and 8% of MONG (Matter Organic Non Glycerol) and *NaCl*. Pure glycerin (local store, 99.6 %) was used as standard.

### 2.2 Preparation of the Catalysts

The glycerol acetylation was catalyzed by acid clay catalysts. Commercial K10, K30 and KSF montmorillonite clays were used, as received, to catalyze the acetylation of pure and crude glycerin. The Al leaching, using acid treatments was performed for K10 clay in order to ameliorate surface acidity and morphologic characteristics. Acid treatments were achieved using aqueous solutions of inorganic (sulfuric, phosphoric and hydrochloric) and organic acids (oxalic, citric, lactic, tartaric and acetic). Briefly, a suspension of the powder clay (20 g) in 1M or 2M acid solution (200 mL) was vigorously stirred during 30 min at boiling temperature. After this period, the solid was separated from liquid by filtration and dried overnight. The powders were finally calcined at 275°C for 3h.

The Amberlyst-15 acid resin was used as a reference due to the fact that it is an ion exchange resin with strong sulfonic groups [20].

### 2.3 Catalysts characterization

XRD patterns were recorded at room temperature on a *Bruker D8 Advance Powder* Diffractometer, using a Bragg-Brentano geometry, under  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm), with a step of 0.02 °/s and the  $2\theta$  range was scanned between 5° to 70°.

The Fourier Transform Infrared (FTIR) spectra were acquired (Perkin Elmer, Spectrum Two IR spectrometer) using a reflectance mode in the range 4000–600  $\text{cm}^{-1}$  and a resolution of 4  $\text{cm}^{-1}$ . A horizontal total attenuated reflection accessory (ATR), from PIKE Technologies, with a ZnSe crystal was used. Four scans were accumulated for each spectrum to obtain an acceptable signal-to-noise ratio. The resulting spectra were treated using the *Kubelka-Munk* function.

Catalytic 1-butene skeletal isomerization tests were carried out in a tubular glass flow reactor, with a catalyst sample of around 500 mg, using 1-butene (5% wt.) mixed with compressed air. All the catalysts were tested for over than 80 min at 398 K. The gaseous effluent was analyzed online using an AutoSystem gas chromatograph (GC) coupled with a Shimadzu, C-R6A Chromatopac integrator.

Scanning Electron Microscope (SEM) analysis accomplished using a JEOL SEM, model 7001F, with a tungsten Field Emission Gun (FEG) SEM with Schottky emission, resolution of 1.2 nm at 15kV, equipped with secondary and backscattered electron detectors, and with an Energy Dispersive Spectroscopy (EDS) light elements detector.

Acetins mixtures produced were analyzed using a CP- 3800 GC (Varian chromatogram analysis) equipped with a flame ionization detector (FID) and a capillary column (Methyl 5 % Phenyl Silicone, 15 m x 0.32 mm). The following temperature program applied was the following: start at 100 °C, increase to 140 °C, 10 °C/min. The injection was made at 280 °C and the detection at 300 °C. The products MAG, DAG and TAG were identified. Commercial montmorillonites, K10, K30, and KSF, were tested, as received, in the acetylation reaction. The main characteristics of raw clay materials are displayed on Table 1.

## 2.4 Catalytic experiments

The acetylation reaction was carried out with a three-necked round flask (500 mL) fitted with a water-cooled condenser and set at 125 °C.

**Table 1 – Characteristics of the Mt K10, K30, and KSF [17] [18] [19]**

Catalyst	K10	K30	KSF
Surface Area (m <sup>2</sup> /g)	240	330	20-40
Apparent Bulk Density (g/L)	300-370	450	800-850
pH	3-4	2.8-3.8	1.5
Pore Volume (mL/g)			
0-80 nm	0.36	0.5	0.023
0-24 nm	0.30	0.44	0.01
0-14 nm	0.26	0.38	0.01

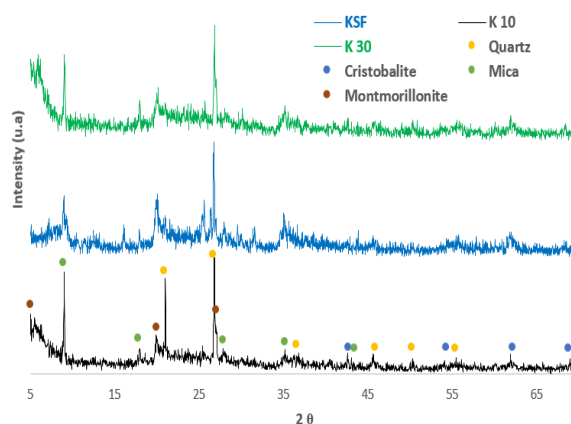
Acetic acid and the catalyst were placed in the reactor, heated from room temperature and kept stirred. When the set temperature was reached, glycerin was injected to the mixture, and the reaction was carried out for a set time. Samples were taken periodically and cooled for GC analysis

## 3 Results and discussion

### 3.1 Catalysts characterization

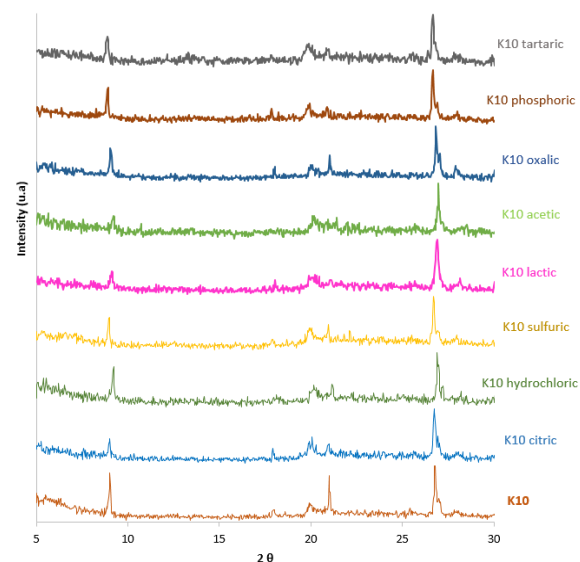
#### 3.1.1 Crystalline phases by XRD

The X-Ray patterns reported in Figure 2 present characteristics corresponding to the commercial catalysts K10, K30, and KSF. It can be seen that, due to their different acid activation, KSF appears to be the most modified catalyst, as diffraction lines tend to be the ones with the lowest intensity, except at the  $2\theta \sim 20^\circ$ , line corresponding to the montmorillonite structure. Furthermore, K10 presents more intense diffraction lines pointing towards the existence of impurities such as mica and quartz [21] [22] [23] [24][25].



**Figure 2 – XRD patterns of raw K10, K30 and KSF.**

When K10 is acid tuned with inorganic and organic acids (1M), the intensity of the diffraction lines is slightly reduced, therefore no significant changes were observed in the samples (Figure 3).



**Figure 3 – XRD patterns of K10 treated with organic and inorganic acids (1M).**

### 3.1.2 Infrared Spectroscopy

FTIR spectra were used to determine surface species of fresh and post reaction catalysts. As shown in Figure 4, the reflectance bands at  $1035\text{ cm}^{-1}$  are assigned to  $\text{Si-O-Si}$  stretching vibrations of the tetrahedral layer, where KSF contains the weakest intensity, corroborating XRD analysis, by being the most attacked by acid. The band at  $910\text{ cm}^{-1}$  represents  $\text{Al-OH-Al}$  bending in the octahedral layers sheet and is observed in all three clays, although in K10 and K30 this band is less intense because hydrochloric treatment attacks aluminum preferentially, leaving the octahedral structure more damaged than the tetrahedral. The bands around  $798, 761, 674, 629$  and  $1100\text{ cm}^{-1}$  indicate the presence of free silica, as quartz (admixture) or cristobalite, also confirmed by X-Ray, which shows an increasing intensity of these bands with the increasing acidity of the catalyst, revealing that KSF has a higher content of these impurities. [26] [27] [28] [29][30]

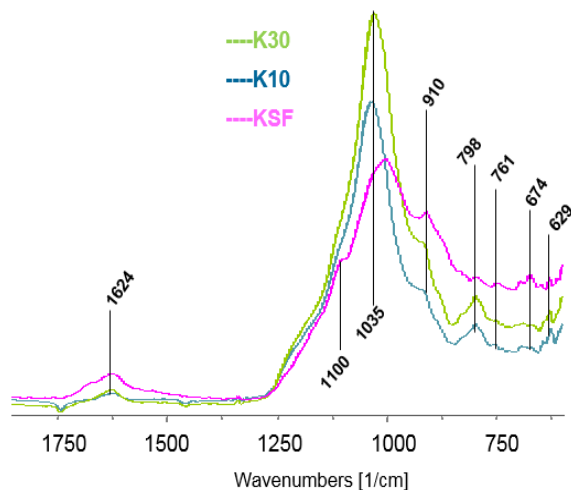


Figure 4 – FTIR spectra of catalysts K10, K30 and KSF ( $2000 - 600\text{ cm}^{-1}$ ).

When K10 is treated with inorganic acids, as can be observed Figure 5, it is clear that the intensity of the band at  $1035\text{ cm}^{-1}$  decreases for both phosphoric and sulfuric, implying that the tetrahedral structure suffers leaching. However, it intensifies with hydrochloric acid due to exposed silica. [23] [31]

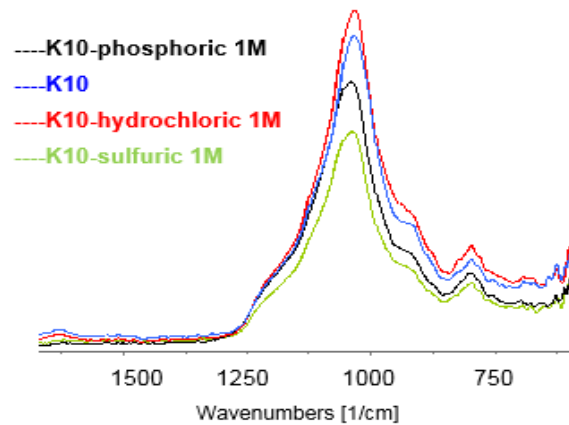


Figure 5 – FTIR spectra of K10 treated with inorganic acids (1M).

Among organic acids (Figure 6), the tartaric acid practically did not change the intensity bands when compared to commercial K10.

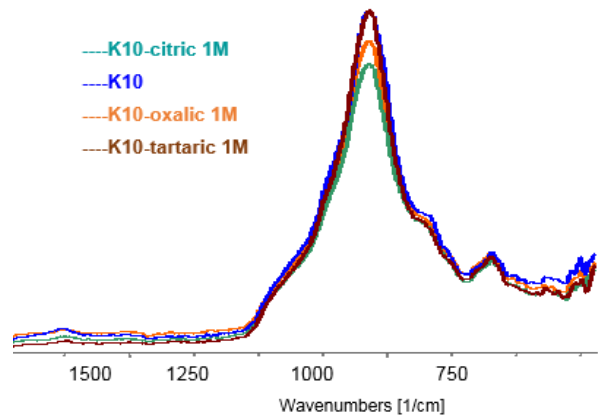
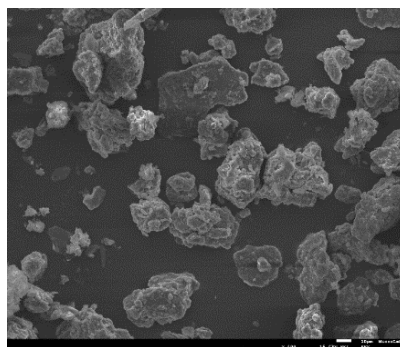


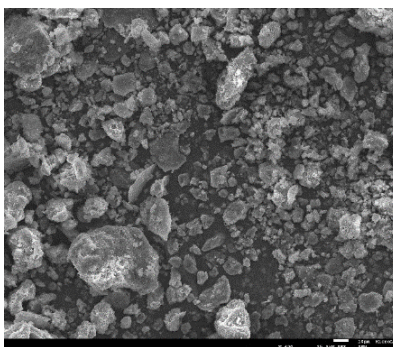
Figure 6 – FTIR spectra of K10 treated with organic acids (1M).

### 3.1.3 SEM-EDS

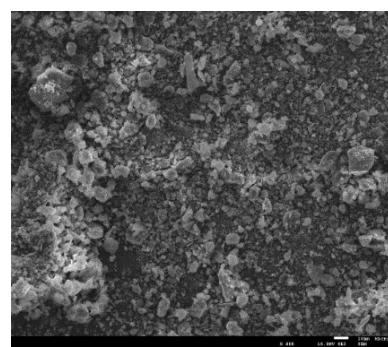
SEM analysis is capable of picturing the surface morphology of solids. The results from Figure 7 show that the grain size is different, with KSF showing bigger and more irregular grains and K10 lowest grain sizes. Using EDS analysis the species O, Na, Mg, Al, K, Ca, Fe, were observed, although in KSF the element sulfur was detected.



KSF ( x 400 ; 10  $\mu$ m )



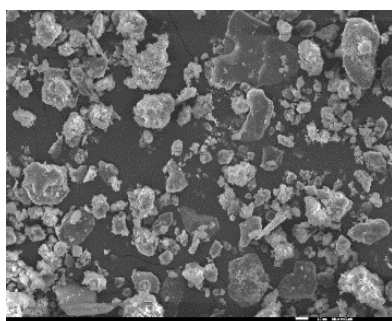
K30 ( x 400 ; 10  $\mu$ m )



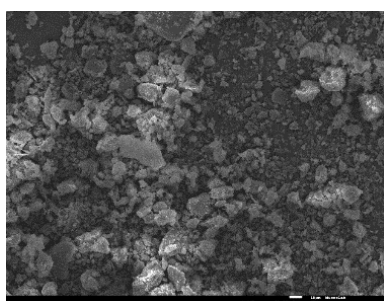
K10 ( x 400 ; 10  $\mu$ m )

**Figure 7 – SEM pictures of the three commercial catalysts K10, K30 and KSF.**

Following the treatment of K10 with organic and inorganic acids it was observed that the majority of the smaller grains of K10 were heavily attack leading to their agglomeration (Figure 8).



Citric 1M ( x 400 ; 10  $\mu$ m )



Sulfuric 1M ( x 400 ; 10  $\mu$ m )

**Figure 8 – SEM picture of the K10 treated with citric and sulfuric acid (1M).**

The acetylating agent used in the present work was acetic acid, known to be a strong organic acid, and

during the 5 hours of the reactions, there may be damage to the structure of the catalyst, leading to a loss of aluminum during the glycerin's acetylation.

**Table 2 – K10, K30, KSF, and K10-acid treated Si/Al atomic by EDS.**

Catalyst		Si/Al atomic ratio	
		Fresh	Post reaction
K30		4.1	4.6 $\pm$ 1.6
KSF		2.3 $\pm$ 0.2	2.7 $\pm$ 1.4
K10	Untreated	3.6	4.6 $\pm$ 1.5
	hydrochloric (1M)	5.9 $\pm$ 0.8	5.5 $\pm$ 1.0
	citric (1M)	5.3 $\pm$ 0.6	5.5 $\pm$ 0.4
	citric (2M)	6.3 $\pm$ 1.6	6.9 $\pm$ 1.9
	tartaric (1M)	6.0 $\pm$ 1.5	5.3 $\pm$ 1.7
	oxalic (1M)	5.4 $\pm$ 0.9	5.7 $\pm$ 1.1
	phosphoric (1M)	5.9 $\pm$ 2.6	6.7 $\pm$ 0.1
	sulfuric (1M)	3.4 $\pm$ 1.0	5.4 $\pm$ 0.4
	sulfuric (2M)	5.5 $\pm$ 1.3	not available
	acetic (1M)	7.1 $\pm$ 1.5	7.2 $\pm$ 1.7
	lactic (1M)	5.4 $\pm$ 0.7	9.3 $\pm$ 2.9
	propionic (1M)	4.7 $\pm$ 1.8	not available

As can be seen on Table 2, there were no significant changes in the atomic ratio Si/Al, although in

some catalysts, namely K10 treated with lactic acid (1M), more pronounced changes in the ratio can be observed.

For the acid treatment in K10 with organic and inorganic acids, results show that the majority of the smaller grains of K10 were heavily attacked leading to their agglomeration (Figure 8).

The acetylating agent used was acetic acid, known to be a strong organic acid, and during the 5 hours of the reactions, damage to the structure of the catalyst could have occurred, leading to a loss of aluminum during the glycerin's acetylation. There were no significant changes in the atomic ratio Si/Al, although in some catalysts, namely K10 treated with lactic acid (1M), more pronounced changes in the ratio could be observed (Table 2).

### 3.1.4 Catalytic Isomerization

Table 3 displays the catalytic activity, expressed as a 1-butene conversion for the Mt K10, K30, and KSF, where its conversion decreases in the order  $K30 > K10 > KSF$ . It is also observed that by increasing temperature, catalytic activity increases.

Despite the fact that this analysis reports that K30 is the most acid catalyst, it cannot ignore the properties of each catalyst, as can be seen in Table 3, where the most acid catalyst is KSF and the most porous is K30. This may indicate that isomerization of 1-butene not only depends on the existing acidity but also their porosity and superficial area.

For the three commercial montmorillonites, it is observed an acid-catalytic isomerization due to the fact that presents ratio cis/trans close to or equal than 1 [32] [33].

For K10 tuned with different acids, the ratio activity is enhanced in general, as well as the cis/trans ratio, although when used citric acid (2M) the cis/trans ratio decreases, probably indicating an excess of aluminum removed from the Montmorillonite sheets or a significant decrease in the porosity of the catalyst.

**Table 3 – 1-Butene conversion at 127 °C in K10, K30 and KSF as well as K10 treated with different acids.**

Catalyst	Conversion (%)	$R_{\text{Butene-1}}$ ( $\mu\text{mol.gcat}^{-1}.\text{s}^{-1}$ )	Cis/trans Ratio
K30	58.1	42.5	1.0
KSF	16.1	11.8	1.4
K10	17.3	12.6	1.3
hydrochloric (1M)	20.3	14.8	1.2
citric (1M)	27.1	20.4	1.2
citric (2M)	6.9	5.0	1.4
tartaric (1M)	28.3	20.7	1.3
oxalic (1M)	30.2	22.1	1.3
phosphoric (1M)	33.2	24.2	1.2
sulfuric (1M)	56.9	41.5	0.9
acetic (1M)	49.4	36.1	1.1
lactic (1M)	47.4	34.6	1.1
propionic (1M)	53.7	40.1	1.1
sulfuric (2M)	63.6	46.5	0.84

### 3.1.5 Acetylation of glycerin

The use of refined glycerin (purity > 99.5%) with an excess of acetic acid at reflux temperature led to the formation of acetins, MAG, DAG, and TAG. All three catalysts achieved a glycerin's conversion superior to 95 % in 3 hours (Figure 9). Selectivity to TAG presents a low value, due to the deactivation of active sites by the formation of water as a by-product, whereas KSF was the one with the highest value.

In the case of crude glycerin (Figure 9), even after 3h of reaction, never reached the same rates as pure glycerin did. The predominant acetin formed was DAG, with MAG following suit. The formation of TAG was not negligible, reaching the highest value when using KSF catalyst, although the difference between the catalysts was minimal. Therefore it was possible to see that the main difference is the presence of 10 % (m/m) of water in the crude glycerin, causing the deactivation of the active sites, which are crucial to formation of TAG.

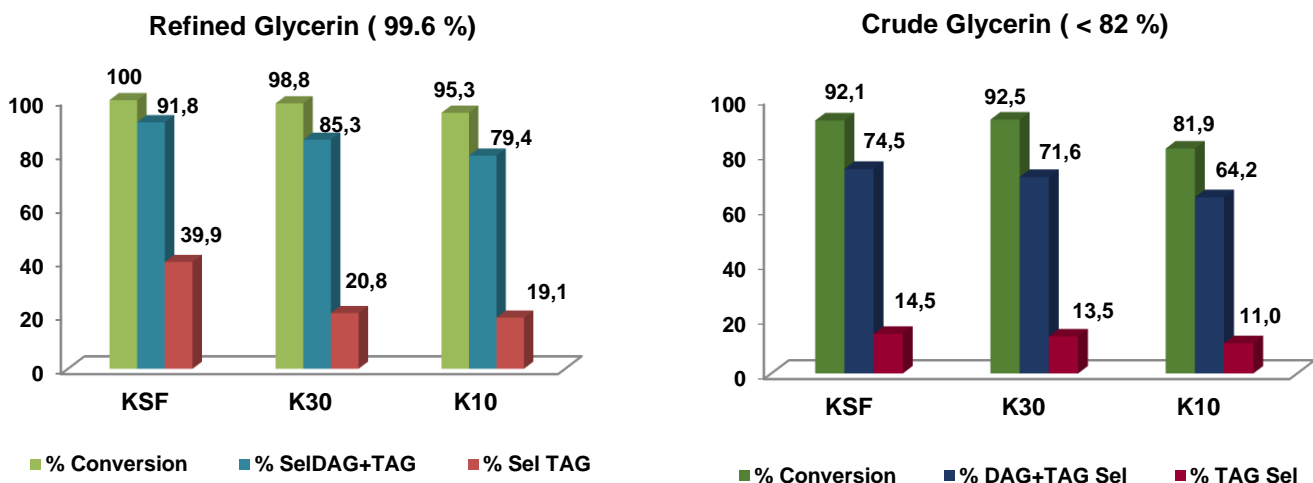


Figure 9 – Results of the acetylation, after 3 hours, with a ratio of acetic acid to glycerin of 9.6:1 (catalyst amount 10% wt. of glycerin) using refined and crude glycerin.

The predominant catalysts that showed excellent catalytic behavior in this reaction were the polymeric sulfonic Amberlyst (standard) and the KSF, seen in Table 4. The main characteristic that these two catalysts have in common is the existence of strong sulfonic groups. [34] [5] [35]

A reaction with the absence of a catalyst, named blank, was performed to affirm that this reaction can occur only due to the use of acetic acid, which is a strong organic acid, and the use of catalysts have the purpose of accelerating the reaction rate.

Table 4 – Results of the acetylation, after 3 hours, with a ratio of acetic acid to glycerin of 9.6:1 (catalyst amount 10% wt. of glycerin)

Catalyst	Conversion (%)	Selectivity (%)		
		MAG	DAG	TAG
Blank	97.0	19.2	63.9	15.9
Amberlyst15	99.0	9.0	53.2	37.9
KSF	100	8.1	51.9	39.9
K30	98.8	14.7	64.5	20.8
K10	95.3	20.6	60.3	19.1

Furthermore, the effect of the refined glycerin's acetylation is reported using different acid treatment in the catalyst K10. Regarding inorganic acids (Table 5), although the hydrochloric acid is stronger than the

sulfuric acid, the latter led to the higher TAG selectivity. This is possible because hydrochloric acid leads to aluminum leaching from the structure, affecting negatively the acidity of the catalyst, through the reduction of Lewis acidity, corroborated by the EDS analysis. On the other hand, catalytic activity estimated through the isomerization of 1-butene is higher when treated with 1M of sulfuric acid than 1M of hydrochloric acid, may be related to the acidity and porosity of the catalyst.

In the category of organic acids, and taking into account the error in the determination of the specific percentage of the peak areas measured by the GC-FID, all acids slightly improved the conversion and selectivity toward TAG, except lactic acid (Table 5), compared to the regular catalyst K10.

It was relevant to analyze the behavior of the tuned catalyst, when more concentrated acid was introduced, treating K10 with 2M of sulfuric acid for inorganic acids and 2M of citric acid for organic acids.

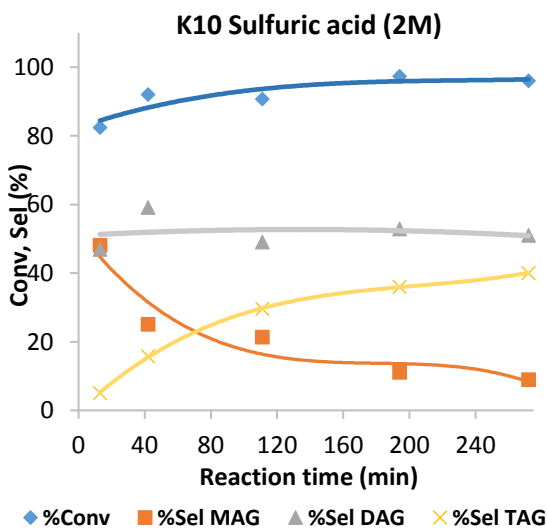
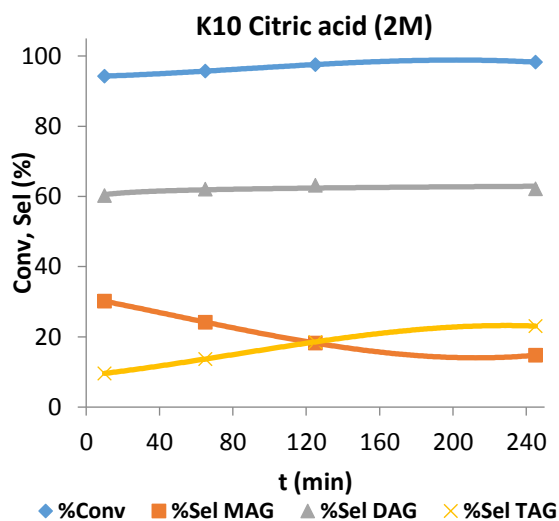
Sulfuric acid (Figure 10) was effective in promoting the formation of TAG, reaching values of 40% in 4 h, while citric acid (Figure 11) only achieved values around 20%. These results corroborate the isomerization test results done to assess intrinsic acidity, which indicated dealumination of the structure and subsequent loss of Lewis acidity

**Table 5 – Summary of the results of glycerin's acetylation during 5 hours, at reflux temperature with a ratio of acetic acid to glycerin of 9.6:1 (catalyst amount 10% wt. glycerin).**

Catalyst	$R_{\text{butene}}(127\text{ }^{\circ}\text{C})$ ( $\mu\text{mol.gcat}^{-1}.\text{s}^{-1}$ )	Si/Al Fraction	Conversion (%)	Selectivity (%)		
				MAG	DAG	TAG
K10 sulfuric2M	46.5	$5.5 \pm 1.3$	97.4	8.9	51.0	40.0*
K30	42.5	4.1	98.4	14.8	60.7	24.5*
K10 sulfuric1M	41.5	$3.4 \pm 1.0$	100	8.5	57.9	33.6
K10 propionic 1M	40.1	$4.7 \pm 1.8$	92.8	18.1	61.3	20.6
K10 acetic 1M	36.1	$7.1 \pm 1.5$	97.9	16.2	58.4	25.4
K10 lactic 1M	34.6	$5.4 \pm 0.7$	98.0	16.5	65.7	17.8
K10 phosphoric 1M	24.2	$5.9 \pm 2.6$	96.2	15.4	62.0	22.6
K10 oxalic 1M	22.1	$5.4 \pm 0.9$	97.4	13.7	60.8	25.6
K10 tartaric 1M	20.7	$6.0 \pm 1.5$	98.0	15.3	62.3	22.4
K10 citric 1M	20.4	$5.3 \pm 0.6$	99.0	11.3	61.4	27.2
K10 hydrochloric 1M	14.8	$5.9 \pm 0.8$	92.0	15.6	59.2	25.3
K10	12.6	3.6	95.2	14.6	64.5	21.0
KSF	11.8	$2.3 \pm 0.2$	99.3	8.1	51.1	40.7*
K10 citric 2M	5.0	$6.3 \pm 1.6$	98.2	14.8	62.1	23.1**

\* - corresponding to 4.5 hours

\*\* - corresponding to 4 hours.


**Figure 10 – Performance of the catalysts K10 treated with sulfuric acid (2M) during 4.5 hours at reflux temperature with a ratio of acetic acid to glycerin of 9.6:1 (catalyst amount 10% wt. glycerin).**

**Figure 11 – Performance of the catalysts K10 treated with citric acid (2M) during 4.5 hours at reflux temperature with a ratio of acetic acid to glycerin of 9.6:1 (catalyst amount 10% wt. glycerin).**



## 4. Conclusion

The conversion of glycerin from biodiesel process into oxygenate fuel additives was studied. The acetylation using acetic acid was carried out using acid heterogeneous catalysts. Commercial K10, K30 and KSF montmorillonite catalysts were used in the pure, and crude, glycerin acetylation with acetic acid. Crude glycerin promoted a decay of the catalytic performances. Being the water and sodium chloride contents the major responsible for such result. The KSF catalyst was the most active showing the highest selectivity towards TAG (39.9 %) underlining the role of the catalyst acidity since it was the commercial material with the lowest surface area and porosity. The K10 and K30 had analogous behaviors regardless their acidity and morphologic differences, with 19.1 and 20.8 % of TAG's selectivity, respectively. It seems that a combined or synergy effect between acidity and morphology control the acetylation performances of the tested.

In order to improve the performances, the K10 clay was treated with inorganic and organic acids. Acid leaching of Al from montmorillonite, among other elements, can improve the acidity and morphologic characteristics. Partial destruction of the montmorillonite structure was observed since Si/Al ratio increased indicating the extraction of a certain quantity of aluminum from the structure. Also, FTIR analysis reflects a little less intensity in the spectrum in both tetrahedral and octahedral sheets. From the organic acids, the ones that exhibit best performance in formatting TAG where citric and oxalic acids (1M) with a selectivity of 27.2 and 25.6 % respectively, where in the inorganic acids it was sulfuric acid (1M) with 33.6 % of selectivity in TAG.

In terms of glycerin's conversion, all catalysts converted more than 95 %, except with propionic acid and hydrochloric acids (1M). Comparing with Si/Al, the three were the ones with the less difference in Si/Al ratio from original K10. However the sulfuric acid (2 M) was the one with the highest achievement in TAG, matching the performance of Amberlyst and KSF.

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