#### PRODUCTION OF BIODIESEL FROM CANOLA OIL (*BRASSICA NAPUS*) USING HYDROESTERIFICATION PROCESS

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#### Abstract

Biodiesel is considered an important substitute of diesel oil. The objective of this work is to produce biodiesel, from esterification of the fatty acid obtained from hydrolysis of canola oil, using powdered niobic acid  $(Nb_2O_5xH_2O)$  as catalyst.

Experiments were conducted following a factorial design  $2^3$ . For both reactions (hydrolysis and esterification) the temperature (250, 275, 300 °C for hydrolysis and 150, 175, 200 °C for esterification) and the mixing velocity (700 rpm<sup>1</sup>) remained constant during all reaction.

At the end of the reaction, the fatty acid was separated from glycerol, the catalyst, when used, can be recovered through filtration. The percentage of free fatty acid was calculated by titration with NaOH 0.25 N (Method proposed by AOCS, American Oil Chemists Society, Ca-40 method).

The best conversion yields obtained in the hydrolysis were observed at 300 °C with 20% of catalyst: at the highest molar ratio (oil:water 1:20) the conversion was 88.5% and at the at lowest molar ratio (oil:water 1:5) the conversion was 84.5%.

The best conversion obtained in the esterification was observed working in excess of methanol (fatty acid: methanol 1:3) and at a temperature of 200  $^{\circ}$ C; the concentration of catalyst is only relevant in the first 40 minutes of reaction. After one hour, even non-catalytic reaction produced high conversions at 200  $^{\circ}$ C.

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This process that integrates hydrolysis and esterification can be used as a potential alternative to transesterification.

#### Riassunto

Il biodiesel è considerato un importante sostituto del diesel.

L'obiettivo di questo lavoro è produrre biodiesel, esterificando l'acido grasso ottenuto dall'idrolisi dell'olio di canola, usando acido niobico in polvere  $(Nb_2O_5xH_2O)$  come catalizzatore.

Gli esperimenti sono stati condotti, seguendo un "factorial design" 2<sup>3</sup>. In entrambe le reazioni, la temperatura (250, 275, 300 °C per l'idrolisi e 150, 175 e 200 °C per l'esterificazione) è mantenuta costante durante i prelievi, così come l'agitazione (700 giri/min.). Al termine della reazione, l'acido grasso è separato dal glicerolo. Il catalizzatore, quando utilizzato, può essere recuperato per filtrazione. La percentuale di acido grasso libero è stato calcolato per titolazione con NaOH 0.25 N [Metodo estratto da AOCS [American Oil Chemists Society (Ca-40)].

Nelle reazioni di idrolisi buone conversioni si sono ottenute, lavorando con il 20% di acido niobico alla temperatura di 300 °C, sia utilizzando un eccesso di acqua, (rapporto molare olio:acqua 1:20 conversione = 88.5 %), sia con una quantità minore (rapporto molare olio:acqua 1:5 conversione = 84.5%).

Nelle reazioni di esterificazione le conversioni migliori si ottengono lavorando in eccesso di metanolo (rapporto molare acido grasso:metanolo 1:3) alla temperatura di 200°C, la presenza di acido niobico è rilevante solo nei primi quaranta minuti di reazione. Dopo un'ora, anche con reazioni condotte in assenza di catalizzatore si ottengono rese elevate.

Keywords: biodiesel, hydrolysis, esterification, acid niobic.

#### Introduction

Biodiesel is traditionally obtained by the transesterification of vegetable oils with methanol or ethanol, catalyzed by NaOH or KOH. In this work biodiesel is produced by a hydroesterification process.

The hydroesterification process shows a certain number of advantages when compared with transesterification of oils, which is the method used to produce first generation biodiesel.

In fact, in the hydrolysis reactions, the glycerol produced contains also fatty acids and water making it easier to separate than that obtained by direct transesterification. This allows to obtain a byhigher grade product (food grade). This never occurs in transesterification where glycerol is generated in the presence of a significant amount of catalyst and methanol (1).

The second advantage is that for this method any fatty feedstock (eg: used oils or fisheries waste) can be used without needing pre-treatment. On the contrary, in the direct transesterification, the feedstock must be sufficiently pure and often requires purification (water, acidity, etc). The highest is the feedstock acidity the better will be the yield of the process. Thus, beef tallow, chicken fat, pork fat, yellow grease, crude palm oil, crude jatropha oil, can be used and be transformed in international biodiesel standards at yields higher than 98% by hydroesterification. Transesterification cannot be efficiently applied with these raw materials. About 80% of the biodiesel production cost is ascribed to fatty material costs. Thus, hydroesterification is a choice that can really improve biodiesel feasibility (1).

The hydroesterification process consists of two stages: hydrolysis and esterification.

Hydrolysis is a chemical reaction between triglycerides and water, producing fatty acids and glycerol (*Fig.1*). Thus, hydrolysis increases the acidity of the fatty material instead of free fatty acid removal through refining.

The ester takes a proton (a hydrogen ion) from the hydroxonium ion. The proton becomes attached to one of the lone pairs on the oxygen which is double-bonded to the carbon.

The transfer of the proton to the oxygen gives it a positive charge, but the charge is actually delocalised much more widely than shown in Figure 1. The next stage of the mechanism involves an attack on the carbon. The positive charge on the carbon atom is attacked by one of the lone pairs on the oxygen of a water molecule (2).



Fig. 1 - Mechanism of the hydrolysis reaction.

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At the end of the first hydrolysis stage, fatty acid and glycerol are separated.

In the second stage, the fatty acid is esterificated with methanol or ethanol producing pure esters. The conversion of fatty acid into ester depends on the quality of raw material and on working conditions. The esterification, then, will be influenced by the quality of the raw material (amount of free fatty acid and the presence of water), temperature of reaction, molar ratio alcohol-acid, and catalyst concentration. If the experiment is carried out in excess of alcohol, the equilibrium can be shifted towards the products of the reaction, thus promoting the conversion to ester.

Figure 2 describes the mechanism of acid esterification: the function of the strong acid is the protonated carboxylic acid (fatty acid). The oxygen of the alcohol attacks the carbonyl of conjugate acid generating a species not yet protonated. The transfer of the proton from the oxygen atom near to radical  $R_2$ -OH group is very fast.

The electrons are delocalised and a molecule of water is removed to form the conjugate acid of ester that losing a proton produces the ester (3).



Fig. 2 - Mechanism of the esterification reaction.

Water, a byproduct of esterification is continuously reused in the hydrolysis stage.

#### Material and methods

#### Experimental design

Experimental design of the tests to be performed and of working conditions was defined before starting the experiments, in order to obtain

useful elements for the established objectives. Planning of experiments by means of the factorial design 2<sup>3</sup> is a statistical tool used for experiments involving several factors, where it is necessary to study, for each response, the combined effect of these factors. With this factorial design it is possible to calculate the degree of dependence between variables and develop models to discriminate and quantify the fundamental dependence as accurately as possible.

The factorial design  $2^k$  is particularly useful in the early stages of experimental work, where many factors could be investigated. It provides the lowest number of experiments for which k factors can be studied in a full factorial design (4-5).

The experiments were conducted following an experimental matrix (created with the program STATISTIC 6.0).

The experiments were carried out according to a plan that comprises eight experiments and three central points obtained from analyses repeated at intermediate conditions respecting those planned regarding: operating temperature, molar ratio and concentration of the catalyst.

Different tests were performed to assess the influence of parameters such as the temperature variation for both reactions, the molar ratio oil/water for hydrolysis, the fatty acid/methanol ratio for esterification, and the concentration of the catalyst.

#### Method

All reactions, hydrolysis and esterification, were conducted in a reactor (Parr Instruments Inc. – Model 4842)-type autoclave, consisting of stainless steel volume of 600 ml and maximum pressure up to 10,000 psi job, with a pipe to extract the sample, automatic rotation and heating mantle.

The percentage of free fatty acid was calculated by titration with NaOH 0.25 N (Method proposed by AOCS, American Oil Chemists Society, Ca-40 method).

Titration determined the amount of sodium hydroxide needed to neutralize the free fatty acids present in solution. In the Erlenmeyer flask there is about 1 g of sample, 25 mL of ethanol, 1 mL of phenolphthalein, 3 drops of 0.1 N NaOH, and the title with NaOH 0.25 N.

Fatty acid composition of canola oil and the analysis of biodiesel samples were conducted by Agilent 6890N gas chromatography apparatus equipped with flame ionization detector.

TABLE 1

### TABLE 2

Experiments	R.M.	T	C
-	(g/mol)	(°C)	(%m/m)
1	5 (-1)	250 (-1)	0 (-1)
2	20 (+1)	250 (-1)	0 (-1)
3	5 (-1)	300 (+1)	0 (-1)
4	20 (+1)	300 (+1)	0 (-1)
5	5 (-1)	250 (-1)	20 (+1)
6	20 (+1)	250 (-1)	20 (+1)
7	5 (-1)	300 (+1)	20 (+1)
8	20 (+1)	300 (+1)	20 (+1)
9 (C)	12.5 (0)	275 (0)	10 (0)
10 (C)	12.5 (0)	275 (0)	10 (0)
11 (C)	12.5 (0)	275 (0)	10 (0)

#### PLANNED EXPERIMENTS OF HYDROLYSIS

#### PLANNED EXPERIMENTS OF ESTERIFICATION

Even oview on ta	R.M.	Т	С
Experiments	(g/mol)	(°C)	(%m/m)
1	1.2 (-1)	150 (-1)	0 (-1)
2	3.0 (+1)	150 (-1)	0 (-1)
3	1.2 (-1)	200 (+1)	0 (-1)
4	3.0 (+1)	200 (+1)	0 (-1)
5	1.2 (-1)	150 (-1)	20 (+1)
6	3.0 (+1)	150 (-1)	20 (+1)
7	1.2 (-1)	200 (+1)	20 (+1)
8	3.0 (+1)	200 (+1)	20 (+1)
9 (C)	2.1 (0)	175 (0)	10 (0)
10 (C)	2.1 (0)	175 (0)	10 (0)
11 (C)	2.1 (0)	175 (0)	10 (0)

#### Hydrolysis

The working conditions used were chosen according to results obtained in experiments made with castor oil and soy (6).

The low level of molar ratio (oil:water 1:5) was chosen because it is near to the stoichiometric ratio (1:3); high level (1:20), because it was chosen to work with an excess water; this parameter (1:20) is to avoid in an industrial process.

For the temperature, the low level (250 °C) was chosen because at 200 °C it would not be possible to obtain a good yield of fatty acid; high level was restricted to 300 °C. In fact the industrial plants that produce fatty acid work at temperatures between 285 to 290 °C.

The concentration of the catalyst was 0% and 20%. Niobic acid was used because among those solid catalyst acid it is the one that give last problems with water (7).

The reagents used in the reactions are: commercial rapeseed oil (initial acidity: 0.17%), distilled water. Powdered niobic acid [(HY-340) supplied from to CBMM (Companhia Brasileira de Mineração e Metalurgia)] was used for both reactions (hydrolysis and esterification).

The reaction conversion yield was evaluated by measuring the acidity index (%) of samples collected at different stages (5, 10, 15, 20, 25, 30, 45, 60 min) of the process.

The percentage of fatty acid formed during the hydrolysis was calculated by the following equation:

Index of acidity (%) =  $A_t = (R*V)/M_a$ 

 $M_a = mass$  of the sample taken

V = volume of 0.25 N NaOH used for titration

R = value ranging between 6.99 and 7.05

Because the acidity calculated at time t is "contaminated" by water and glycerol, the final values are calculated by reference to the dry sample.

Efficiency of Hydrolysis (%) =  $R = A_t \times \{[(A_s - A_u) \times 100]/A_s\} + A_t$ 

 $A_t$  = acidity at the time t

 $A_s =$  the dry acidity

 $A_u = acidity of the sample 60 min.$ 

At the end of reaction the product was decanted in a separator funnel for one hour, fatty acid and glycerol were separated.

The glycerol was eliminated and fatty acid was washed (two times) with distillated water and then heated at 110-120  $^{\circ}$ C.

At the end of the hydrolysis, the fatty acid was separated from glycerol while the catalyst, when used, can be recovered through filtration.

#### Esterification

The low level of molar ratio (fatty acid:methanol 1:1.2) was chosen because it is near to stoichiometric ratio (1:1); high level (1:3), because it was chosen to work with an excess of alcohol. The lowest (150  $^{\circ}$ C) and highest temperature (200  $^{\circ}$ C) were chosen according to what is reported in literature (8-9).

The concentration of the catalyst was between 0% and 20%.

The reagents used in the reactions are: fatty acid (from hydrolysis of canola oil), anhydrous methanol as esterification agent.

Instruments and methodology are the same used in the reaction of hydrolysis.

The esterification's efficiency was calculated by the equation:

**Efficiency** (%) =  $[(A_{bco}-A_a)/A_{bco}]*100$ 

 $A_{bco}$  = acidity of white sample (taken before the T reactor reaches the value set)  $A_a$  = acidity of the sample time t

At the end of the reaction the product was centrifuged to separate the catalyst and then it was heated to remove water, which is a by-product of the reaction of esterification.

#### **Results and discussion**

The results of experiments are reported in Table 3 for hydrolisys and Table 4, for esterification.

#### Hydrolysis

The concentration of catalyst is relevant in the first 30 minutes of reaction working at a temperature of 250 °C, at the lowest molar ratio (oil:water 1:5 *Fig. 3* up) and at the highest molar ratio (oil:water 1:20 *Fig. 3* down).

The reactions carried out at temperature of 300 °C have variable results: when using niobic acid the best conversion yields were obtained with a small amount of water; without  $Nb_2O_5$  the best conversion yields were obtained at the highest molar ratio.

This behaviour can be explained by the fact that canola oil, compared to other oils, has more unsaturated fatty acids, and therefore it is a reactive oil, even in the absence of  $Nb_2O_5$ .

This experiment shows the reversible nature of the hydrolysis reaction. On the whole the best conversion yields were obtained working with a small amount of water and 20% of niobic acid.

#### Esterification

The best yield obtained in the esterification was observed working with excess methanol (fatty acid:methanol 1:3) and at a temperature of 200 °C, the concentration of catalyst is only relevant in the first 40 minutes of reaction (*Fig.4* up). After one hour, even non-catalytic reaction produced high conversion yields at 200 °C. The reactions carried out at low temperature (150 °C) good yields were obtained with niobic acid.

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# MR= MOLAR RATIO OIL:WATER (g/mol); T= TEMPERATURE (°C); C= AMOUNT OF NB<sub>2</sub>O<sub>5</sub> (% m/m); R= YIELD FROM 5 TO 60 MIN. (%); RS = YIELD OF DRIED SAMPLE (%). THE EXPERIMENTS RESULTS OF HYDROLYSIS

Experiments	RM	T	C	R5	${f R}_{10}$	$\mathbf{R}_{15}$	$\mathbf{R}_{20}$	$\mathbf{R}_{25}$	$\mathbf{R}_{30}$	$\mathbf{R}_{45}$	${f R}_{60}$	$\mathbf{R}_{\mathrm{S}}$
1	5	250	0	2.2	5.1	7.3	12.2	17.8	26.5	39.0	55.2	65.3
2	20	250	0	1.4	ю	7.2	13.6	24.4	28.0	44.4	64.4	69
3	5	300	0	2.9	37.3	51	55.6	57.9	57.5	57.3	56.7	75.7
4	20	300	0	60.7	74.5	76.5	72.1	70.9	74.0	70.5	72.8	77.0
5	5	250	20	6.6	22.6	34.9	43.5	48.8	56.4	59.8	70.3	71.5
6	20	250	20	18.2	43.7	46.3	48.4	55.1	64.6	65.1	70.7	82.8
L	5	300	20	37.8	60.0	70.5	84.4	82.6	87.6	86.8	84.5	85.5
8	20	300	20	6.8	43.2	51.3	41.8	62.6	66.8	73.0	86.3	88.5
6	12.5	275	10	10.7	55.5	68.3	75.0	72.3	72.0	73.0	81.9	84.1
10	12.5	275	10	11.0	55.9	68.9	75.4	72.8	71.9	72.5	82.6	84.2
11	12.5	275	10	10.6	55.7	68.5	75.0	72.1	72.1	71.8	81.3	85.0

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Fatty acids, obtained from hydrolysis of canola oil, were analised by Agilent 6890N gas chromatography apparatus equipped with flame ionization detector.

This analysis is to assess the degree sample of purity. After the hidrolysis reaction, 1ml of product was taken and placed in a test tube of 5 mL.





*Fig. 3* - Reaction of hydrolysis with different temperatures and percentages of niobic acid, molar ratio costant (1:5 up and 1:20 down)

Experiments	RM	Τ	C	$\mathbf{R}_{10}$	$\mathbf{R}_{20}$	$\mathbf{R}_{30}$	${f R}_{40}$	$\mathbf{R}_{50}$	${f R}_{60}$	$\mathbf{R}_{\mathrm{S}}$
	1.2	150	0	7.4	18.4	25.9	33.3	37.4	44.4	53.2
2	с,	150	0	23.5	31.7	37.8	49.6	53.4	58.9	59.1
3	1.2	200	0	31.2	43.4	48	51.9	55.2	58.2	59.3
4	3	200	0	60.4	65.7	75.2	75.8	81.8	83.8	85.6
5	1.2	150	20	13.9	35.8	45	49.3	48.9	54.4	63.1
6	ю	150	20	57.7	61.7	74.2	74.0	75.2	75.4	79.1
L	1.2	200	20	71.7	70.6	72.2	70	75.1	73.3	75
8	3	200	20	77.2	85.1	89.7	93.6	87.0	88.7	88.1
6	2.1	175	10	69.3	85.6	6.98	87	84.1	85.0	62.6
10	2.1	175	10	69.3	85.5	87.6	87.2	85.2	85.3	62
11	2.1	175	10	70	86.4	87.7	87.7	85.0	85.4	62.1

MR= MOLAR RATIO OIL:WATER (g/mol); T= TEMPERATURE (°C); C= AMOUNT OF NB<sub>2</sub>O<sub>5</sub> (% m/m); R= YIELD FROM 5 TO 60 MIN. (%); RS = YIELD OF DRIED SAMPLE (%). THE EXPERIMENTS RESULTS OF ESTERIFICATION

TABLE 4

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*Fig.4* - Reaction of esterification with different temperatures and percentages of niobic acid, molar ratio costant (1:1.2 up and 1:3 down)

The sample was diluted in chloroform P.A. (in proportion 1:1 m/m), to remove any impurities still present. The test tube was put in centrifuge for ten minutes.

The supernatant was taken  $(1\mu L)$  and it was injected into the gas chromatograph, after the addition of internal standard.

The chromatograms of the experiments that produced the best conversions (for hydrolysis) are shown in Figures 5 and 6.



*Fig.6* - Chromatogram T=300 °C, R.M.=1:20 e Nb<sub>2</sub>O<sub>5</sub> =20%

The chromatograms show that varying the conditions of reaction, the yields of the process were changed, but the purity of the product was good. As shown in the Table 5, the reaction products have a purity greater than 90%.

#### TABLE 5

Molar Ratio	<b>Temperature</b> (°C)	Catayst (%)	Acidity Titrated (%)	Fatty acid (%)
1:5	300	20	85.5	94.62
1:20	300	20	88.5	95.51

RESULTS OF THE PERCENTAGES OF FATTY ACID IN SAMPLE OF HYDROLYSIS REACTIONS

Also the products of esterification reactions were subjected to chromatographic analysis.

Figure 7 shows the chromatogram of sample taken before the fatty acid is transformed into ester, in fact peaks of ester are not visible. At the end of the esterification, the peaks of the different esters are distinguished very well, mainly oleic ester (Figure 8).



Fig. 7 - Chromatograms white sample T=100 °C, R.M.=1:3 e 20% di Nb<sub>2</sub>O<sub>5</sub>



Fig. 8 - Chromatograms T=200 °C, R.M.=1:3 20% di Nb<sub>2</sub>O<sub>5</sub>

#### Statistic data analysis

The results obtained in the experiments were used to build a linear regression (with software statistic 6.0), it was made for all experiments at the different times and it determined the parameters statistically significant, with confidence levels of 95%. The linear regression model was created with experimental data. The mathematical equation written below, describes the linear regression model used:

$$\begin{split} \mathbf{Y} = \ \beta_0 + \beta_1 \ R.M. + \beta_2 T. + \beta_3 C. + \beta_4 \ R.M. *T. + \beta_5 R.M. *C. + \ \beta_6 \ T. \\ *C + \ \beta_7 \ R.M. *T*C. + \ \epsilon \end{split}$$

The coefficients to estimate are:  $\beta_0$ ,  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ,  $\beta_4$ ,  $\beta_5$ ,  $\beta_6$ ,  $\beta_7$ . The statistical analysis was carried out encoding variables as -1 and +1, because those used in the experimental program have different units of measurement (°C, %) (Table 6).

ESTIMATEI Estimate: E*=	D EFFECT	S FOR CO $B_0 = INTF$ $3 = NB_2O_5$	NVERSIO FOR ERCEPT; B B <sub>4</sub> = R.M. <sup>3</sup>	NS OBTAI HYDROL I <sub>1</sub> = MOLA T; B <sub>5</sub> = R	NED IN T XSIS REA R RATIO; .M.*C. ; B	THE DIFFH ACTION. B <sub>2</sub> = TEM 6 = T.*C.; ]	ERENT TII IPERATUF B <sub>7</sub> = R.M.* Sent the	ME (FRON RE; T.*C.; ` fferct	15 TO 60	MIN.),
0			STATIST	LUES UN	NIFICAN	CE (P> 0.0	<b>1</b> 5)			-
min.	β0	β <sub>1</sub>	ß2	ß3	β4	β5	β6	₿7	*w	${ m R}^2$
5	10.76±0.13	-1.69±0.13	8.85±0.13	16.63±0.13	-7.10±0.13	-8.02±0.13	$1.04 \pm 0.13$	-14.22±0.13	0.03	0.99
10	55.71±0.08	5.62±0.08	30.91±0.08	14.25±0.08	-3.91±0.08	-3.51±0.08	-12.47±0.08	-15.06±0.08	0.05	0.99
15	68.54±0.11	$5,.8{\pm}0.11$	39.38±0.11	16.59±0.11	-0.27±0.11	-9.29±0.11	-19.08±0.11	-15.06±0.11	0.09	0.99
20	75.13±0.07	-0.36±0.07	38.60±0.07	15.32±0.07	-3.52±0.07	-13.42±0.07	-16.42±0.07	-15.20±0.07	0.04	0.99
25	72.38±0.13	5.70±0.13	36.19±0.13	19.20±0.13	-0.76±0.13	-12.52±0.13	-15.54±0.13	-12.45±0.13	0.14	0.99
30	72.03±0.04	4.48±0.04	30.72±0.04	20.05±0.04	-0.34±0.04	-12.52±0.04	-14.02±0.04	-14.11±0.04	0.01	0.99
45	72.46±0.20	6.37±0.20	23.73±0.20	14.51±0.20	$1.05 \pm 0.20$	-10.65±0.20	-6.23±0.20	-10.63±0.20	0.32	0.99
60	81.91±0.23	7.66±0.23	10.71±0.23	14.87±0.23	2.86±0.23	-6.56±0.23	4.18±0.23	-2.19±0.23	0.43	0.99

TABLE 6

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Table 6 shows the values of the parameters estimated for every variable and its interaction, standard deviation and coefficient of multiple determination ( $R^2$ ). The values are reported by the influence of that the variables have on yield Y; it is the transformation of the triglyceride into fatty acid during times of reaction (from 5 to 60 min.).

Table 7 shows the linear regression models for hydrolysis reaction. The models obtained confirmed that the temperature is the most influential variable in the system; the second is catalyst. Molar ratio is considerable when niobic acid is used, in fact using  $Nb_2O_5$ , the best yields are obtained working with a small amount of water.

#### TABLE 7

#### REGRESSION MODELS OBTAINED WITH VALUES OF REGRESSION COEFFICIENTS FOR HYDROLYSIS. CALCULATED FOR THE CON-VERSION OBTAINED IN THE HYDROLYSIS REACTIONS.

min.	Model
5	10.76 -0.85 R.M.+4.43T+5.83C-3.55RM*T-4.01R.M.*C+0.52T*C-7.11R.M.*T*C
10	55.71+ 2.81R.M.+15.45T+8.31C-1.95RM*T-1.75R.M.*C-6.24T*C-7.53R.M.*T*C
15	68.54 + 2.69RM + 19.69T + 7.12C - 4.65RM*C - 9.54 T*C -7.53 RM*T*C
20	75.13+ 19.30T + 8.30C - 1.76RM*T - 6.71RM*C - 8.21 T*C - 7.60 RM*T*C
25	72.38- 2.85RM + 18.09T + 7.66C- 6.26RM*C - 7.77 T*C - 6.22 RM*T*C
30	72.03+ 2.24RM + 15.36T + 9.60C - 0.17RM*T - 5.41RM*C - 7.01 T*C - 7.06 RM*T*C
45	72.46 +3.19RM + 11.86T + 7.25C - 5.32RM*C - 3.12 T*C - 5.32 RM*T*C
60	81.91 +3.83RM + 5.35T + 7.43C + 1.43RM*T – 3.28RM*C + 2.09 T*C - 1.10 RM*T*C

Figure 9 represents the values observed on predicted values for hydrolysis. The linear regression models created are appropriate because the values are near to the line and the values of  $R^2$  are equal to 0.99.



*Fig. 9* - Graphic of observed values on predicted values for hydrolysis reaction after 60 minutes.

In Tables 8 e Figure 10 the estimated effects for conversion obtained in the different time and the linear regression model for esterification reported, respectively.

#### TABLE 8

#### REGRESSION MODELS OBTAINED WITH VALUES OF REGRESSION COEFFICIENTS FOR ESTERIFICATION

min	model
10	42.85 + 11.82RM + 17.25T + 12.25C - 3.16RM*T +2.09 T*C - 6.43 RM*T*C
20	m51.55 +9.50RM + 14.65 T + 11.74C -2.5 5 RM*T*C
30	58.51 + 10.73RM + 12.77T + 11.77C + +0.94RM*C - 2.09T*C -3.37 RM*T*C
40	62.19 – 11.06RM + 10.63 T + 9.53C + 0.82RM*T + 1.02RM*C -0.56 T*C -1.08 RM*T*C
50	64.25 – 10.10RM + 10.53T + 7.31C - 1.02 T*C - 3.13 RM*T*C
60	67.16 + 8.86T +5.82C + 0.69RM*T – 0.48RM*C - 0.82 T*C - 2.08 RM*T*C

The Figure 10 represents the values observed on predicted values for esterification. The linear regression models created are appropriate because the values are near to the line and the values of  $R^2$  are equal to 0.99.



*Fig. 10* - Graphic of observed values on predicted values for esterification reaction after 60 minutes.

#### Conclusion

For hydrolysis reactions, the best conversions rates were obtained at 300 °C with 20% of catalyst: at the highest molar ratio (oil:water 1:20) the conversion rate was 88.49% and at the lowest molar ratio (oil:water 1:5) the conversion was 84.53%.

For esterification reactions, the best conversion rates were obtained working with excess methanol (molar ratio fatty-acid:methanol 1:3) and at a temperature of 200 °C. in the presence of  $Nb_2O_5$ .

The research has allowed us to obtain some important results such as: - Simplifying the process,

- Good separation of the product (which shows a low degree of impurity),

- Confirmation that the process can be used for other feedstocks,

- Contained costs,

Nevertheless, there also some critical aspects:

niobic acid: shows low impact for laboratory reactions, while experiments on prototype plants seem to indicate a significant role temperature: has a significant influence on process time as a function of its yield.

It is important to evaluate the possibility of optimising some parameters that can have a certain effect on such choices (temperature, niobic acid percentage, time and efficiency of the process).

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