OPEN
JOURNAL
SYSTEMS
ISSN: 2675-3065

Environment (Brazil), v.3, n.4. 002-013 (2021)

Environment (Brazil)

Manuel et al

Catalytic efficiency of bone extracted CaO for the trans-sterification reaction

Albano Kanga Manuel[1,2], Pedro Guilherme João[1,2], Isaú Alfredo Bernardo Quissindo[3], Kabongo Mutobola Celestino[2,4]

[1]*Faculty of Engineering at Agostinho Neto University, Luanda-Angola.*
[2]*Laboratory of Catalysis, Fine Chemistry and Renewable Energies (LACAFINER), Luanda-Angola.*
[3]*Faculty of Agrarian Sciences from José Eduardo dos Santos University (UJES), Huambo-Angola.*
[4]*Higher Polytechnic Institute of Moxico (ISPM), Moxico-Angola. (Corresponding author: kabongomutobola19@gmail.com).*

(Paper of event: Special Edition - Angola) Submitted on: 21/04/2021 Revised on:15/05/2021 Accepted on: 18/05/2021

ABSTRACT

In this work, it was made a comparative study of biodiesel synthesis by transesterification reaction of *mufuko* oil with methanol in the presence of NaOH and a heterogeneous catalyst based on CaO and MgO extracted from bovine bones. The catalyst was prepared by extraction of Ca2+ and Mg2+ ions from bones with acetic acid, and precipitation of $CaCO3$ and $MgCO3$ followed by calcination at 550 ºC to obtain CaO and MgO. The activation of the catalyst was performed at 200 ºC. The CaO and MgO composition of the catalyst was 97.50% and 1.75% respectively. Tomography analysis showed an abrasive crystalline structure and RD-X showed a parallelepiped shape with a density of 3.30 g/cm3. The biodiesel synthesis carried out using NaOH as catalyst showed a yield of 74.6% while with CaO, the same was around 69.8%. The biodiesel obtained by our heterogeneous catalyst falls within the admissible limit values of the international quality standards defined by ASTM-D and EN/ISO. Thus, this study provides a new process of preparation of heterogeneous catalyst based on CaO and MgO, low cost and efficient to be used in the synthesis of biodiesel with an environmental advantage because values the use of waste organic matter.

Keywords: Transesterification, Biodiesel, CaO and MgO catalyst, Bovine bones.

Eficiência catalítica de CaO extraído de ossos de origem bovina para reação de transesterificão

RESUMO

Neste estudo fez-se um estudo comparativo de síntese de biodiesel por reacção de transesterificação de óleo de *mufuko* com o metanol em presença de NaOH e de um catalisador composto de 97,50% de CaO e 1,75% de MgO extraído de ossos de origem bovina. Esse catalisador foi preparado por extracção dos iões Ca2+ e Mg2+ dos ossos com o ácido acético e precipitação em $CaCO3$ e $MgCO3$ seguida de calcinação à 550 ºC para obter o CaO e MgO. A activação do catalisador realizou-se à 200 ºC. A análise deste catalisador por tomografia e RX-D mostrou uma estrutura cristalina abrasiva e uma forma paralelepipédica com uma densidade de 3.30 g/cm3. A síntese de biodiesel realizada usando NaOH como catalisador apresentou um rendimento de 74.6% enquanto que com este catalisador, o rendimento situou-se em torno de 69.8%. O biodiesel obtido por reação de transesterificação catalisada por CaO e MgO enquadra-se nos valores limites admissíveis dos padrões internacionais de qualidade definidos pelas normas ASTM-D e EN/ISO. Assim este trabalho aporta um novo processo de preparação de um catalisador heterogéneo à base de CaO e MgO; a baixo custo e eficiente para ser usado na síntese de biodiesel com vantagem ambiental, pois valoriza o uso de resíduos de matérias orgânicas.

Palavras-Chaves: Transesterificação, Biodiesel, Catalisador de CaO e MgO, Ossos de bovinos.

Manuel, A.K., João, P.G., Quissindo, I.A.B., Celestino, K.M. (2021). Catalytic efficiency of bone extracted CaO for the trans-sterification reaction. **Environment (Brazil)**, v.3, n.4, p.02-13.

1. Introduction

In general, biodiesel is defined as a mono - alkyl ester of fatty acids from vegetable or animal oil and is produced mainly by the transesterification reaction of these oils in the presence of a short chain alcohol such as methanol, ethanol, propanol, or butanol (Cordeiro, 2014). This process decreases the viscosity of the oil and consequently improves diesel engine performance (Shu & Yang, 2017).

The reaction occurs in homogeneous or heterogeneous catalytic medium and can be influenced by some factors such as the purity of the reactants, the type of alcohol, the type of catalyst, the oil / alcohol molar ratio, the agitation of the mixture, the temperature, and the reaction time.

Homogeneous catalysis in alkaline medium is the predominant technological route for biodiesel production due to its greater speed, simplicity, and efficiency. However, homogeneous catalysts have the disadvantage of being in the same phase as the reactants, products, and waste, requiring various methods of separation and washing, which hinders the final purification step of the biodiesel obtained (Singh & Prata, 2014).

Acid catalytic transesterification is not widely used, mainly because it is a slower reaction than basic catalysis. However, it has the advantage of not being affected by the presence of free fatty acids in the feedstock, of not producing soap during the reaction and of simultaneously catalysing esterification and transesterification reactions (Gustavo, 2016).

Heterogeneous catalysis, in the case of CaO and SrO, can achieve yields of about 98% and their catalysts are easily removed from the process by simple filtration, but the cost of their preparation is higher (Wenlei, Hong, & Lingong, 2017). Thus, the need arises to prepare a heterogeneous catalyst that can be easily removed from the reaction mixture and reused more often. In this case the feedstock should be abundant, low cost and environmentally sustainable.

Therefore, in this work, similar to the researchers Vâny et al. (2018), who prepared the catalyst from chicken eggshells for transesterification, it is proposed to prepare a catalyst based on calcium oxide extracted from bones of bovine origin whose waste is an environmental problem.

2. Material and Methods

2.1. Material

The materials used for calcium precipitation are:

- Test tube, pipette and funnel;
- Lamp, tripod and asbestos net;
- Wooden tweezers;
- Cylinder;
- Balance;
- Erlenmeyer flask;
- Heating plate.

2.2. Preparation methods

Applied in study the Colsar (1980) methodology in a total leaching in sulfuric acid of heterogeneous copper and cobalt minerals followed by selective precipitation according to the pH and oxidation-reduction potential of each metal, to the organic compounds but using the acid acetic to extract calcium from bones and calcination after precipitation. Thus, the preparation of the catalyst from bones of bovine origin took place in three ways with different processes, namely:

1. Selective extraction of Ca^{2+} ion from bones by dissolving in 10% CH_3COOH followed by precipitation with Na_2CO_3 to obtain $CaCO_3$ and $MgCO_3$, which in turn were subjected to calcination at 550 ºC to form CaO and MgO.

2. Complete bone leaching in concentrated H_2SO_4 precipitating $CaSO_4$ and $MgSO_4$ which were subjected to calcination at 500 ºC to obtain CaO and MgO.

3. Direct pyrolysis of bones at 900 ºC to obtain the ash composed of CaO and MgO.

The steps for preparing the catalyst from bones of bovine origin by the first route are:

1. Extraction of calcium from bones of bovine origin by leaching in acetic acid;
2. Precipitation of calcium and magnesium with Na_2CO_3;
3. Drying and heat treatment of the catalyst at 550 ºC;
4. Physico-chemical characterization and application in transesterification;
5. Evaluation of reaction and economic efficiency

The characterization of the catalyst was done using the methods of 3D-tomography, RX-D and Electron Scanning Microscopy. The study of the reaction kinetics and the oil conversion rate for biodiesel was carried out by applying the differential method and by monitoring the acidity index as a function of time (Colsar, 1980). The efficiency of the CaO catalyst was evaluated by comparison with that of NaOH under the same working conditions.

In the analysis of the catalytic activity of NaOH and CaO + MgO in the transesterification reaction, the formula proposed by Colsar (1980) was used:

$$\frac{1}{A} - \frac{1}{A0} = k.t,$$

Where:
- A is the fatty acid concentration after a certain reaction time.
- A0 is the concentration of fatty acid at the beginning of the reaction.

The units for each variable are:
- Reaction time: min
- Concentration: mg KOH/g
- Speed constant – k: L/mol.s

3. Results and discussion

3.1 Preparation of the catalyst

The preparation of the CaO catalyst from bones of bovine origin was carried out in three procedural routes mentioned above. The first route is to extract calcium from the bones with CH3COOH (Leaching):

Bone + $CH_3COOH \rightarrow Ca^{2+} + Mg^{2+}$ + organic waste.

Figure 1 shows the bone reagents, acetic acid and the Ca^{2+} and Mg^{2+} ion solution with waste.

Figure 1 - Crushed bones, acetic acid, and the dissolution of calcium with waste

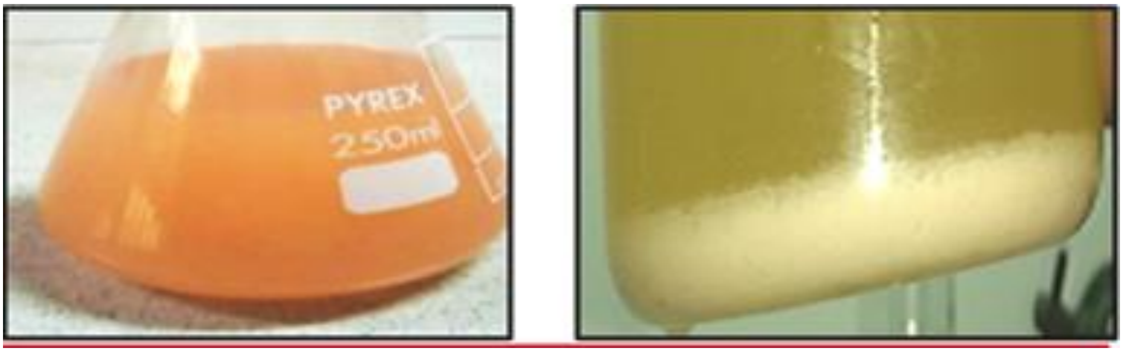
Bone ***CH_3COOH*** ***Ca^{2+}, Mg^{2+}, waste***

Source: Authors (2021)

Acetic acid selectively discontents calcium and magnesium, made after analysis of food seasoning sauce with vinegar. It is known that vinegar is mainly composed of acetic acid, from which it was used for the operation of calcium extraction from crushed bones. This was done in 3 (three) hours at the temperature of 85 and 100 ºC and a agitation of about 300 r/min. In this process, the organic residues were separated from the $(CH3COO)_2$ Ca and $(CH3COO)_2$ Mg solution by filtration. Anhydrous 50% w / v NaOH was added until MgO precipitation at pH 13 separated also by filtration.

It was noted that magnesium was not depleted. Then Ca2+ was precipitated in $CaCO_3$ by adding Na_2CO_3 as shown in the following Figure 2, on the right an organic sediment and a overflow of calcium and magnesium solution with about 11.24 mg/mL% and 4.1 mg/mL, respectively.

Figure 2 - Ca^{2+} leaching, Mg^{2+} photo on the left and Ca^{2+} precipitation in $CaCO_3$, photo on the right



Source: Authors (2021)

The operation was repeated several times to optimize the extraction. After precipitation, a white precipitate formed at the bottom of the conical flask, consisting of Ca CO_3 and $MgCO_3$ resulting from the following reactions:

$$Ca^{2+} + Mg^{2+} + CO^{32-} \rightarrow Ca\ CO_3 + MgCO_3$$

Then the calcium and magnesium bicarbonate were calcined at 550 ºC to produce calcium oxide and magnesium oxide:

$$Ca\quad CO_3 \quad + \quad 550°C \quad 550°C\ MgCO_3 \quad \rightarrow \quad CaO + MgO + 2CO_2$$

This is re-calcined before being placed in the form of 0.5 mm diameter and 2 mm high tablets as shown in figure 3.

Figure 3 – Wafer-shaped catalyst

Source: Authors (2021)

The pellet-shaped catalyst is activated by subjecting it to a temperature of 200°C for 5 hours. Calcium and magnesium exist only in the oxidation state +2 and its activation consists of increased size and intermolecular sites by heating the tablet. This will allow for greater contact surface and opening of insert pores thus allowed reaction acceleration. Heating decreases the ionic bond strength between oxygen and calcium thus allowing the hydrogen bridge connection with acetic acid in the reactional mechanism of transesterification. That's why cooling mode is important for structural repositioning. Brutal cooling allows the fixation of molecules in the excited position with weak iniocbonds.

The second route of CaO preparation consists of precipitation of Ca^{2+} and Mg^{2+} into $CaSO_4$ and $MgSO_4$ using concentrated H_2SO_4 (Figure 4) followed by calcination of these precipitates at 550 ºC to obtain CaO, MgO and sulphides.

Figure 4 – White precipitate of $CaSO_4$ and $MgSO_4$

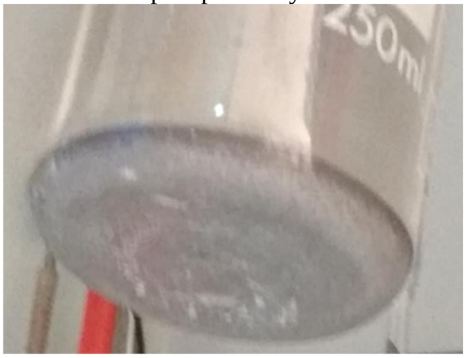
Source: Authors (2021)

At the same methode as the Paul Colsar process, which uses sulfuric acid for total leaching of copper and cobalt operation followed by differential precipitation by pH variation, the same used to dissolve the bovine bone by dissolving all organic material and precipitate calcium and magnesium at pH inferable to 4. This precipitate was taken to calcination with desulfurization whose result of analisis by volumetry of complexation referred to above.

The third route of preparation of CaO catalyst is bone pyrolysis at 900 ºC obtaining a ash consisting of 55.42% CaO, 4.82% MgO and 42.4% phosphates.

To obtain CaO, phosphates were removed with a 10% citric acid solution. The ash passes from cizenta color to gray white color consisting of 86.75% CaO, 4.82% MgO and 9.2% phosphates.

Figure 5 – Removal of phosphates by dissolution in citric acid



Source: Authors (2021)

For n fact, leaching with sulfuric acid involved the formation of cácio sulfate. Calcination of the calcination produces calcium oxide, sulphur oxide and sulphides as illustrated by the following equation:

$$\mathrm{CaSO4} \quad 550^{\circ}\mathrm{C} \rightarrow \mathrm{CaO} + \mathrm{SO_2} + \mathrm{CaS} + \mathrm{S_2}$$

Similarly, direct calcination at 900 °C also produces sulphides and phosphates by bone having contained these elements in their composition.

When the leaching process with acetic acid was observed, selective extraction was observed by dissolution of cácio and magnesium. From this, the preparation of CaO catalyst was used in this work with this procedure that does not present any traces of sulphides or phosphates that are considered, in addition to additional costs of reagents and refining, as catalytic poison (catalytic inhibitor).

3.2 Calcium extraction yield from bovine bones and its composition

The extraction yield is the percentage ratio of the extracted amount of calcium (g) per amount of it contained in the sample and its chemical composition was determined by volumetry. Table 1 shows the calcium extraction yield and its composition.

Table 1 - Calcium extraction yield from bone and its composition

Sample	Crushed bones (g).	Calcium: in bone (g).	Calcium extracted (g).	Extraction yield (%).	Composition CaO (%)	CaO recalcined (%)
1	100	68.45	37.60	54.95	91.60	97.50
2	100	68.45	37.90	55.32	91.40	97.60
3	100	68.45	37.90	55.31	91.90	97.70
4	100	68.45	37.70	55.14	91.70	97.40
5	100	68.45	37.80	55.22	91.50	97.50
Average	**100**	**68.45**	**37.70**	**52.21**	**91.60**	**97.55**

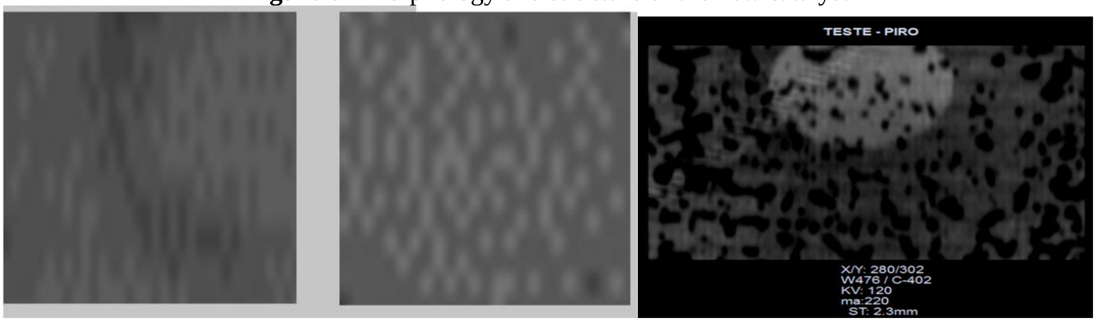
Source: Authors (2021)

The extraction yield by leaching with acetic acid is 52.21% and the CaO composition is 91.60%. After recalcination at 550ºC calcium and magnesium contents of 97.50% and 1.75% respectively were obtained.

3.3 Physico-chemical characterization of the catalyst prepared by leaching

Figures 6 and 7 present the structure tests by D-RX, density, and morphology by -3D tomography and Scanning Microscopy, respectively.

Figure 6 - Morphology and structure of the new catalyst



Source: Authors (2021)

The structure and chemical composition of calcium oxide determined by RX-D is of abrasive crystalline type with the parallelepiped shape with a density of 3.30 g/cm3 by tomography and a concentration of 97.5% by volumetry.

3.4 Catalytic activity of NaOH and CaO in the transesterification reaction

The catalytic activity of NaOH and CaO was studied by determining the speed of the transesterification reaction which provided the optimum time for each catalyst. The activity and selectivity of the CaO catalyst were evaluated by comparison with those of NaOH under the same working conditions.

The study of kinetics and the conversion rate from oil to biodiesel was carried out by monitoring acidity index as a function of reaction time.

The order of the reaction was determined by applying the integral method from experimental data of the evolution of the acidity concentration during the reaction as a function of time. Table 2 illustrates the conversion rate by the accumulated loss of acidity as a function of time for the transesterification reaction of mufuko oil with methanol using NaOH as a catalyst. That is, the conversion rate accumulated and´calculated by the difference between the inical concentration and the final or subsequent concentration multiplied by 100.

Table 2 - Conversion rate of fatty acids to FAAM, biodiesel in the transesterification of oil with methanol using NaOH as catalyst

Time (min)	A.I. (mg KOH/g)	Conversion rate (%)
0	5.95	0
15	3.12	47.6
26	2.30	61.4
45	1.60	73.1

56	0.58	90.5
70	0.51	94.3

Source: Authors (2021)

It is observed in Table 2 the evolution of biodiesel formation as a function of time and the conversion rate of oil to biodiesel. For the determination of the order, it was used the integral method of Van'Hoff based on the calculation of the specific speed constant from the expression of the reaction speed. For this purpose, the experimental data of sample collection at different time during the reaction were considered.

We experimented successively the adjustment of data for the integral equations different orders (zero, 1st and 2nd) in order to determine the specific speed constant. Table 3 shows the calculations for the determination of this constant that was adjusted with the equation of the integral method of the 2nd order reaction.

The results of the reaction velocity constant are shown in table 3.

Table 3 - Determination of specific rate constant, k, of the reaction of transesterification of *mufuko* oil with methanol using NaOH as catalyst

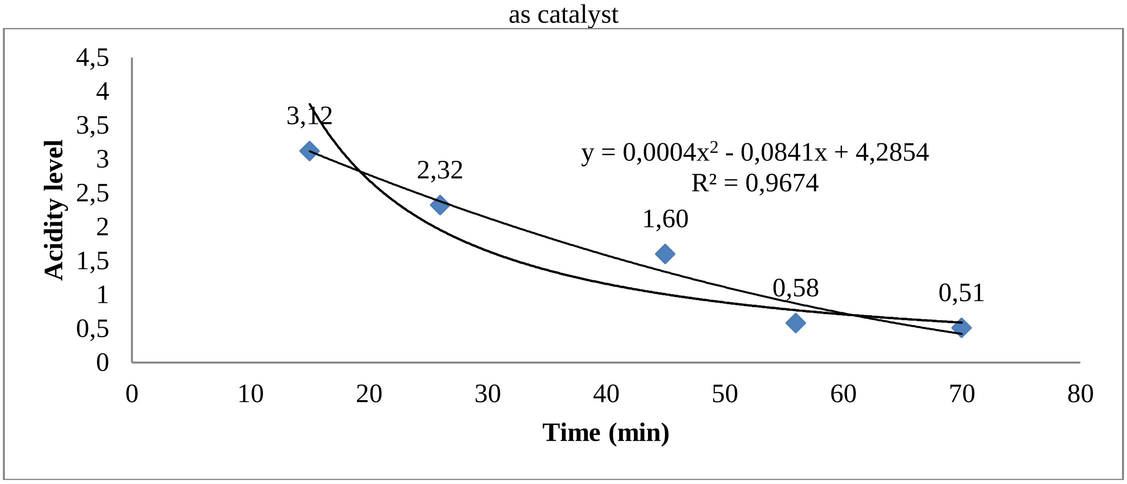
Reaction time (min)	Acidity level (Mg KOH/g)	Speed constant, k (L/mol.s)
0	5.95	0.000169
15	3.12	0.000167
26	2.32	0.000168
45	1.60	0.000166
56	0.58	0.000167
65	0.37	0.000169

Source: Authors (2021)

The table 3 shows the constancy of the speed constant on average of 0.000168 l/mol,s. That is, the integral equation of order 2 corresponds to the occurrence of this reaction.

It is possible to observe figures 7 and 8 which represent respectively the kinetics curve of the mufuko oil transesterification reaction (loss of reactant as a function of time) and the conversion rate into biodiesel (product formation as a function of time).

Figure 7 - Reagent loss as function of time with continuous sampling in oil transesterification with methanol and NaOH as catalyst

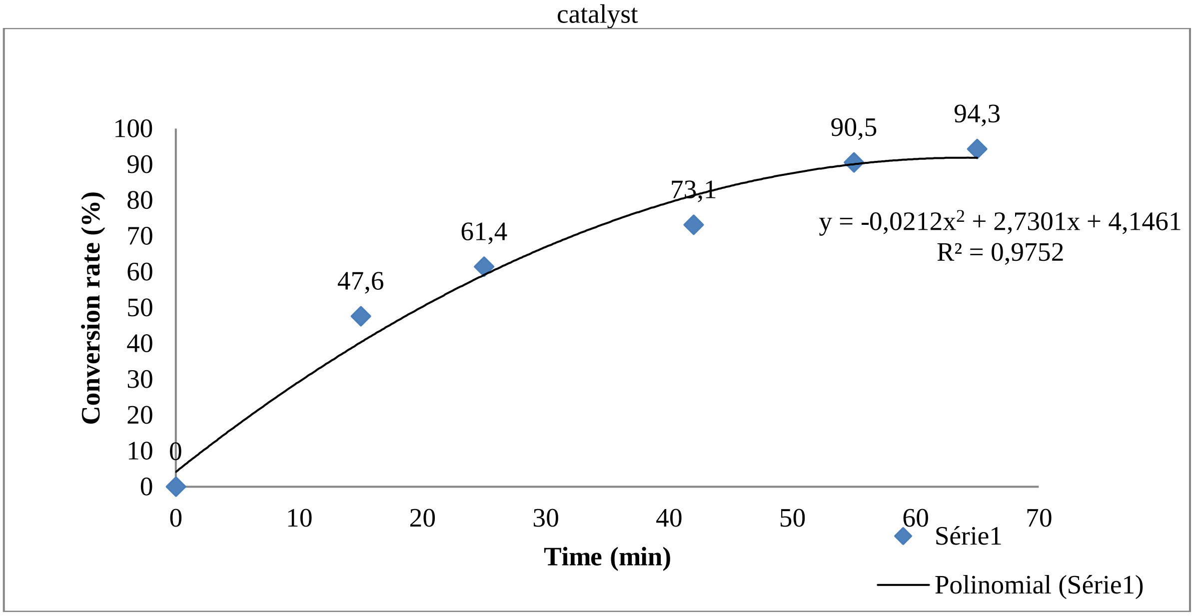


Source: Authors (2021)

The following figure shows the loss of acidity as a function of time in the occurrence of transesterification rection. From 5.95 to 3.12 it is phase in which the esterification in the presence of sulfuric acid as catalyst. From 3.12 to 0.51, transesteifiation was observed in the presence of sodium oxide as a catalyst. This is the substitution of acid group by the methyl group of biodiesel formation. The polynomial trend presents a regression of 96.74% Corresponding to a perfect correlation adjustment of the above-mentioned equation of the 2nd order reaction.

In figure 8 a conversion rate of 94.3% of glycerides from mufuko oil into biodiesel mono methyl esters can be observed.

Figure 8 - The product formation as a function of time (conversion rate of fatty acids to FAAM) using NaOH as catalyst



Source: Authors (2021)

The conversion rate of fatty acids to mono-methyl-esters, biodiesel, is 94.3% in the process with continuous sampling from the in-batch reactor. It is found that the reaction reaches dynamic equilibrium (low speed) between 70 and 90 minutes.

The kinetic study of the transesterification reaction of mufuko oil with methanol using the catalyst (CaO) was carried out monitoring also the loss of oil acidity index as a function of time. The conversion rate of the same into biodiesel was also determined from experimental data.

Table 4 - Conversion rate of fatty acids into FAAM, biodiesel in transesterification of oil with methanol using CaO as catalyst

Time: (min)	Sample (g)	Titration: VNaOH 0.5N (mL)	Index, acidity (mg KOH/g)	Conversion rate (%)
0	1.00	6.1	6.15	0
10	0.97	3.8	3.71	39.67
20	1.02	2.5	2.66	56.74
35	1.01	1.8	1.86	69.74
50	0.95	1.5	1.44	76.20
75	0.94	1.1	1.04	82.70
110	1.01	0.7	0.75	87.41
150	1.00	0.5	0.51	91.32
180	1.02	0.5	0.35	94.60

Source: Authors (2021)

Order of the reaction was determined by applying the integral method from experimental data of the evolution of the acidity concentration during the reaction as a function of time. Table 2 illustrates the conversion rate by the accumulated loss of acidity as a function of time for the transesterification reaction of *mufuko* oil with methanol using CaO as a catalyst. That is, the conversion rate accumulated and calculated by the difference between the initial concentration and the final or subsequent concentration multiplied by 100.

Similarly, the speed constant (k) of the reaction and its value was also determined as illustrated in table 5.

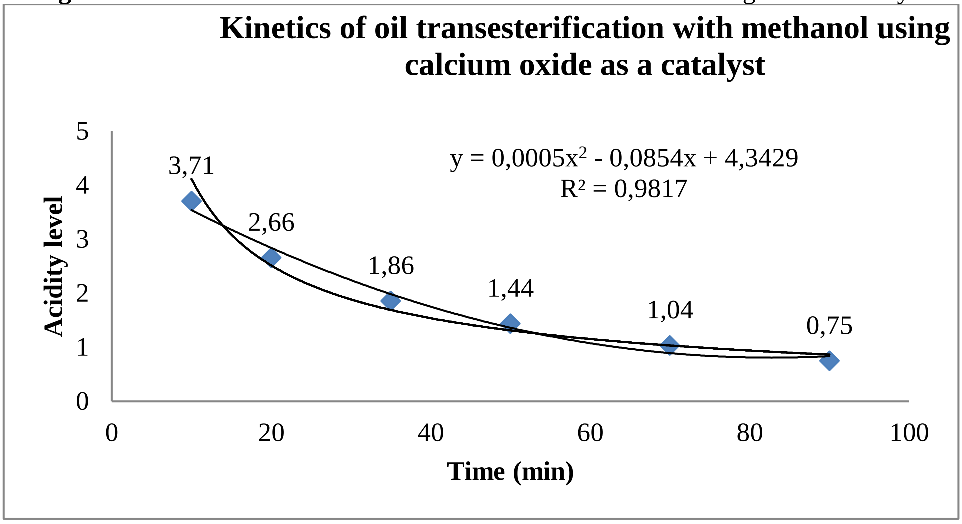
Table 5 - Determination of specific speed constant, k, of the reaction of transesterification of mufuko oil with methanol using CaO as catalyst

Reaction time(min)	Acidity level (mol)	Speed constant, k, (L/mol.s)
0	6.15	0.000171
10	3.71	0.000177
20	2.66	0.000179
35	1.86	0.000174
50	1.44	0.000178
75	1.04	0.000176
110	0.75	0.000178

Source: Authors (2021)

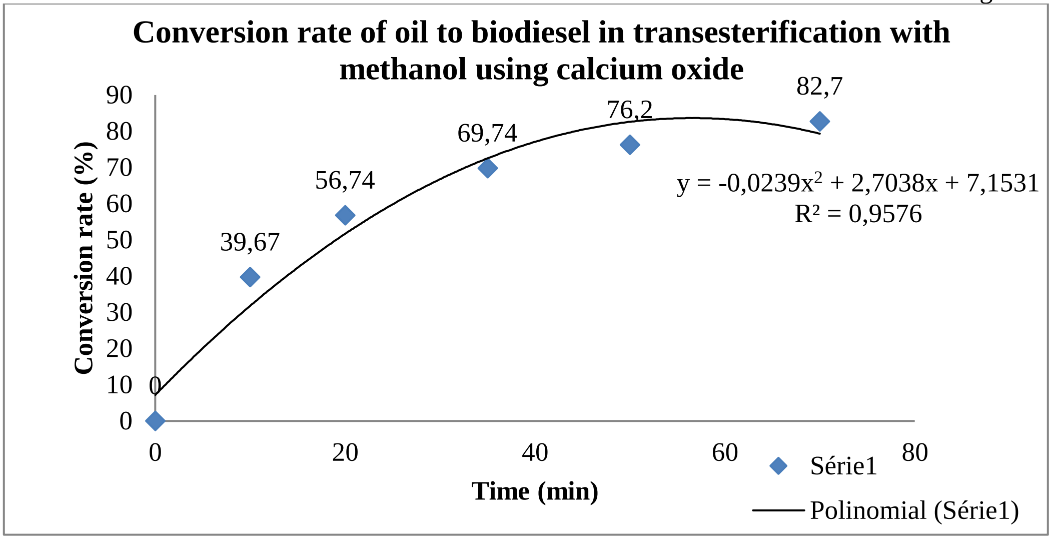
It is also possible to observe the velocity constant conforms to a 2nd order reaction by its integral equation: referenced above. The straight-line fitting and regression of reactant concentration variation and biodiesel formation as function of time are presented in figures 9 and 10.

Figure 9 - Kinetics of trans-esterification of oil and methanol using CaO as catalyst



Source: Authors (2021)

Figure 10 - Conversion rate of oil to biodiesel from the transesterification reaction with methanol using CaO as catalyst



Source: Authors (2021)

Figures 8 and 10 show that NaOH catalyst (94.3%) has the higher conversion rate compared to CaO (82.7%) considering the same working conditions as the reaction time (65 minutes), temperature (65 ºC) and oil/ethanol ratio (1/6). CaO reaches a conversion rate of 94.7% after 110 minutes.

Knowing that selectivity highlights the relative velocities of two or more simultaneous reactions and gives the catalyst the tendency to favour one of the possible products in processes where there is the possibility of secondary reactions occurring, CaOH has less activity than NaOH and therefore has greater selectivity. As NaOH is a liquid, it has a greater contact and agitation surface area with better diffusion to facilitate simultaneous reactions with the mono-, di- and triglycerides present in the oil. The low selectivity of CaO is noticed when its electronic and geometric nature favours, in humid environment, the saponification reaction. This catalyst has the advantage of being reusable.

The yield of biodiesel production (69.05%) by transesterification reaction using CaO as a catalyst is lower than that obtained when using NaOH as a catalyst (74.50%) in 65 minutes. The same performance is obtained when a time of about 110 minutes is observed with CaO.

That value of conversion rate falls within the permissible limits for converting oil into biodiesel by the use of known conventional catalysts. This translates the efficiency of this catalyst prepared based on calcium oxide extracted from bovine bone. Heterogeneous catalysts are mainly alkaline-ground oxides and metals that are active and can reach the reaction yield greater than 98% without presenting any saponification or oxidation problems in the moist medium (Cordeiro, 2014).

Heterogeneous catalysts are easily eliminated from the process by simple filtration, but the cost of their preparation is higher. Thus, the need arose to look for methods of preparation of a heterogeneous catalyst that can be easily removed from the reactional and reusable mixture, but whose raw material is abundant, low cost and environmentally sustainable.

Therefore, in this work, it is proposed to prepare a catalyst based on calcium oxide extracted from bones of bovine origin whose residues constitute an environmental problem.

4. Conclusion

This study presents a new process of preparation of heterogeneous catalyst based on CaO, at low cost and efficient to be used in the synthesis of biodiesel, thus valuing the organic residues of bovine bones. CaO has an advantage over NaOH due to the ease of its recovery at the end of the reaction and the possibility of its reuse. The values of the physical-chemical parameters of biodiesel obtained in both processes are within the limits allowed by international quality standards of the ASTM and EN / ISO standards. The transesterification reaction time in the catalytic medium with CaO was longer to reach the optimum yield and conversion rate of the oil in biodiesel of the homogeneous catalytic system with NaOH, but CaO has the advantage that both esterification and transesterification reactions occur simultaneously with high acid oils, considered unsuitable for transesterification. More research can be done with this catalyst to analyze possible structural changes that can increase its activity and capacity for use.

5. References

Colsar, P. (1980). Procédé métalurgique d´extraction de cuivre e cobalte du minerai hétérogenites. de minerais hééerogenites.Montreal - Canáda: Université de monteral.

Cordeiro, U. (2014). Cientific bases for the preparation of hetergeous catalysts. 11Th international symposium, 6 -10 July. p. 82.

Gustavo, V. P. (2016). Substâcia encontrada na casca de ovo substitui com vantagens catalisadores usados na síntese de biodiesel. Pesquisa LEC-ICEx,Brasil, 2-3.

Shu, Q., & Yang, B. (2017). Predicting the viscosity of biodiesel fuels based on the mixture topological index method fuel (Vol. 86). (A. k. A., Trad.) Yew York. Acess date: May 2019. Avalable: http://www. biodiesel.tec. org.br.

Singh, B., & Prata, S. U. (2014). http://www.biofuel.product.org/87.2355. Acess date: March 2021. Avaliable: http://www.Eu.J.Lipid Sci.Tecnol.br: http://www.Eu.J.Lipid Sci.Tecnol.br.

Wenlei, X., Hong, P., & Lingong, C. (Setembro de 2017). Cobalt catalyst on ZSM - 5 beaded silics oxid-fiber for Fischer - Trosch synthesis. Journal of molecular catlysts, pp. 2 - 3.