Natural and Activated Allophane Catalytic Activity Based on the Microactivity Test in Astm Norm 3907/D3907M-2019

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Received: 27 January 2020; Accepted: 9 March 2020; Published: 27 April 2020

Abstract: The optimal conditions of the catalytic activation of allophane were evaluated for possible use as a catalyst within a fluidized bed catalytic cracking unit (FCC). The physicochemical properties of natural allophane and activated allophane were studied by using an alkaline activating agent, followed by a hydrothermal treatment. For the characterization, analytical techniques were used: Fourier transform infrared spectroscopy, particle size, (BET) surface area, thermogravimetry (TGA), X-ray diffraction (XRD), chemisorption, X-ray fluorescence (XRF), atomic force microscopy (AFM), and chromatography. The catalytic evaluation was determined by the (MAT) micro activity test equipment constructed according to ASTM D-3907/D3907M-2019. In addition, the Navier–Stokes 3D equations (nonlinear partial derivatives) were studied, which allow studying molecular dynamics contributing substantively to chemical kinetics describing the process of decomposition of crude oil in thermal cracking, determining the maximum temperature at which it retains its properties through the action of heat.

Keywords: Ecuadorian allophane; catalytic cracking; physicochemical characterization; catalytic evaluation; Navier–Stokes

1. Introduction

The fluidized catalytic cracking (FCC) process converts heavy cuts into light ones. Generally, the feed is vacuum gas oil, providing boiling points around 450 °C due to the high molecular weight of this type of hydrocarbon. The products obtained include dry gases, liquefied petroleum gas, light oil, heavy oil and mainly gasoline, diesel, and kerosene.

One of the characteristics of the FCC process is that the catalyst used for this unit is selective and must be designed according to the specific process and conditions (operation, feeding characteristics) in the Esmeraldas State Refinery in which it will be applied. Therefore, the catalysts can have a great effect on the production and on the economic aspect due to the volume of feed processed daily [1].

Allophane is a nanoporous micro clay with an undefined crystalline structure. It consists of organic material and has a high moisture content due to its hygroscopic property and extensive surface area. It adsorbs large amounts of water due to its hygroscopic property; its adsorption capacity can be in a range of [20, 50]% by weight of water [2].

The geographical location of allophane sample collection was established by the Institute of Geological and Energy Research (IIGE), located in the province of Santo Domingo de los Tsáchilas, covering an area greater than 4000 km².
This process began with the drying and grinding of different samples of natural allophane; consequently the samples were physically characterized by BET (Brunauer, Emmett, Teller) surface area tests, particle size, and Fourier transform infrared spectroscopy (FT-IR), and then alkaline fusion was performed followed by a hydrothermal treatment. Finally, the samples were washed, filtered, and dried. The activated samples were evaluated and characterized by the following tests: BET surface area (Brunauer, Emmett, Teller), particle size, Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TGA), chemisorption, X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray fluorescence (XRF), and chromatography.

The test method for the determination of the activity of catalytic fluidized cracking (FCC) catalysts in equilibrium or deactivated in the laboratory is evaluated on the basis of the mass conversion percentage of the diesel feed in a microactivity unit, with equipment constructed according to ASTM D-3907/D3907M-2019.

The Navier-Stokes 3D equations govern the behavior of any fluid, allowing molecular dynamics to be studied, contributing substantively to chemical kinetics.

The dynamics of catalysis attempts to quantitatively explain the forces and vector fields of moving fluids, such as crude oil in the fluidized catalytic cracking process.

2. Materials and Methods

2.1. Physicochemical Characterization Tests

2.1.1. Particle Size

The method used to determine particle size is characterized using Stokes’s law, analyzing the velocity of the particles. It consists of registering the images by two digital cameras where the particles that pass through a beam of light are projected, obtaining as a result granulometric distribution curves in real time [3], for which the RETSCH TECHNOLOGY frame granulometric analysis system, model CAMZISER was used.

2.1.2. Surface Area BET

This is a method of measuring the physical adsorption capacity (fisisorption) where the gas molecule is fixed in the solid molecule and also controls the quality of the catalysts. The factors that affect the surface area are the porosity and the size and geometric shape of the particle since the surface area increases when the particle size decreases.

The amount of gas absorbed by the sample depends directly on the temperature, characterized by having a good adjustment of the adsorption curves, BET area units are m\(^2\)/g. This method is a standard because it allows you to control the speed of the chemical interaction between gases and solids or liquids. Nitrogen generally makes contact with the degassed solid, thus obtaining a balance between adsorbed molecules and gas phase molecules that depend on the temperature and pressure of the gas. “Allophane containing 70–80% by weight has a specific N\(_2\) BET surface of >300 m\(^2\)/g” [4].

The HORIBA surface area equipment, model SA-9600, was used to determine this parameter.

2.1.3. Fourier Transform Infrared Spectroscopy (FTIR)

This method is characterized by using a sweep that passes through the absorption lines being the Fourier transform which allows us to obtain the classic spectrum form, allowing us to identify the different functional groups.

“The infrared (IR) vibration of aluminum-rich allophane ranges from 975 cm\(^{-1}\) to 1020 cm\(^{-1}\) (Al/Si equal 1), with the main range being 1005 cm\(^{-1}\) that provides a ratio of (Al/Si equal 1.3). The most characteristic infrared band of allophane is 348 cm\(^{-1}\). However, this band can only be assigned to allophane if illite, montmorillonite, kaolinite, and halloysite are absent” [5]. In Figure 1, we present the FTIR spectrum of activated allophane.
Using the FTIR PERKIN ELMER device, model Spectrum Two.

![FTIR active allophane results.](image)

**Figure 1.** FTIR active allophane results.

2.1.4. X-ray Diffraction (XRD)

The X-ray diffraction technique is based on the incidence, with a certain angle $\theta$, of an X-ray beam on a flat sample. The intensity of the diffracted radiation resulting from the interaction of the beam with the solid is a function of the distance between the crystalline planes that configure the structure and the angle of diffraction $\theta$ [6].

This method was carried out in BRUKER equipment, model: D8 ADVANCE, with Difrac plus software for measurement, and EVA and TOPAS 4.2 for the identification and quantification of the crystalline phases present in each of the samples.

Specifically for allophane, X-ray diffraction indicates a generalized dispersion and is weak due to the particle size and the undefined crystallographic structure, characteristic of this type of amorphous clay.

2.1.5. Chemisorption Temperature-Programmed Desorption (TPD)

This method is characterized by working with high temperatures; the heat of adsorption is high, the speed and energy of activation are high (not activated) and low (activated), and there is characteristic coverage of a monolayer or less.

This analytical method consists of determining the number, type, and strength of the active sites that are on the surface of a catalyst where the amount of gas or liquid on the solid is measured followed by an increase in temperature, which varies over time in a controlled way.

For this investigation, the activated allophane and natural allophane are worn out using ammonia that stabilizes when adsorbed under acidic conditions, entering the pores and saturating the sample. Afterwards, increasing temperatures are applied to the sample to finally be quantified by the detector, allowing the gas concentration to be measured; in this way, the desorbed gas volume and the temperature desorption are obtained. Finally, the value of the acid sites is determined by a ratio of ammonia detected in a specific amount of sample.

It is assumed that one molecule is adsorbed for each experimentally determined active site [7]. The equipment used is an automatic characterization system of catalysts, model AUTOCHEM 2920, brand Micrometrics.

2.1.6. Atomic Force Microscopy (AFM)

The method used for this test is non-contact because the distance between the cantilever and the surface is 10 nm. For this reason, there is no force action preventing contamination and damage of the
samples due to the generation of images. However, this image has lower than lateral resolution and
scanning speed.

Atomic force microscopy for the allophane allows us to check the diameter of the particle that is
less than or equal to 50 nm. This means that the images obtained by this characterization confirm the
presence of nano particles due to their spongy form with abundant fine holes, maintaining a relationship
with the specific area [8].

The equipment used for this test is an PARK SYSTEMS; model: PARK NX10 AFM Atomic
Force Microscopy.

2.1.7. Thermogravimetry (TGA)

The method allows us to identify the endothermic temperature, which for this type of clay occurs
at 150 °C, as it provides dehydration of water present in the sample. Also, the curve does not present
any inflections and is characterized by a continuous model similar to the identification of the active
phase of the catalysts.

The thermal analysis allows us to identify quantitative weight data when the previously set
temperature under a dynamic temperature program varies, working at a certain pressure, allowing us
to know the degradation of the sample.

This procedure begins with a warming of the estimated sample of 10–15 mg to 25 °C until a final
temperature of 420 °C, using nitrogen as a purge gas that covers the microbalance; the curves obtained
at the end of the process are known as thermograms (thermal decomposition), represented by the
variation of the mass as a function of time or temperature. These curves indicate the loss of weight
caused by different aspects such as physical transformations (pure and activated allophane) and
chemical reactions where the combustion of hollin (allophane mixture—heavy crude) is appreciated.
Specifically, the weight diagram as a function of temperature allows us to obtain information on the
stability and composition of the residue obtained at the end of the experiment.

2.1.8. X-ray Fluorescence (XRF)

The method is used when X rays crosses the wavelength and is quantitatively recorded by the
X-ray count. In this way, the elemental composition (total content) of samples (pure and activated
allophane) is obtained physically. This method is also known as a non-destructive test because when
exposed by high-energy X-ray radiation, the sample does not present any type of modification.

The test begins with the mechanical preparation where the sample is dried, to decrease the
particle size to approximately 75 microns, and then a quartet is performed to obtain a representative
sample. The samples pass to the physical–chemical preparation area, where fusion is performed in
order to obtain a homogeneous glazed disc for analytical reading. In instrumental reading, an X-ray
fluorescence spectrometer is used per dispersive wavelength in which the optical part is housed for the
identification and quantification of certain elements.

The elements determined for this study are the identification and quantification of silica and
alumina present in the allophane due to the ratio of silicon/aluminum equal to one, as mentioned above.

The adsorption capacity is influenced by the Si/Al ratio due to its chemical composition, since the
lower the number of aluminum atoms, the fewer exchange cations, so the silicon content is inherently
hydrophobic, generating an affinity with hydrocarbons.

The allophane is characterized by containing in its structure elements considered predominant
such as aluminum and silicon. This synthesis originates from soils from volcanic ash that generally
indicate a greater presence of silicon.

“The allophane Al/Si ratio is in the range 1.3–1.4. The said allophane is called allophane or
allophane flow of silica and represents an intermediate between the allophanes of soils rich in Al (Al/Si
= 2 known as allophane proto-imologite or allophane of imologite type) and allophanes rich in Si (Al/Si
= 1 is phazom or allophane-type allophane)” [9].
A decrease in Si/Al implies an increase in the aluminum content, avoiding an interaction between them, since the AlO₄-tetrahedra are far from each other.

The equipment used for the method is BRUKER S8 TIGER.

2.1.9. Apparent Density

This is a physical property that describes soil compaction, representing the relationship between solids and space, allowing us to evaluate the strength of the material (allophane with an apparent density of 1.9 g/mL) [10] and thus to convert the concentrations to mass and volume. Additionally, it refers to the direct relationship with the type of circulation and fluidization of the catalyst in the reactor.

For this, the pycnometer method was used at room temperature.

2.2. Characterization of Hydrocarbon

2.2.1. API Gravity (°API)

This technique allows us to determine the API gravity by the hydrometer method, which is used for petroleum and non-volatile liquid derivatives, and fundamentally allows us to determine the volume of commercialization and the transformation from mass to volume. The volume of the sample varies directly with the immersion of the hydrometer (2H) graduated in °API. Once this value has been registered, the respective temperature is measured, for which a correction at a standard temperature of 60 [°F] must be performed, using the respective °API correction table for the sample analyzed [11].

2.2.2. Sulfur Content

This is based on the determination of the sulfur content in percentage by mass of petroleum and its derivatives, complying with permissive limits. For this reason, the method consists of making an X-ray source (analyzer) influence the sample for an approximate time of 1–5 min, in a range of 0.015–5.0% by mass of sulfur [12].

The equipment used is an Oxford Instruments sulfur analyzer (Lab X-3500).

2.2.3. Viscosity

The Saybolt viscosity measurement for petroleum products (viscous) in a temperature range of 70–210 [°F] allows us to analyze the fluid pumping as a function of the temperature, making known the manipulation of the products. In the measuring equipment, the operating temperature (thermoregulator) is adjusted, and the sample is placed in the equipment and the respective orifice until reaching the indicated temperature. Finally, the process is uncorked, and the sample in the package is matched to the capacity line taking into account the time measurement [13].

2.2.4. Conradson Carbon Residue

The method it allows us to determine the carbon residue amount that is obtained after evaporation and the pyrolysis of a crude oil or heavy fuel under specified conditions, intending to provide some relative indication of coke formation, which serves as an approximation of the tendency of the fuel to form deposits in vaporization.

To carry out this characterization, the ASTM D-189 STANDARD was followed, where a certain amount of sample is placed in a crucible, and the residue is subjected to cracking and carbonization reactions during a fixed heating period. The remaining residue is expressed as a percentage of the original sample; the results must exceed 5% of the Conradson carbon residue due to the material used [14].

2.2.5. Ashes

This method covers the ash determination in mass percentage of distillates and petroleum products; for the realization of this characterization, the ASTM D-482 STANDARD was followed.
This test method covers the determination of ash in the range of 0.001–0.180% by mass of distilled and residual fuels, gas turbine fuels, crude oils, lubricating oils, waxes, and other petroleum products in which any present material that generates ash is normally considered as impurity or undesirable contaminant [15].

The experimental procedure continues once the content of the Conradson carbon is finished by finally subjecting it to a calcination temperature close to 800 °C for a set time (4 h) to finally obtain the required ash value.

2.2.6. Paraffin

Paraffin is a mixture of hydrocarbons, solid and crystalline, completely derived from the portion of crude oil designated as paraffin distillate, by solidification at low temperature and pressure.

This method consists of quantifying paraffins by gas chromatography in hydrocarbons that do not exceed the temperature range of 200 °C. The lower limit of detection for a single component or group of hydrocarbons is 0.05% by mass.

The Agilent Technologies 5977E MS gas chromatograph equipment was used.

2.3. Test Microactivity (Fixed Bed Reactor)

The microactivity test is based on ASTM D 3907 (standard test method for testing fluid cracking FCC catalysts by the microactivity test); with this method, the activity of the catalyst of the fluidized catalytic cracking unit (FCC) is evaluated. The test method consists of carrying out the respective tests with a catalyst sample in the fixed bed reactor (designed under the parameters established by this standard), which comes into contact with the respective hydrocarbon sample [16].

The catalyst (4 g) is placed in the temperature-controlled reactor until it reaches 482 °C and is operated with a gas in an inert atmosphere (nitrogen) prior to a purge with synthetic air cleaning; subsequently, the preheated hydrocarbon sample is injected at 40 °C where the weight and the necessary execution time are verified; finally, the gases and liquid products generated are collected.

2.4. Characterization of Liquid Product

Gas Chromatography

The gas chromatography method volatilizes the sample. This effectively vaporizes the sample to the gas phase and separates its various components using a capillary column filled with a stationary (solid) phase and an inert carrier gas (helium). As the components separate, they elute from the column at different times, identifying retention times [17].

An Agilent Technologies 5997E MSD gas chromatograph, model 7820 A GS SISTEM, was used. Additionally, the detailed hydrocarbon analysis (HAD) was applied to obtain quantitative results. The detailed DHA hydrocarbon analysis allows quantitative determination of the carbon chains existing in the liquid sample, as well as the number of octanes and specific gravity that are necessary parameters for the analysis of the product obtained.

An Agilent Technologies 5997E MSD gas chromatograph, model 7820 A GS SISTEM APLICATION CRUDE DHA, was used.

3. Results

3.1. Characterization of Natural Allophane

3.1.1. Humidity

For the physical characterization of the natural allophane, the drying (24 h at 60 °C) and grinding processes were carried out.
Table 1 shows the initial experimental humidity of the different allophane samples in which this variation in humidity can be established by geographical location.

Table 1. Initial Moisture of Natural Allophane.

| Sample | Initial Moisture of Natural Allophane |  |
|--------|-------------------------------------|--|
|        | Natural Allophane Weight (g) | Dry Natural Allophane Weight (g) | Water Weight Contained (g) | Humidity (%) |
| AN-1   | 5 | 2.5161 | 2.4839 | 50 |
| AN-2   | 5 | 2.5161 | 2.4839 | 50 |
| AN-3   | 5 | 2.1676 | 2.8324 | 57 |
| AN-4   | 5 | 2.1676 | 2.8324 | 57 |
| AN-5   | 5 | 2.4890 | 2.5110 | 50 |
| AN-6   | 5 | 2.4890 | 2.5110 | 50 |
| AN-7   | 5 | 2.4927 | 2.5073 | 50 |
| AN-8   | 5 | 2.4927 | 2.5073 | 50 |
| AN-9   | 5 | 2.3759 | 2.6241 | 53 |
| AN-10  | 5 | 2.3759 | 2.6241 | 53 |
| AN-11  | 5 | 3.9041 | 1.0959 | 22 |
| AN-12  | 5 | 3.9041 | 1.0959 | 22 |
| AN-13  | 5 | 2.6545 | 2.3455 | 47 |
| AN-14  | 5 | 2.6545 | 2.3455 | 47 |
| AN-15  | 5 | 2.6545 | 2.3455 | 47 |

The average humidity of each of the samples is within the range of 20–50% moisture by weight established by KAUFHOLD STEPHAN.

3.1.2. Particle Size Test

The percentage retention ranges in the particle size test were established by the State Emerald Refinery for the case of the catalyst used in the fluidized catalytic cracking process. Subject to these values, >20%, 40%, 60%, 80%, and >80%, in all natural samples, a percentage retention greater than 80% was identified; a particle size in that percentage of retention greater than 0.08 mm (Table 2) determined that the particle size should be reduced for subsequent tests.

Table 2. Particle size distribution by sample.

| Pure Sample | Retention Percentage |
|-------------|----------------------|
|             | >20 mm | 40 mm | 60 mm | 80 mm | >80 mm |
| AN-1        | 0.01   | 0.18  | 0.85  | 1.75  | 97.2   |
| AN-2        | 0.01   | 0.17  | 0.85  | 1.81  | 97.16  |
| AN-3        | 0.00   | 0.10  | 0.53  | 1.23  | 98.13  |
| AN-4        | 0.01   | 0.12  | 0.57  | 1.28  | 98.03  |
| AN-5        | 0.01   | 0.22  | 1.07  | 2.24  | 96.56  |
| AN-6        | 0.01   | 0.22  | 1.08  | 2.25  | 96.43  |
| AN-7        | 0.01   | 0.27  | 1.25  | 2.43  | 96.03  |
| AN-8        | 0.01   | 0.19  | 0.87  | 1.72  | 97.20  |
| AN-9        | 0.01   | 0.14  | 0.70  | 1.49  | 97.67  |
| AN-10       | 0.01   | 0.14  | 0.78  | 1.70  | 97.37  |
| AN-11       | 0.00   | 0.05  | 0.28  | 0.72  | 98.95  |
| AN-12       | 0.00   | 0.06  | 0.35  | 0.85  | 98.75  |
| AN-13       | 0.01   | 0.21  | 1.04  | 2.21  | 96.54  |
| AN-14       | 0.01   | 0.21  | 1.03  | 2.12  | 96.63  |
| AN-15       | 0.01   | 0.16  | 0.80  | 1.73  | 97.31  |

3.1.3. Surface Area Test

By testing, BET surface area in Table 3 identified that natural samples 3, 4, and 15 have a surface area greater than or equal to 300 m²/g, which is within the range set by KAUFHOLD STEPHAN. It was
also possible to see that the AN-11 and AN-12 samples were outside the characteristic ranges of an FCC catalyst; for this reason, they were not considered in the following tests since the total surface area of the solid has an important effect on the speed of reaction. The smaller the particle size of the catalyst, the greater the surface area.

The results of the BET surface area of each sample are presented below.

Table 3. BET surface area calculations (pure material).

| Natural Allophane | Essays | Empty Cell [g] | Sample Cell [g] | Area [m²/g] | Superficial Area [m²/g] | Average Surface Area [m²/g] |
|-------------------|--------|---------------|----------------|------------|--------------------------|-----------------------------|
| AN-1              | 1      | 10.05         | 10.1659        | 33.94      | 292.83                   | 286.44                      |
|                   | 2      | 10.2022       | 10.3171        | 32.73      | 284.85                   |                             |
|                   | 3      | 10.0495       | 10.1754        | 35.46      | 281.65                   |                             |
| AN-2              | 1      | 10.2021       | 10.3234        | 33.76      | 278.31                   | 273.22                      |
|                   | 2      | 10.0568       | 10.1806        | 31.71      | 256.13                   |                             |
|                   | 3      | 10.2017       | 10.3269        | 35.71      | 285.22                   |                             |
| AN-3              | 1      | 10.0499       | 10.1671        | 36.87      | 314.59                   | 322.78                      |
|                   | 2      | 10.0501       | 10.1632        | 37.37      | 330.41                   |                             |
|                   | 3      | 10.2025       | 10.3164        | 36.83      | 323.35                   |                             |
| AN-4              | 1      | 10.2021       | 10.3171        | 36.14      | 314.26                   | 302.92                      |
|                   | 2      | 10.0538       | 10.1686        | 34.86      | 303.65                   |                             |
|                   | 3      | 10.2013       | 10.3163        | 33.45      | 290.86                   |                             |
| AN-5              | 1      | 10.0544       | 10.1778        | 25.02      | 202.75                   | 191.61                      |
|                   | 2      | 10.2093       | 10.3284        | 23.60      | 198.15                   |                             |
|                   | 3      | 10.0505       | 10.1947        | 25.08      | 173.92                   |                             |
| AN-6              | 1      | 10.2021       | 10.3278        | 25.5       | 202.86                   | 202.07                      |
|                   | 2      | 10.0497       | 10.1757        | 26.36      | 209.20                   |                             |
|                   | 3      | 10.2021       | 10.3306        | 24.95      | 194.16                   |                             |
| AN-7              | 1      | 10.2019       | 10.3276        | 25.9       | 206.04                   | 232.09                      |
|                   | 2      | 10.0495       | 10.1559        | 25.08      | 235.71                   |                             |
|                   | 3      | 10.0498       | 10.1712        | 30.9       | 254.53                   |                             |
| AN-8              | 1      | 10.2022       | 10.3176        | 28.19      | 244.28                   | 238.48                      |
|                   | 2      | 10.202       | 10.3199        | 28.24      | 239.52                   |                             |
|                   | 3      | 10.0499       | 10.1681        | 27.38      | 231.64                   |                             |
| AN-9              | 1      | 10.0537       | 10.1709        | 34.05      | 290.52                   | 290.64                      |
|                   | 2      | 10.2023       | 10.3198        | 34.32      | 292.08                   |                             |
|                   | 3      | 10.0476       | 10.1646        | 33.85      | 289.31                   |                             |
| AN-10             | 1      | 10.0503       | 10.1676        | 35.35      | 301.36                   | 282.33                      |
|                   | 2      | 10.2023       | 10.3258        | 31.84      | 257.81                   |                             |
|                   | 3      | 10.2017       | 10.3158        | 32.84      | 287.81                   |                             |
| AN-11             | 1      | 10.0485       | 10.1873        | 5.54       | 39.91                    | 41.37                       |
|                   | 2      | 10.2014       | 10.3433        | 5.68       | 40.02                    |                             |
|                   | 3      | 10.0501       | 10.1979        | 6.53       | 44.18                    |                             |
| AN-12             | 1      | 10.2021       | 10.3529        | 6.67       | 44.23                    | 44.01                       |
|                   | 2      | 10.2014       | 10.3531        | 6.55       | 43.17                    |                             |
|                   | 3      | 10.0507       | 10.1979        | 6.57       | 44.63                    |                             |
| AN-13             | 1      | 10.200        | 10.3173        | 32.99      | 281.24                   | 279.91                      |
|                   | 2      | 10.0501       | 10.1735        | 33.79      | 273.82                   |                             |
|                   | 3      | 10.0403       | 10.1657        | 35.7       | 284.68                   |                             |
| AN-14             | 1      | 10.2021       | 10.3238        | 32.98      | 270.99                   | 249.81                      |
|                   | 2      | 10.0496       | 10.1612        | 28.08      | 251.61                   |                             |
|                   | 3      | 10.2019       | 10.317         | 26.11      | 226.84                   |                             |
| AN-15             | 1      | 10.0475       | 10.1674        | 37.06      | 309.09                   | 300.00                      |
|                   | 2      | 10.2002       | 10.3188        | 36.05      | 303.96                   |                             |
|                   | 3      | 10.0403       | 10.1659        | 35.89      | 285.74                   |                             |

The cell is a quartz vessel that contains approximately 0.15 g of the sample of the starting material.
3.1.4. Fourier Transform Infrared Spectroscopy Assays (FT-IR)

The absorption band at 1640 cm\(^{-1}\) H\(_2\)O and the infrared (IR) vibration ranges of allophane rich in aluminum bonds (Si-O-AL) are shown at 1300–800 cm\(^{-1}\). The characteristic infrared band of allophane is 348 cm\(^{-1}\); however, this band can only be assigned to allophane if it is absent from illite, montmorillonite, kaolinite, and halloysite. None of the different natural samples is free of the above-mentioned minerals, as the numerical values are shown in Table 4. Table 4 shows the main bands of the different samples of natural allophane identifying the vibration bands of water molecules (OH groups), deformation caused by H\(_2\)O, and allophane rich in aluminum. The numerical value of natural allophane AN-7 and AN-8 is out of range; for that reason, we discarded them for the following tests.

Table 4. FT-IR infrared spectra for main bands of natural allophane.

| Natural Allophane | Vibration of Water Molecules, OH Groups | Deformation Caused by H\(_2\)O | Allophane Rich in Aluminum | Infrared Band Characteristic of the Allophane Absent from Illite, Montmorillonite, Kaolinite, and Halloysite |
|-------------------|----------------------------------------|-------------------------------|---------------------------|---------------------------------------------------------------|
|                   | cm\(^{-1}\)                           |                               |                           |                                                               |
| AN-1              | 3452.00                               | 1642.3                        | 997.17                    | 527.37                                                        |
|                   | 3435.5                                | 1639                          | 990.55                    | 484.36                                                        |
|                   | 3442.1                                | 1639                          | 993.86                    | 484.9                                                         |
| AN-2              | 3435.5                                | 1635.7                        | 983.94                    | 487.67                                                        |
|                   | 3462                                  | 1639                          | 990.55                    | 487.61                                                        |
|                   | 3455.3                                | 1639                          | 987.25                    | 484.61                                                        |
| AN-3              | 3329.6                                | 1635.7                        | 970.70                    | 438.05                                                        |
|                   | 3329.5                                | 1635.7                        | 983.94                    | 447.97                                                        |
|                   | 3435.5                                | 1635.7                        | 983.94                    | 434.36                                                        |
| AN-4              | 3326.3                                | 1642.3                        | 970.70                    | 481.06                                                        |
|                   | 3448.7                                | 1635.7                        | 983.94                    | 467.82                                                        |
|                   | 3440.7                                | 1639                          | 993.94                    | 467.82                                                        |
| AN-5              | 3458.6                                | 1635.7                        | 993.86                    | 497.6                                                         |
|                   | 3458.6                                | 1635.7                        | 987.25                    | 504.22                                                        |
|                   | 3462                                  | 1635.7                        | 993.86                    | 497.6                                                         |
| AN-6              | 3450.5                                | 1635.8                        | 998.77                    | 469.36                                                        |
|                   | 3452                                  | 1632.4                        | 997.17                    | 469.7                                                        |
|                   | 3452                                  | 1635.7                        | 987.25                    | 474.44                                                        |
| AN-7              | 1635.7                                | 1036.9                        | 471.13                    |
|                   | 1635.7                                | 1036.9                        | 474.44                    |
|                   | 1639                                  | 1040.2                        | 471.13                    |
| AN-8              | 1635.7                                | 1036.9                        | 471.13                    |
|                   | 1645.6                                | 1036.9                        | 471.13                    |
|                   | 1639                                  | 1036.9                        | 467.82                    |
| AN-9              | 3545.4                                | 1642.3                        | 980.63                    | 498.2                                                         |
|                   | 3441.2                                | 1635.7                        | 974.01                    | 504.22                                                        |
|                   | 3458.6                                | 1639                          | 974.01                    | 497.6                                                         |
| AN-10             | 3458.6                                | 1642.3                        | 974.01                    | 500.9                                                         |
|                   | 3448.7                                | 1639                          | 980.63                    | 510.83                                                        |
|                   | 3447.6                                | 1638.6                        | 981.78                    | 503.33                                                        |
| AN-11             | 3448.7                                | 1635.7                        | 1013.7                    | 494.3                                                         |
|                   | 3455.3                                | 1639                          | 1020.3                    | 487.67                                                        |
|                   | 3448.7                                | 1639                          | 1023.6                    | 487.7                                                         |
| AN-12             | 3448.7                                | 1642.3                        | 1017.0                    | 507.52                                                        |
|                   | 3455.3                                | 1639                          | 997.17                    | 507.52                                                        |
|                   | 3452                                  | 1632.4                        | 983.94                    | 507.52                                                        |
| AN-13             | 3455.3                                | 1639                          | 1003.8                    | 500.9                                                         |
|                   | 3452                                  | 1639                          | 1013.7                    | 497.6                                                         |
|                   | 3452                                  | 1639                          | 1020.3                    | 494.3                                                         |
3.1.5. X-ray Diffraction (XRD)

The analysis of X-ray diffraction is a molecular phenomenon that lies in making an X-ray beam affect the solid, being an analytical technique in which light is diffracted, allowing us to identify the internal structure of the molecules, the average size of crystals, the possible special groups, the crystalline planes and chemical species of a complex catalyst, state of dispersion on the support, etc. Specifically for allophane, X-ray diffraction indicates a generalized and weak dispersion due to the particle size and the undefined crystallographic structure, characteristic of this type of amorphous clay. The presence of the following minerals was determined by the X-ray diffraction test: quartz (SiO₂), albite (NaAlSi₃O₈), anortite (Ca(Al₂Si₂O₈)), cristobalite (SiO₂), actinolite (Ca₁.₇₃Na₀.₈₅Mg₁.₈₈Fe²⁺₂.₇₂Al₀.₂₁Fe³⁺₀.₃₂Mn²⁺₀.₁₆Si₇.₆₈Al₀.₃₂O₂₂(OH)₂), group N K-ferdespato (sancidine microcline orthoclase) (KAlSi₃O₈), chlorite group (Mg₃.₇₅Fe²⁺₁.₂₅Al₂SiO₁₀(OH)₈), tridymite (SiO₂), and gibbsite Al(OH)₃. The results obtained are indicated in Table 5.

3.1.6. Chemisorption

This method allows us to recognize the nature of the chemical process presented by the allophane, using desorption at programmed temperature (TPD). This consists of determining the number, type, and strength of the active sites that are on the surface of a catalyst where the amount of gas in the solid is measured followed by an increase in temperature, which varies over time in a controlled manner. Ammonia was used for stabilization when adsorbed in acidic places, getting into the pores and saturating the sample, applying increasing temperatures in the sample, to finally be quantified by the detector allowing us to measure the gas concentration. In this way the volume of desorbed gas and the desorption temperature are obtained. The value of the acid sites is determined by an ammonia ratio detected in a specific amount of sample. We assume that one molecule is adsorbed for each experimentally determined active site.

Through the chemisorption test, the acidity was determined by identifying the Lewis and Bronsted sites in the samples. It is worth mentioning that not all existing acid centers in the samples can be considered active development centers for the chemical reaction, since only a part of them will have enough acid to catalyze the reaction.

The determination of the active allophane active sites is shown in Table 6. Table 6 contains the amount of ammonia adsorbed by the sample in the TPD test.

3.1.7. Determination of Major Elements by X-Ray Fluorescence (WD-XRF)

This method determined the concentrations of the elements in the form of oxides (see Table 7) for the following elements: sodium, magnesium, aluminum, silica, phosphorus, sulfur, potassium, calcium, titanium, manganese, and iron in the natural samples. These percentages allowed calculation of the Si/Al ratio and the percentage of allophane in each natural sample as shown in Table 8. The ratio of SiO₂/Al₂O₃ oxides determines the percentage of allophane in each natural sample according to Equations (1) and (2).

- If SiO₂/Al₂O₃ < 6

\[
\text{Allophane\%} = \frac{\text{SiO}_2\% + 0.282 \times \text{SiO}_3\%}{0.89}
\]  

(1)

- If SiO₂/Al₂O₃ > 6

\[
\text{Allophane\%} = \frac{\text{Al}_2\text{O}_3\% + 3.545 \times \text{Al}_2\text{O}_3\%}{0.89}
\]

(2)
Table 5. Determination of minerals by X-ray diffraction (XRD) of pure allophane.

| CODE | QUARTZ (%) | ALBITE (%) | ANORTHITE (%) | CRISTOBALITE (%) | ACTINOLITE (%) | GROUP N K-FELDSPAR (SANCIDINE MICROCLINE ORTHoclase) (%) | CHLORITE GROUP (%) | TRIDYMITE (%) | GIBBSITE (%) |
|------|------------|------------|---------------|------------------|----------------|---------------------------------------------------------------------------------------------------|-------------------|--------------|-------------|
|      | SiO₂       | NaAlSi₃O₈  | Ca₆Al₂Si₄O₁₀   | SiO₂             | C₄₁₋₅Ca₂₋₄M₈₋₁₂Fe²⁺₂₋₄Al₃₋₄Fe³⁺₀₋₂Mn²⁺₀₋₂Si₉₋₁₄Al₀₋₂O₉₀₋₈(OH)₂₀ | KAlSi₃O₈         | M₈₋₁₂Fe²⁺₂₋₄Al₃₋₄Si₀₋₂O₁₀(OH)₂₀ | SiO₂          | Al(OH)₃     |
| AN-1 | 10.5       | 13.3       | 26.1           | 10.3             | 17.6           | 13.3                                                                                               | 2                 | 6.9          | -           |
| AN-2 | 10.5       | 13.3       | 26.1           | 10.3             | 17.6           | 13.3                                                                                               | 2                 | 6.9          | -           |
| AN-3 | 10.9       | 0.4        | 23.5           | 13.8             | 17.9           | 22.9                                                                                               | 2                 | 8.3          | -           |
| AN-4 | 11.5       | 1.3        | 27             | 14.7             | 20.1           | 22.9                                                                                               | 2                 | 2.9          | -           |
| AN-5 | 10.4       | 4.3        | 34.4           | 7.7              | 21.4           | 12.6                                                                                               | 2                 | 6.4          | -           |
| AN-6 | 10.4       | 4.3        | 34.4           | 7.7              | 21.4           | 12.6                                                                                               | 2                 | 6.4          | -           |
| AN-9 | 13.8       | -          | -              | 15.3             | 20.2           | 15.3                                                                                               | -                 | 48.8         | -           |
| AN-10| 13.8       | -          | -              | 15.3             | 20.2           | 15.3                                                                                               | -                 | 48.8         | -           |
| AN-13| 14.2       | -          | -              | 13.2             | 18.6           | 13.2                                                                                               | -                 | 49.5         | -           |
| AN-14| 14.2       | -          | -              | 13.2             | 18.6           | 13.2                                                                                               | -                 | 49.5         | -           |
| AN-15| 14.2       | -          | -              | 13.2             | 18.6           | 13.2                                                                                               | -                 | 49.5         | -           |
Table 6. Results of active sites of pure allophane.

| Sample | Active Sites | Active Sites/g | Sample | Active Sites | Active Sites/g |
|--------|--------------|----------------|--------|--------------|----------------|
| AN-1   | 15           | 267            | AN-9   | 29           | 536            |
| AN-2   | 15           | 267            | AN-10  | 18           | 329            |
| AN-3   | 15           | 296            | AN-11  | 17           | 287            |
| AN-4   | 15           | 247            | AN-12  | 13           | 247            |
| AN-5   | 21           | 316            | AN-13  | 13           | 235            |
| AN-6   | 22           | 376            | AN-14  | 29           | 524            |
| AN-7   | 25           | 335            | AN-15  | 23           | 426            |
| AN-8   | 26           | 466            |        |              |                |

Table 7. Results of the determination of major elements by X-ray fluorescence (WD-XRF).

| Sample | Na<sub>2</sub>O (%) | MgO (%) | Al<sub>2</sub>O<sub>3</sub> (%) | SiO<sub>2</sub> (%) | P<sub>2</sub>O<sub>5</sub> (%) | SO<sub>2</sub> (%) | K<sub>2</sub>O (%) | CaO (%) | TiO<sub>2</sub> (%) | MnO<sub>2</sub> (%) | FeO<sub>2</sub> (%) | PPC (%) |
|--------|---------------------|---------|-------------------------------|---------------------|-------------------------|-----------------|-----------------|---------|-----------------|-----------------|-----------------|---------|
| AN-1   | 0.988               | 2.741   | 23.677                        | 38.687              | 0.11                    | -               | -               | -       | 0.842           | -               | 5.611           | -       |
| AN-2   | 0.988               | 2.741   | 23.677                        | 38.687              | 0.11                    | -               | -               | -       | 0.842           | -               | 5.611           | -       |
| AN-3   | <0.02               | 1.398   | 27.41                         | 36.077              | 0.084                   | <0.05           | 0.242           | 0.975   | 0.854           | 0.046           | 6.321           | 25.16   |
| AN-4   | <0.02               | 1.398   | 27.41                         | 36.077              | 0.084                   | <0.05           | 0.242           | 0.975   | 0.854           | 0.046           | 6.321           | 25.16   |
| AN-9   | <0.02               | 1.031   | 30.316                        | 28.674              | 0.064                   | <0.05           | 0.091           | 0.547   | 0.989           | 0.087           | 10.04          | 26.18   |
| AN-10  | <0.02               | 1.031   | 30.316                        | 28.674              | 0.064                   | <0.05           | 0.091           | 0.547   | 0.989           | 0.087           | 10.04          | 26.18   |
| AN-13  | <0.02               | 1.37    | 30.894                        | 31.646              | 0.06                    | <0.05           | 0.084           | 0.642   | 0.977           | 0.132           | 9.823           | 22.09   |
| AN-14  | <0.02               | 1.37    | 30.894                        | 31.646              | 0.06                    | <0.05           | 0.084           | 0.642   | 0.977           | 0.132           | 9.823           | 22.09   |
| AN-15  | <0.02               | 1.239   | 29.219                        | 29.732              | 0.056                   | <0.05           | 0.008           | 0.39    | 0.919           | 0.123           | 9.288           | 26.39   |

Table 8. Results of the ratio of Si/Al and % of allophane in natural samples.

| Natural Sample | Si/Al Ratio | % Allophane |
|----------------|-------------|-------------|
| AN-1           | 1.63        | 55.63       |
| AN-2           | 1.63        | 55.63       |
| AN-3           | 1.31        | 51.88       |
| AN-4           | 1.32        | 51.88       |
| AN-9           | 0.94        | 41.24       |
| AN-10          | 0.94        | 41.24       |
| AN-13          | 1.02        | 45.51       |
| AN-14          | 1.02        | 45.51       |
| AN-15          | 1.02        | 42.76       |

3.1.8. Atomic Force Microscopy, AFM

Atomic force microscopy allows us to determine the pore size of the natural allophane particle. This means that the images obtained by this characterization confirm the presence of nano particles due to their spongy shape with abundant fine holes, maintaining a relationship with the surface area. Figure 2 shows examples of the microscopy of natural allophane.
### Table 8. Results of the ratio of Si/Al and % of allophane in natural samples.

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|----------------|-------------|-------------|
| AN-1           | 1.63        | 55.63       |
| AN-2           | 1.63        | 55.63       |
| AN-3           | 1.31        | 51.88       |
| AN-4           | 1.32        | 51.88       |
| AN-9           | 0.94        | 41.24       |
| AN-10          | 0.94        | 41.24       |
| AN-13          | 1.02        | 45.51       |
| AN-14          | 1.02        | 45.51       |
| AN-15          | 1.02        | 42.76       |

- If SiO$_2$/Al$_2$O$_3$ < 6
  \[
  \text{% Allophane} = \text{SiO}_2\% + 0.282 \times \text{Si} \times 0.89
  \]

- If SiO$_2$/Al$_2$O$_3$ > 6
  \[
  \text{% Allophane} = \text{SiO}_2\% + 3.545 \times \text{Si} \times 0.89
  \]

### 3.1.8. Atomic Force Microscopy, AFM

Atomic force microscopy allows us to determine the pore size of the natural allophane particle. This means that the images obtained by this characterization confirm the presence of nanoparticles due to their spongy shape with abundant fine holes, maintaining a relationship with the surface area. Figure 2 shows examples of the microscopy of natural allophane.

![Figure 2. (a) Microscopy of natural allophane 3, (b) Natural allophane 4.](image)

### 3.2. Physicochemical Characterization of Activated Allophane

#### 3.2.1. Allophane Activation Process

The optimized activation process was carried out by the alkaline fusion method, using sodium hydroxide as the activating agent followed by hydrothermal treatment by the following procedure:

- Dry the sample for 24 h at a temperature of 60 °C.
- Grind the sample.
- Mix 120 g of commercial sodium hydroxide (NaOH) with 100 g of dried allophane, maintaining a ratio of alkaline activator/raw material equal to 1.2.
- Calcinate the resulting product in the flask at 600 °C for 1 h.
- Dissolve the fused alkaline product in distilled water (water/fused alkaline product ratio = 5 mL/g).
- Stir the resulting alkaline product at 800 rpm for 1 h and 1100 rpm for 30 min until a homogeneous hydrogel is achieved; this hydrogel is placed in a 1000 mL PTFE (Teflon) polytetrafluoroethylene reactor.
- Homogeneous hydrogel aging for 72 h.
- Submit the homogeneous hydrogel obtained at 80 °C for a period of 18 h for hydrothermal treatment.
- Wash and filter the material obtained with distilled water until a neutral pH is obtained in order to remove excess hydroxide.
- Dry the samples in the oven at 60 [°C] for 1 h.

The activation process by alkaline fusion followed by a hydrothermal treatment is presented in the following diagram, Figure 3 [18].

#### 3.2.2. Physico–Chemical Characterization of Activated Allophane

- **Fourier Transform Infrared Spectroscopy (FT-IR)**
  
  The spectrum has four broad absorption bands. The structural OH groups and the OH groups associated with the absorbed water are indicated by the absorption bands close to 3500 cm$^{-1}$.

  The absorption band at 1640 cm$^{-1}$ H$_2$O and the infrared (IR) vibration ranges of allophane rich in aluminum bonds (Si-O-AL) are shown at 800–1300 cm$^{-1}$.
The characteristic infrared band of allophane is 348 cm\(^{-1}\); however, this band can only be assigned to allophane if it is absent from illite, montmorillonite, kaolinite, and halloysite. None of the different natural samples is free from the minerals mentioned above, as the numerical values are shown in Table 9.

**Table 9.** Fourier Transform Infrared Spectroscopy (FT-IR) Results.

| Sample | Vibration of Molecules of Water, OH Groups | Deformation Caused by H\(_2\)O | Allophane Rich in Aluminum | Infrared Band Characteristic of the Allophane Absent from Illite, Montmorillonite, Kaolinite, and Halloysite |
|--------|------------------------------------------|---------------------------------|---------------------------|---------------------------------------------------------------------------------|
|        | cm\(^{-1}\)                             |                                 |                           |                                                                                 |
| AA-1   | 3364.92                                  | 1638.65                         | 1000.48                   | 553.96                                                                          |
|        | 3395.87                                  | 1631.90                         | 1002.23                   | 553.96                                                                          |
|        | 3424.03                                  | 1637.4                          | 975.61                    | 546.36                                                                          |
| AA-2   | 1660.2                                   | 1002.68                         | 550.16                    |                                                                                 |
|        | 1656.4                                   | 1000.07                         | 542.56                    |                                                                                 |
|        | 1664                                     | 1004.44                         | 557.76                    |                                                                                 |
| AA-3   | 3396.26                                  | 1620.57                         | 997.33                    | 553.82                                                                          |
|        | 3393.13                                  | 1618.75                         | 994.56                    | 555.60                                                                          |
|        | 3382.44                                  | 1618.34                         | 990.85                    | 556.06                                                                          |
| AA-4   | 3391.09                                  | 1633.24                         | 995.13                    | 557.66                                                                          |
|        | 3390.30                                  | 1632.64                         | 996.44                    | 552.27                                                                          |
|        | 3399.18                                  | 1630.55                         | 999.20                    | 559.43                                                                          |
| AA-5   | 3402.03                                  | 1632.69                         | 1000.92                   | 556.61                                                                          |
|        | 3404.70                                  | 1632.10                         | 1003.42                   | 560.9                                                                           |
|        | 3403.29                                  | 1632.96                         | 1001.69                   | 558.88                                                                          |
Table 9. Cont.

| Sample  | Vibration of Molecules of Water, OH Groups | Deformation Caused by H₂O | Allophane Rich in Aluminum | Infrared Band Characteristic of the Allophane Absent from Illite, Montmorillonite, Kaolinite, and Halloysite |
|---------|---------------------------------------------|---------------------------|---------------------------|-------------------------------------------------------------------------------------------------|
|         | cm⁻¹                                        |                           |                           |                                                                                                |
| AA-6    | 3396.53                                    | 1633.32                   | 995.79                    | 556.61                                                                                           |
|         | 3396.55                                    | 1632.76                   | 995.71                    | 552.32                                                                                           |
|         | 3397.63                                    | 1633.84                   | 996.16                    | 556.61                                                                                           |
| AA-7    | 3399.93                                    | 1632.36                   | 1004.21                   | 554.11                                                                                           |
|         | 3398.23                                    | 1633.36                   | 1004.18                   | 555.22                                                                                           |
|         | 3397.91                                    | 1633.39                   | 1005.09                   | 560.32                                                                                           |
| AA-8    | 3396.23                                    | 1634.03                   | 1004.56                   | 557.64                                                                                           |
|         | 3395.40                                    | 1631.72                   | 1003.25                   | 541.50                                                                                           |
|         | 3394.01                                    | 1632.17                   | 1007.30                   | 548.26                                                                                           |
| AA-9    | 3382.41                                    | 1624.29                   | 1001.91                   | 559.98                                                                                           |
|         | 3390.87                                    | 1624.10                   | 1003.13                   | 560.41                                                                                           |
|         | 3391.77                                    | 1625.06                   | 1002.89                   | 558.55                                                                                           |
| AA-10   | 3377.28                                    | 1621.44                   | 996.81                    | 559.91                                                                                           |
|         | 3397.20                                    | 1629.26                   | 995.44                    | 558.07                                                                                           |
|         | 3389.79                                    | 1628.62                   | 996.29                    | 557.91                                                                                           |
| AA-11   | 3384.41                                    | 1636.80                   | 1004.90                   | 554.95                                                                                           |
|         | 3382.81                                    | 1635.13                   | 1004.80                   | 565.80                                                                                           |
|         | 3383.99                                    | 1633.37                   | 1005.31                   | 561.81                                                                                           |
| AA-12   | 3387.96                                    | 1634.04                   | 1006.68                   | 558.45                                                                                           |
|         | 3385.78                                    | 1630.51                   | 1007.19                   | 554.93                                                                                           |
|         | 3387.73                                    | 1632.92                   | 1006.96                   | 558.64                                                                                           |
| AA-13   | 3401.21                                    | 1623.39                   | 1006.46                   | 553.86                                                                                           |
|         | 3411.85                                    | 1623.48                   | 1006.60                   | 557.70                                                                                           |
|         | 3409.59                                    | 1625.29                   | 1006.14                   | 557.42                                                                                           |
| AA-14   | 3390.01                                    | 1629.90                   | 1007.52                   | 557.56                                                                                           |
|         | 3392.63                                    | 1626.86                   | 1009.42                   | 561.10                                                                                           |
|         | 3403.47                                    | 1620.24                   | 1007.39                   | 556.71                                                                                           |
| AA-15   | 3398.75                                    | 1626.61                   | 1005.79                   | 549.42                                                                                           |
|         | 3399.49                                    | 1625.56                   | 1005.97                   | 553.72                                                                                           |
|         | 3403.86                                    | 1627.94                   | 1008.30                   | 554.19                                                                                           |

Table 9 shows the main bands of the different samples of activated allophane. The numerical values of the infrared vibration bands identified the presence of allophane and of illite, montmorillonite, kaolinite, and halloysite according to the vibration ranges.

3.2.3. Analysis of Particle Size

The percentage retention rates in the particle size test were established by the State Emerald Refinery for the case of the catalyst used in the fluidized catalytic cracking process subject to these values, >20%, 40%, 60%, 80%, and >80%. In all activated samples, a percentage of retention greater than 80% was identified; the particle size in that percentage of retention is greater than 0.08 mm (Table 10). Therefore, particle size should be reduced for subsequent tests.

Table 10. Average Size of activated allophane.

| Activated Samples | <20 mm | 20 mm | 40 mm | 60 mm | >80 mm |
|-------------------|--------|-------|-------|-------|--------|
| AA-1              | 0.00   | 0.04  | 0.23  | 0.58  | 99.15  |
| AA-2              | 0.01   | 0.45  | 2.25  | 4.91  | 92.38  |
| AA-3              | 0.02   | 0.72  | 3.80  | 8.75  | 86.72  |
| AA-4              | 0.03   | 1.03  | 5.38  | 12.26 | 81.30  |
Table 10. Cont.

| Activated Samples | <20 mm | 20 mm  | 40 mm  | 60 mm  | >80 mm |
|-------------------|--------|--------|--------|--------|--------|
| AA-5              | 0.03   | 1.10   | 5.85   | 13.21  | 79.81  |
| AA-6              | 0.03   | 1.19   | 6.34   | 14.11  | 78.33  |
| AA-7              | 0.04   | 1.28   | 7.00   | 15.61  | 76.08  |
| AA-8              | 0.03   | 1.07   | 5.82   | 13.38  | 79.70  |
| AA-9              | 0.03   | 1.00   | 5.32   | 12.30  | 81.35  |
| AA-10             | 0.03   | 0.94   | 4.72   | 10.94  | 83.37  |
| AA-11             | 0.02   | 0.69   | 3.47   | 8.00   | 98.88  |
| AA-12             | 0.01   | 0.39   | 1.93   | 4.34   | 93.33  |
| AA-13             | 0.00   | 0.06   | 0.32   | 0.74   | 98.88  |
| AA-14             | 0.00   | 0.05   | 0.27   | 0.64   | 99.04  |
| AA-15             | 0.00   | 0.05   | 0.23   | 0.59   | 99.13  |

3.2.4. Superficial Area BET

Allophane samples activated by the alkaline fusion method followed by hydrothermal treatment showed a BET surface area greater than 300 m²/g, which is within the range established by KAUFHOLD STEPHAN in activated samples 3, 6, 11, and 15. The other samples are outside the characteristic range of the allophane and at the same time of an FCC catalyst; for this reason, they were not considered in the following tests since the total surface area of the solid has an important effect on the reaction rate. The smaller the size of a catalyst particle, the greater the surface area.

The results of the BET surface area of each sample are presented below, Table 11.

Table 11. Results of superficial area BET of activated allophane.

| Samples | Essays | Empty Cell (g) | Cell with Sample BET (g) | Area BET (m²/g) | Superficial Area (m²/g) | Average of Superficial Area (m²/g) |
|---------|--------|----------------|--------------------------|-----------------|------------------------|-----------------------------------|
| AA-1    | 1      | 10.0500        | 10.1662                  | 33.94           | 292.08                 | 285.1324                          |
|         | 2      | 10.2000        | 10.3198                  | 32.73           | 284.11                 |                                    |
|         | 3      | 10.0500        | 10.1625                  | 31.41           | 279.20                 |                                    |
| AA-2    | 1      | 10.2024        | 10.3217                  | 27.95           | 234.28                 | 228.9463                          |
|         | 2      | 10.2003        | 10.3234                  | 27.94           | 226.97                 |                                    |
|         | 3      | 10.0524        | 10.1634                  | 25.04           | 225.59                 |                                    |
| AA-3    | 1      | 10.0537        | 10.1701                  | 35.12           | 301.72                 | 302.0292                          |
|         | 2      | 10.2060        | 10.3240                  | 36.66           | 310.68                 |                                    |
|         | 3      | 10.0462        | 10.1635                  | 34.45           | 293.69                 |                                    |
| AA-4    | 1      | 10.1998        | 10.3118                  | 28.86           | 257.68                 | 271.6072                          |
|         | 2      | 10.0504        | 10.1553                  | 30.3100         | 288.94                 |                                    |
|         | 3      | 10.2028        | 10.2962                  | 25.0500         | 268.20                 |                                    |
| AA-5    | 1      | 10.0506        | 10.1757                  | 24.87           | 198.80                 | 201.2320                          |
|         | 2      | 10.2029        | 10.3208                  | 25              | 212.04                 |                                    |
|         | 3      | 10.2022        | 10.3169                  | 22.12           | 192.85                 |                                    |
| AA-6    | 1      | 10.0504        | 10.1422                  | 35.75           | 389.43                 | 402.6160                          |
|         | 2      | 10.0500        | 10.1603                  | 45.47           | 412.24                 |                                    |
|         | 3      | 10.2021        | 10.3106                  | 44.07           | 406.18                 |                                    |
| AA-7    | 1      | 10.2019        | 10.3228                  | 13.27           | 109.76                 | 99.8721                           |
|         | 2      | 10.0503        | 10.1922                  | 10.49           | 73.93                  |                                    |
|         | 3      | 10.2019        | 10.3174                  | 13.39           | 115.93                 |                                    |
| AA-8    | 1      | 10.0492        | 10.161                   | 20.22           | 180.86                 | 188.5667                          |
|         | 2      | 10.2014        | 10.3139                  | 21.27           | 189.07                 |                                    |
|         | 3      | 10.0500        | 10.1636                  | 22.24           | 195.77                 |                                    |
| AA-9    | 1      | 10.2014        | 10.3157                  | 27.2            | 237.97                 | 250.6459                          |
|         | 2      | 10.0493        | 10.1472                  | 24.59           | 251.17                 |                                    |
|         | 3      | 10.2017        | 10.3213                  | 31.43           | 262.79                 |                                    |
Table 11. Cont.

| Samples | Essays | Empty Cell (g) | Cell with Sample BET (g) | Area BET (m²/g) | Superficial Area (m²/g) | Average of Superficial Area (m²/g) |
|---------|--------|----------------|--------------------------|----------------|------------------------|----------------------------------|
| AA-10   | 1      | 10.2018        | 10.3210                  | 28.01          | 234.98                 | 247.3363                         |
|         | 2      | 10.0502        | 10.1658                  | 27.45          | 237.46                 |                                   |
|         | 3      | 10.0499        | 10.1682                  | 31.89          | 269.57                 |                                   |
| AA-11   | 1      | 10.2012        | 10.3160                  | 36.21          | 315.42                 | 325.3312                         |
|         | 2      | 10.0493        | 10.1657                  | 37.13          | 318.99                 |                                   |
|         | 3      | 10.2018        | 10.3201                  | 40.41          | 341.59                 |                                   |
| AA-12   | 1      | 10.0498        | 10.1792                  | 10.40          | 80.37                  | 86.4101                          |
|         | 2      | 10.2024        | 10.3225                  | 10.58          | 88.20                  |                                   |
|         | 3      | 10.2018        | 10.3239                  | 11.07          | 90.66                  |                                   |
| AA-13   | 1      | 10.0495        | 10.1792                  | 10.12          | 78.03                  | 81.1681                          |
|         | 2      | 10.0490        | 10.1728                  | 9.58           | 77.38                  |                                   |
|         | 3      | 10.2019        | 10.2337                  | 10.73          | 88.10                  |                                   |
| AA-15   | 1      | 10.0222        | 10.3350                  | 45.17          | 340.14                 | 336.5539                         |
|         | 2      | 10.0503        | 10.1661                  | 40.29          | 347.93                 |                                   |
|         | 3      | 10.0501        | 10.1677                  | 37.82          | 321.60                 |                                   |

3.2.5. X-ray Diffraction (XRD)

The presence of the following minerals was determined by the X-ray diffraction test: quartz, anortite, actinolite, group N K-ferdespato (Sanidine microcline orthoclase), faujasite, and sodium aluminum silicate, as can be seen in Table 12. Specifically for allophane, X-ray diffraction indicates a weak generalized dispersion, due to particle size and undefined crystallographic structure, characteristic of this type of amorphous clay.

Table 12. Mineral determination by X-ray diffraction of activated allophane.

| Sample | Quartz (%) | Anortite (%) | Actinolite (%) | Group N K-Feldspar (Sanidine Microcline Orthoclase) (%) | Faujasite | Silicate of Aluminum and Sodium |
|--------|------------|--------------|----------------|------------------------------------------------------|-----------|--------------------------------|
| AA-3   | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE |
| AA-6   | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE |
| AA-11  | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE |
| AA-15  | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE | POSSIBLE PRESENCE |

3.2.6. Chemisorption

The determination of the active allophane activated sites is represented in Table 13. Table data contains the amount of ammonia adsorbed by the sample in the TPD test.

Table 13. Active site results of activated allophane.

| Sample | Active Sites | Active Sites/g |
|--------|--------------|----------------|
| AA 3   | 23           | 393            |
| AA 6   | 27           | 357            |
| AA 11  | 12           | 211            |
| AA 15  | 9            | 173            |
3.2.7. Determination of Greater Elements by X-ray Fluorescence (WD-XRF)

This method determined the concentrations of the elements in the form of oxides (see Table 14) for the following elements: sodium, magnesium, aluminum, silica, phosphorus, sulfur, potassium, calcium, titanium, manganese, and iron in natural samples. These percentages allowed calculation of the Si/Al ratio and the percentage of allophane in each activated samples as shown in Table 14. The ratio of SiO$_2$/Al$_2$O$_3$ oxides determines the percentage of allophane in each activated sample according to Equations (1) and (2).

Table 14. XRF results of activated allophane.

| Sample | Na$_2$O (%) | MgO (%) | Al$_2$O$_3$ (%) | SiO$_2$ (%) | P$_2$O$_5$ (%) | SO$_3$ (%) | K$_2$O (%) | CaO (%) | TiO$_2$ (%) | Mn$_2$O$_3$ (%) | Fe$_2$O$_3$ (%) | PPC (%) |
|--------|-------------|---------|-----------------|-------------|----------------|-----------|-----------|---------|-------------|----------------|----------------|--------|
| AA-3   | 9.122       | 3.053   | 21.902          | 32.562      | <0.01          | <0.05     | 0.207     | 2.145   | 0.699       | 0.059          | 5.396          | 23.46  |
| AA-6   | 7.767       | 3.382   | 21.521          | 32.631      | <0.01          | <0.05     | 0.208     | 2.335   | 0.832       | 0.076          | 5.734          | 24.08  |
| AA-11  | 4.611       | 2.603   | 21.567          | 26.485      | <0.01          | <0.05     | 0.478     | 3.693   | 1.129       | 0.08           | 12.573         | 23.71  |
| AA-15  | 1.566       | 3.608   | 22.346          | 27.61       | <0.01          | <0.05     | 0.72      | 5.575   | 1.134       | 0.105          | 11.988         | 24.07  |

Table 15 shows the results of the Si/Al ratio and the percentage of allophane of the activated samples. The Si/Al ratio of allophane is close to 1 according to [6] and [18]. The results obtained according to the test are greater than estimated since we performed desalumination of the samples by the activation method, which means we eliminated aluminum atoms. Thus, the lower the amount of aluminum, the greater the Si/Al ratio, and a high silicon content is inherently hydrophobic, so both elements have an affinity for hydrocarbons. An important factor to consider is that not all existing acid centers can be considered active centers for the development of a specific chemical reaction; only a part of them will have sufficient acid strength to catalyze that reaction in principle.

Table 15. Si/Al ratio of activated allophane.

| Sample | Ratio Si/Al | % Allophane |
|--------|-------------|-------------|
| AA-3   | 1.49        | 46.83       |
| AA-6   | 1.52        | 46.93       |
| AA-11  | 1.23        | 38.09       |
| AA-15  | 1.24        | 39.71       |

The percentage of allophane in the samples is less than 50%.

3.2.8. Catalytic Cracking Stage

- **Heavy crude.** Product obtained of the Emeraldas Refinery.
- **Reaction temperature.** Using a thermogravimetry (TGA) device, a general scan of the crude oil was carried out, from 25 to 500 °C, with a heating rate of 10 °C/min using a nitrogen atmosphere. The objective was the evaluation of the heavy oil based on time and temperature behavior. The result of this test is seen in Figure 10.
- **Time of reaction.** Tests were performed using a heating rate of 10 [°C/min], from 25 °C to the reaction temperature, and an analysis time of 90 min.
- **Catalyst mass/heavy crude mass ratio for the microactivity test.** A 50/50 ratio of catalyst/crude oil mass was used as specified by ASTM D3907/D3907M-19.

As can be seen in Figures 4 and 5, the greatest loss of mass was obtained in the first 40 min of reaction; after this period, the mass loss was insignificant, so we decided to keep the analysis time at 90 min.
• Time of reaction. Tests were performed using a heating rate of 10 °C/min, from 25 °C to the reaction temperature, and an analysis time of 90 min.

• Catalyst mass/heavy crude mass ratio for the microactivity test. A 50/50 ratio of catalyst/crude oil mass was used as specified by ASTM D3907/D3907M-19.

As can be seen in Figures 4 and 5, the greatest loss of mass was obtained in the first 40 min of reaction; after this period, the mass loss was insignificant, so we decided to keep the analysis time at 90 min.

Figure 4. Thermogravimetric curves at 420 °C.

Figure 5. Thermogravimetric curves at 420 °C.

3.3. TCE (Testing Catalyst Equipment) Design and Specifications

The design of the equipment is based on reproducing operating conditions for the FCC in the refinery based on the Standard Test Method for Testing Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test ASTM D3907/D3907M-19.

Inside the reactor a defined mass of catalyst particles (natural and activated allophane) rises together with a certain amount of hydrocarbon from the base upwards, without axial dispersion. During the course of the reaction, the reagents are in contact with the catalyst until they separate at the top.

The design specifications shown in Table 16 were determined. These generally describe the operating conditions with which the contact time is maintained. Under these conditions, the reagents
react with the catalyst inside the reactor (riser), reaching the desired conversion, according to the commercial specifications for the FCC in the refinery.

Table 16. TCE Specifications of Design.

| Reactor | Diameter mm | Length mm |
|---------|-------------|-----------|
| Stripper | 40          | 400       |
| Operating pressure | Activity psi | 20         |
| Feed | Maximum g/min | 5          |
| N2 pressure | Activity psi | 20         |
| Operating temperature | Maximum °C | 700        |
| Catalyst Inventory | Maximum g | 5          |
| | Minimum g | 2          |

These operating conditions allow us to obtain a contact time of 15 min as expressed by the standard, ensuring that the allophane does not rise too much when the load is injected or due to the increase in the number of moles caused by the formation of the cracking gas product. Higher speeds produce agglomeration in the mesh of the reactor stripper region with possible leaks to the condenser, Figure 6.

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The design specifications shown in Table 16 were determined. These generally describe the operating conditions with which the contact time is maintained. Under these conditions, the reagents react with the catalyst inside the reactor (riser), reaching the desired conversion, according to the commercial specifications for the FCC in the refinery.

3.4. Construction and Operation Details

The MAT consists essentially of a reactor, a condenser and a gas recuperator, distributed in a metal structure and interconnected by pipes and fittings that allow the supply of gases and gasoil. In addition, the MAT is assisted by a control panel that allows recording temperatures at one point, as well as energizing and controlling the electrical resistance. The reactor was turned from a stainless steel bar. It consists of the following areas: preheating, radiation, riser, stripping, and dome. The preheating, radiation, stripping, and dome areas are spliced with metal gaskets by flanges. The preheating zone, located at the bottom of the reactor, and spliced by flanges to the radiation zone, makes it possible for the residence time of the drag gas to be prolonged in order to improve the heat transfer to the fluid prior to its entry to the nozzle. In the radiation zone is the heating system, with which the allophane (catalyst) temperature rises; a nozzle is installed in the center that allows the impeller gas to escape. The stripping zone, attached to the radiation and dome zone, constitutes a low-pressure zone where separation of the catalyst and cracked gases occurs.

The stripper is coupled with the dome; inside of the stripper, a mesh is located, which allows the gases to escape from the cracking, free of catalyst particles. The reactor parts can be seen in Figures 7–9.

Figure 6. Condenser.
The preheating zone, located at the bottom of the reactor, and spliced by flanges to the radiation zone, makes it possible for the residence time of the drag gas to be prolonged in order to improve the heat transfer to the fluid prior to its entry to the nozzle. In the radiation zone is the heating system, with which the allophane (catalyst) temperature rises; a nozzle is installed in the center that allows the impeller gas to escape. The stripping zone, attached to the radiation and dome zone, constitutes a low-pressure zone where separation of the catalyst and cracked gases occurs.

The stripper is coupled with the dome; inside of the stripper, a mesh is located, which allows the gases to escape from the cracking, free of catalyst particles. The reactor parts can be seen in Figures 7–9.

Figure 7. Stripper.

Figure 8. Reactor.

Figure 9. Microactivity test device.

The condenser, built as a vertically located concentric tube heat exchanger, has a widened upper stripping zone that helps condensable gas fractions precipitate and be collected at the bottom, as indicated in Figure 7.

3.5. Characterization And Properties of Heavy Crude

The results of the analysis of heavy oil used as feed in the MAT are reported in Table 17. With the thermogravimetry (TGA) data, it is established that the weighted average temperature corresponds to 420 °C. With this value, and with the specific weight (0.9593), the characterization factor of Watson and Nelson (Kw or KUOP) is calculated (Table 18). This parameter allows determination of the chemical nature of the cargo next to mixed hydrocarbons and branched cycles, with little presence of naphthenes or slightly substituted aromatics.

Table 17. Characterization parameters of heavy crude.

| Parameters | Unit | Magnitude | Test |
|------------|------|-----------|------|
| Density API, 60 °F | ° API | 16.4 | ASTM D-287 |
| Specific gravity | 60°F/60 °F | 0.9593 | ASTM D-1298 |
| Absolute density | g/cm 3 | 0.99593 | - |
| Percentage of Sulphur | %, masa | 2.397 | ASTM-D130 |
| Viscosity, Second Seybolt Furol, SSF | s | 25 | ASTM D-88 |
| Cinematic viscosity, to 210 °F | St | 0.4864 | ASTM D-445 |
| Cinematic viscosity, to 100 °F | St | 1.4195 | - |
| Coal Conradson | %, mass | 11.97 | ASTM D-189 |
| Ashes | %, mass | 0.045 | - |
The condenser, built as a vertically located concentric tube heat exchanger, has a widened upper stripping zone that helps condensable gas fractions precipitate and be collected at the bottom, as indicated in Figure 7.

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| Parameters                                      | Unit       | Magnitude | Test         |
|-------------------------------------------------|------------|-----------|--------------|
| Density API, 60 °F                              | ° API      | 16.4      | ASTM D-287   |
| Specific gravity 60°F/60 °F                      |            | 0.9593    | ASTM D-1298  |
| Absolute density                                 | g/cm³      | 0.99593   | -            |
| Percentage of Sulphur                            | %, masa    | 2.397     | ASTM-D130    |
| Viscosity, Second Seybolt Furol, SSF             | s          | 25        | ASTM D-88    |
| Cinematic viscosity, to 210 °F                   | St         | 0.4864    | ASTM D-445   |
| Cinematic viscosity, to 100 °F                   | St         | 1.6195    |              |
| Coal Conradson                                   | %, mass    | 11.97     |              |
| Ashes                                           | %, mass    | 0.045     | ASTM D-189   |
| Paraffins                                        | %, mass    | 2.123     | -            |

Table 17. Characterization parameters of heavy crude.

| Property                                         | Unit       | Result    |
|--------------------------------------------------|------------|-----------|
| Factor KUOP                                      | -          | 9.5710    |
| Molecular weight                                 | kg/mol     | 292.15    |

Table 18. Properties of heavy crude calculating from experimental analysis.

3.6. Group of Particle Properties

A solid catalyst possesses properties of a fluid, in our case, essentially when allophane is dry, so that they exert pressure on the walls of the container that contains them. They can also flow or descend through a hole whereby they intersect and adhere due to the pressure. Some of the important characteristics such as density vary depending on surface rigidity, shape, and type of cross-linking and packaging [19].

Apparent Density of the Packed Catalytic Bed

In solids, the density does not vary due to pressure and temperature, unlike liquids. The set of particles packaging and crosslinking has a different behavior. Thus, in order to determine the gross or apparent density of natural and activated allophane, a certain amount of natural or activated allophane is poured into a tared specimen, and the weight of the allophane is related to the volume occupied. Several measurements are made with different quantities, and the average is taken in order to quantify the mass of natural and activated allophane that occupies a certain volume.

Table 19 shows the changes in density as the amount of activated allophane 15 in a specimen is increased, calculated from the mass that a volume occupies. On the other hand, Figure 10 shows linear behavior between the amount of the activated allophane and the volume it occupies, different from the density, since it relates mass, and volume increases. This allows saying that the density is an extensive property, due to the packing of the particles that asymptotically approximate a constant value.
Table 19. Apparent Density of the Packed Catalytic bed.

| AA-15 | Volume, [cm³] | Mass, g | Density, [g/cm³] |
|-------|--------------|--------|-----------------|
| 1     | 0.451        | 0.451  | 0.4510          |
| 2     | 1.0367       | 0.5183 | 0.5183          |
| 3     | 1.6493       | 0.5497 | 0.5497          |
| 4     | 2.3808       | 0.5952 | 0.5952          |
| 5     | 3.0609       | 0.6122 | 0.6122          |
| 6     | 3.6737       | 0.6123 | 0.6123          |
| 7     | 4.2653       | 0.6093 | 0.6093          |
| 8     | 4.9901       | 0.6238 | 0.6238          |
| 9     | 5.7248       | 0.6361 | 0.6361          |
| 10    | 6.324        | 0.6324 | 0.6324          |

Figure 10. Volume occupied by the mass of active allophane particles in a 10 mL test tube.

3.7. Microactivity MAT Test

The microactivity test is performed with the purpose of evaluating the activity of the circulating catalyst in the FCC unit by reproducing a catalytic cracking reaction. Heavy oil was used as the power source.

Catalyst microactivity is calculated with Equation (3):

$$X = \frac{M_f - y(M_L + M_Q) - M_M}{M_f} \times 100$$  \hspace{1cm} (3)

where:

- $X$ conversion [% mass/mass]
- $M_L$ difference in weight between the initial and final value of the condenser [g]
- $y$ fraction by weight of the sample treated in the porcelain crucible
- $M_f$ difference in weight between the initial and final value of the syringe [g]
- $M_Q$ difference in weight of the cotton with which the remainder of the lines and joints of the reactor dome to the condenser is cleaned [g]
- $M_M$ difference in weight of cotton that cleans the dome, rings, and mesh [g]

Table 20 shows the results of equilibrium catalyst samples (ECat) (new catalyst), reported as mass percentage (% M/M), evaluated in the TCE, and the results of the microactivity test reported by GRACE DAVISON Company, the supplier for the refinery (Paucar M, 2011).

Table 20. Conversion (X) evaluated through the Micro Activity Test and TCE of the Equilibrium Catalyst (ECat), (RESIDCAT® R 137).

| MAT X, % M/M | TCE supplier % X, % M/M |
|-------------|------------------------|
| 11.80       | 77                     |
| 11.06       | 76                     |

*a Results taken from “Study of the activity of the circulating catalyst in the fluidized catalytic cracking unit (FCC) of the Esmeraldas State Refinery (REE)”, Marco Favio Paucar Sánchez (2011).*
Table 20 shows the results of equilibrium catalyst samples (ECat) (new catalyst), reported as mass percentage (% M/M), evaluated in the TCE, and the results of the micro activity test reported by GRACE DAVISON Company, the supplier for the refinery (Paucar M, 2011).

**Table 20.** Conversion (X) evaluated through the Micro Activity Test and TCE of the Equilibrium Catalyst (ECat), (RESIDCAT® R 137).

| MATX, % M/M | TCE supplier | X, % M/M |
|------------|--------------|----------|
| 11.80      | 77           |          |
| 11.06      | 76           |          |

*Results taken from “Study of the activity of the circulating catalyst in the fluidized catalytic cracking unit (FCC) of the Esmeraldas State Refinery (REE)”, Marco FAVIO Paucar Sánchez (2011).*

The activity results reported by the MAT are inferior to the company results that supplies the catalyst in the refinery carried out in TCE (testing catalyst equipment). The results cannot be compared directly because the laboratory equipment is different, one with a fluid bed (TCE) and the other with a fixed bed (MAT). For this reason, in order to improve reproducibility between the different laboratories that perform the microactivity test (MAT), the results must be corrected by the calibration curve obtained from reference equilibrium catalysts with conversion within the useful range of the method proposed by ASTM D-3907 [19]. This will allow us to obtain data comparable to the activity of the commercial process.

The GS-MS gas chromatography analysis with DETAILED HYDROCARBON ANALYSIS (DHA) application of the cracked liquid product in the MAT of the different samples is found in Tables 21–26.

**Table 21.** Liquid products of catalytic cracking MAT.

| Sample | Octane Number | n-Paraffins | Iso-Paraffins | Olefins | Naphthenes | Aromatics |
|--------|---------------|-------------|--------------|---------|------------|-----------|
| New catalyst FCC 1 | 20.119 | 14.301 | 2.694 | 0.213 | 0.431 | 2.480 |
| New catalyst FCC 2 | 23.263 | 6.521 | 3.671 | 0.129 | 5.088 | 7.854 |
| Natural Allophane | 12.755 | 6.299 | 1.714 | 0.622 | 0.278 | 3.842 |
| Activated Allophane 11 | 22.682 | 19.551 | 0.794 | 0.242 | 0.117 | 1.978 |
| Activated Allophane 15 | 21.570 | 10.946 | 2.295 | 0.463 | 0.736 | 7.130 |

**Table 22.** Total composition results by group type and carbon number, as a percentage of the mass of catalyst New FCC 1.

| Carbon | n-Paraffins, % | Isoparaffins, % | Olefins, % | Naphthenes, % | Aromatics, % | Total, % |
|--------|----------------|-----------------|------------|---------------|--------------|----------|
| C8     | -              | -               | -          | -             | 1.139       | 1.139    |
| C9     | 0.096          | 1.939           | -          | 7.836         | 0.671       | 10.542   |
| C10    | 0.226          | 1.903           | -          | 0.409         | 3.292       | 5.829    |
| C11    | 1.626          | 1.564           | 0.139      | 0.195         | 1.778       | 5.302    |
| C12    | 1.291          | 0.402           | -          | 0.250         | 2.789       | 4.733    |
| C13    | 1.706          | 0.132           | -          | -             | -           | 1.838    |
| C14    | 2.131          | -               | -          | -             | -           | 2.131    |
| TOTAL  | 2.131          | 5.941           | 0.139      | 8.690         | 9.669       | 31.514   |

**Total Oxygenates:** 35.599
**Total Heavies:** 32.887
**Grand Total:** 100.000
Table 23. Total composition results by group type and carbon number, as a percentage of the mass of catalyst New FCC 2.

| Carbon | n-Paraffins, % | Isoparaffins, % | Olefins, % | Naphthenes, % | Aromatics, % | Total, % |
|--------|----------------|-----------------|------------|----------------|--------------|----------|
| C8     | 0.079          | 0.153           | 0.109      | 0.486          | 0.827        | 1.540    |
| C9     | 0.116          | 0.124           | 0.124      | 0.515          | 0.755        | 1.367    |
| C10    | 0.174          | 0.349           | -          | 0.286          | 1.063        | 1.654    |
| C11    | 0.329          | 1.744           | 0.098      | 0.051          | 0.282        | 2.505    |
| C12    | 0.602          | 0.291           | 0.069      | -              | 0.588        | 1.550    |
| C13    | 1.726          | 0.291           | 0.068      | -              | -            | 2.139    |
| C14    | 12.878         | -               | -          | -              | -            | 12.878   |
| TOTAL  | 15.903         | 2.883           | 0.234      | 0.571          | 2.934        | 22.526   |

Total Oxygenates: 
Total Heavies: 49.283
Total unknowns: 28.192
Grand Total: 100.000

Table 24. Total composition results by group type and carbon number, as a percentage of the mass of natural allophane 3.

| Carbon | n-Paraffins, % | Isoparaffins, % | Olefins, % | Naphthenes, % | Aromatics, % | Total, % |
|--------|----------------|-----------------|------------|----------------|--------------|----------|
| C8     | -              | -               | -          | 0.045          | 0.045        | 0.045    |
| C9     | 0.031          | -               | -          | 0.220          | 0.251        | 0.471    |
| C10    | 0.078          | 0.176           | -          | 0.046          | 1.122        | 1.422    |
| C11    | 0.157          | 0.434           | 0.026      | 0.151          | 0.612        | 1.379    |
| C12    | 0.973          | 0.734           | 0.252      | 0.125          | 3.130        | 5.214    |
| C13    | 1.114          | 0.521           | 0.408      | -              | -            | 2.044    |
| C14    | 4.569          | -               | -          | -              | -            | 4.569    |
| TOTAL  | 6.922          | 1.865           | 0.686      | 0.322          | 5.128        | 14.924   |

Total Oxygenates: 
Total Heavies: 33.572
Total unknowns: 51.504
Grand Total: 100.000

Table 25. Total composition results by group type and carbon number, as a percentage of the mass of activated allophane 11.

| Carbon | n-Paraffins, % | Isoparaffins, % | Olefins, % | Naphthenes, % | Aromatics, % | Total, % |
|--------|----------------|-----------------|------------|----------------|--------------|----------|
| C9     | 0.024          | -               | -          | 0.025          | 0.137        | 0.161    |
| C10    | 0.127          | -               | -          | 0.025          | 0.646        | 0.799    |
| C11    | 0.124          | 0.400           | -          | 0.070          | 0.522        | 1.116    |
| C12    | 0.438          | 0.194           | 0.067      | 0.040          | 1.327        | 2.067    |
| C13    | 1.983          | 0.283           | 0.202      | -              | -            | 2.468    |
| C14    | 18.929         | -               | -          | -              | -            | 18.929   |
| TOTAL  | 21.626         | 0.877           | 0.269      | 0.135          | 2.633        | 25.540   |

Total Oxygenates: 
Total Heavies: 35.994
Total unknowns: 38.466
Grand Total: 100.000
Table 26. Total composition results by group type and carbon number, as a percentage of the mass of activated allophane 15.

| Carbon | n-Paraffins, % | Isoparaffins, % | Olefins, % | Naphthenes, % | Aromatics, % | Total, % |
|--------|----------------|-----------------|------------|---------------|--------------|----------|
| C8     | 0.035          | -               | -          | -             | 0.094        | 0.129    |
| C9     | 0.105          | 0.035           | -          | 0.151         | 0.466        | 0.757    |
| C10    | 0.229          | 0.188           | -          | 0.253         | 3.150        | 3.820    |
| C11    | 0.054          | 0.790           | 0.228      | 0.092         | 3.316        | 4.479    |
| C12    | 0.892          | 1.163           | 0.092      | 3.606         | 2.084        | 4.591    |
| C13    | 1.687          | 0.304           | 0.186      | -             | -            | 2.178    |
| C14    | 9.038          | -               | -          | -             | -            | 9.038    |
| TOTAL  | 12.041         | 2.479           | 0.506      | 0.856         | 9.110        | 24.992   |

Total Oxygenates: -
Total Heavies: 36.221
Total unknowns: 38.787
Grand Total: 100.000

3.7.1. Catalytic Cracking Dynamics

The catalysis dynamics aims to quantitatively explain the forces and vector fields of moving fluids. The 3D Navier–Stokes equations govern the behavior of any fluid; in that sense chemical reactions are closely related to the fluid dynamics inside these complex systems.

**Dimensional analysis**

We will define the respective dimensional units of each of the variables and physical constants that appear in the solution of the Navier–Stokes 3D equation:

**Cinematic viscosity**

\[ \nu = \frac{\eta}{\rho_0} \left[ \frac{m^2}{s} \right] \]

**Dynamic viscosity**: \( \eta \), [pa·s], where [pa]: Pascal pressure unit
Initial pressure of equilibrium output: \( p_0 \), [pa]
Fluid density: \( \rho_0 \), [kg/m³], where kg is kilogram and m³ cubic meters.

Logistics probability function: \( P(x, y, z, t) = \frac{1}{1 + e^{x-y-z}} \), it is the real number \( 0 \leq P \leq 1 \).

Equilibrium condition: \( r = \frac{k}{\mu} t = \frac{p_0}{2\rho_0 \eta} t = |u_e|t, [m] \).

Output speed of fluid field at equilibrium: \( u = -2\nu(1-P)\nabla r [m/s] \).
Position, \( r = (x^2 + y^2 + z^2)^{1/2}[m] \).
Attenuation coefficient: \( \mu \), [1/m]

Growth coefficient: \( k = \frac{p_0}{2\rho_0 \eta} [1/s] \).
Concentration: \( C = C_0 e^{-\frac{k}{\mu} t} \).

The speed of the fluid needs to be defined by: \( u = -2\nu \frac{\nabla P}{\rho_0} \), where \( P(x, y, z, t) \) is the logistic probability function \( P(x, y, z, t) = \frac{1}{1 + e^{x-y-z}} \), \( r = (x^2 + y^2 + z^2)^{1/2} \), defined as \( (x, y, z) \in \mathbb{R}^3, t \geq 0 \). \( P \) is the general solution of 3D Navier–Stokes equation, which satisfies Equations (4) and (5), allowing the dynamic analysis of an incomprehensible fluid:

\[ \frac{\partial u}{\partial t} + (u \cdot \nabla) u = -\frac{\nabla P}{\rho_0} \left( (x, y, z) \in \mathbb{R}^3, t \geq 0 \right) \]  (4)

where, \( u \in \mathbb{R}^3 \) is a vector of known speed, \( \rho_0 \) is constant fluid density and pressure \( p = p_0 P \in \mathbb{R} \).
Speed and pressure are dependent on \( r \) and \( t \). We will write the incompressible condition as follows:

\[
\nabla \cdot u = 0 \quad \left( (x, y, z) \in \mathbb{R}^3, \ t \geq 0 \right)
\]

(5)

**Theorem 1.** Navier–Stokes 3D solutions. The fluid velocity is given by \( u = -2v \nabla P \), where \( P(x, y, z, t) = \frac{1}{1 + e^{k(t-wx^2+y^2+z^2)^{1/2}}} \), defined in \( (x, y, z) \in \mathbb{R}^3, \ t \geq 0 \); it is the general solution of the Navier–Stokes equation, which satisfies Equations (4) and (5).

Prove: first, We set equivalence \( u = \nabla \theta \) and replace it in Equation (4). Taking into account that \( \nabla \theta \) is anti rotational, \( \nabla \times \nabla \theta = 0 \), leads to:

\[
(u, \nabla) u = (\nabla \theta, \nabla) \nabla \theta = \frac{1}{2} \nabla (\nabla \theta \cdot \nabla \theta) - \nabla \times (\nabla \times \nabla \theta) = \frac{1}{2} \nabla (\nabla \theta \cdot \nabla \theta)
\]

We can write:

\[
\nabla \left( \frac{\partial \theta}{\partial t} + \frac{1}{2} (\nabla \theta \cdot \nabla \theta) \right) = \nabla (-p)
\]

This is equivalent to:

\[
\frac{\partial \theta}{\partial t} + \frac{1}{2} (\nabla \theta \cdot \nabla \theta) = \frac{\Delta p}{\rho_0}
\]

where \( \Delta p \) is the difference between the current pressure \( p \) and some reference pressure \( p_0 \). Now replace \( \theta = -2v \ln(P) \); the Navier–Stokes equation becomes:

\[
\frac{\partial p}{\partial t} = \frac{\Delta p}{\rho_0} p,
\]

(6)

The external force is zero, so there is a constant force \( F \) due to the pressure variation in a cross section \( \sigma \). Where \( \sigma \) is the total cross-section of all events that occur in cavitation and bubble formation including loss of energy, absorption, and creation of shock waves.

\[
F = p \sigma_2 = p_0 \sigma_1
\]

\[
\Delta p = p - p_0 = \left( \frac{\sigma_1}{\sigma_2} - 1 \right) p_0 = -(1 - P)p_0 ,
\]

(7)

Inserting Equation (6) in Equation (7) we have

\[
\frac{\partial p}{\partial t} = -\mu k(1 - P)p
\]

(8)

To verify Equation (5), \( \nabla \cdot u = 0 \), we need to obtain \( \nabla r = \left( \frac{x}{r}, \frac{y}{r}, \frac{z}{r} \right) \),

\[
\nabla^2 r = \nabla \cdot \nabla r = \frac{y^2 + z^2 + (x^2 + y^2) \left( x^2 + y^2 + z^2 \right)^{3/2}}{r^2} = \frac{2}{r}
\]

\[
\nabla \cdot u = -2v \nabla \cdot \frac{\Delta p}{p} = -2v \mu(1 - P) \nabla \nabla r
\]

(9)

Replace the respective values for the terms: \( \nabla^2 P \) and \( |\nabla P|^2 \) of Equation (9). The Laplacian of \( P \) it can be written as follows:

\[
\nabla^2 P = \mu(1 - 2P) \nabla P \cdot \nabla r + \mu (P - P^2) \nabla^2 r
\]

(10)

\[
= \mu^2 (1 - 2P) (P - P^2) \nabla r^2 + \mu (P - P^2) \nabla^2 r
\]

(11)
\[= \mu^2(1 - 2P)(P - P_2) + \mu\left(P - P_2\right)^2 \tag{12} \]

Using the gradient \( \nabla P = \mu(P - P_2)\nabla r \), module \( |\nabla P|^2 = \mu^2(P - P_2)^2|\nabla r|^2 \) and \( \nabla^2 P \) in Equation (10). Equations (11)–(13) can be seen in references [20–22].

\[\left[ \nabla^2 P - \frac{|\nabla P|^2}{P^2} \right] = 0 \tag{13} \]

Replace Equations (9) and (10) in Equation (13); we obtain the main result of the Navier–Stokes equations, this solution represents a fixed point of an implicit function \( f(t, r) \) where \( f(t, r) = P - \frac{2}{\mu r} = 0 \)

\[P = \frac{1}{1 + e^{k(t - \mu(x^2 + y^2 + z^2)^{1/2})}} = \frac{2}{\mu(x^2 + y^2 + z^2)^{1/2}} \left( (x, y, z) \in \mathbb{R}^3, t \geq 0 \right) \tag{14} \]

Placing the parameters \( k \) based on the variables of fluid mechanics, we have:

\[P = \frac{1}{1 + e^{\frac{kt}{\mu} - \mu(x^2 + y^2 + z^2)^{1/2}}} \left( (x, y, z) \in \mathbb{R}^3, t \geq 0 \right), \tag{15} \]

### 3.7.2. Application of 3D Navier–Stokes in Reaction Dynamics

Starting from Equation (14), which describes in a probabilistic way the solution of the Navier–Stokes 3D equations, we can find the fundamental values of the model, that is, \( k \), the constant of growth or decrease of the reaction and \( \mu \), the absorption coefficient. Taking into account that experimentally, through a TGA thermobalance, we know the variable reaction \( P(x, y, z, t) \) that depends on space \( (x, y, z) \) and time \( t \), we can obtain:

\[P(x, y, z, t) = \frac{C_0}{C(x, y, z, t) + C_0}, \tag{16} \]

where \( C_0 \) which represents the concentration of the analyzed crude, is its mass and depends on space and time \( (x, y, z, t) \). In an analogous way, using Equation (14), we obtain \( k, \mu, b \) through two regressions.

\[P = \frac{1}{\mu r}, \tag{17} \]

\[\ln\left(\frac{1 - P}{P}\right) + \frac{2}{P} = kt + b, \tag{18} \]

### Vector speed field

The knowledge of the velocity vector field allows us to evaluate the behavior of the field, Figure 11, especially as regards stability, especially when turbulence occurs or the fluid becomes complex, making the industrial use of the fluid difficult.

\[u = -2\nu\mu(1 - P)\nabla r, \tag{19} \]

\[u = -2\nu\mu(1 - P)\frac{1}{r}(x, y, z), \]

\[u = -2\nu\mu\left(\frac{1}{(x^2 + y^2 + z^2)^{1/2}} - \frac{2}{\mu(x^2 + y^2 + z^2)}\right)(x, y, z), \]

\[\left(\frac{x}{(x^2 + y^2 + z^2)}\right)' \left(\frac{y}{(x^2 + y^2 + z^2)}\right)' \left(\frac{z}{(x^2 + y^2 + z^2)}\right)' \]
4. Discussion

Allophane is a material with a high water absorption capacity, which is why it was dried at 60 °C so as not to change its average drying properties.

The physicochemical characterization was established according to the BET surface area results of the samples analyzed; in the case of natural allophane, the selected samples were 3, 4, and 15. In the case of the activated allophane, samples were established as 3, 6, 11, and 15.

By the chemisorption test, the acidity was determined by identifying active centers in the samples. Not all existing acid centers can be considered active development centers for the chemical reaction since only a part will have enough acid to catalyze the reaction. The surface acidity of the allophane was modified by the ion exchange method or desaluminization synthesis (alkaline fusion method at 600 °C, followed by a treatment), obtaining the Si/Al ratio in the case of the activated allophane.

Among the variables analyzed in the allophane activation process such as: agitation speed, aging time, hydrotreatment time, and the NaOH/allophane ratio, the most important variables were the aging time and the hydrotreatment time since they define the amount of aluminum present in the allophane and at the same time, establish the Si/Al ratio. This ratio is a factor that influences catalytic activity.

The microactivity test showed lower conversion values in the mass–mass percentage of the product obtained compared to the conversion of the catalyst at equilibrium (RESIDCAT® R 137 because the operating conditions were not those indicated by the standard since it was modified according to the refinery operating conditions.

5. Conclusions

- The BET surface area of a catalyst is an influential property in the development of the catalytic cracking reaction; in the case of the natural allophane, it was determined that samples 3, 4, and 15 had a numerical value greater than or equal to 300 m²/g of surface area as shown in Table 3. In the case of the activated allophane, i.e., the surface area in general, the different samples decreased the numerical value with the exception of samples 3, 6, 11, and 15.
- The active sites were determined by means of the chemisorption test for natural and activated allophane. In the case of activated allophane, in general, it increases the active sites compared to natural allophane. In addition, the presence of nano particles was corroborated by atomic force microscopy (AFM) due to its spongy form with abundant fine pores, maintaining a relationship with the surface area, since the greater the porosity, the greater the surface area of contact. The activity was confirmed by means of the microactivity test.
- The natural and activated allophanes were within the characteristic range of the vibration bands identified in the FT-IR, identifying allophane of aluminum-rich soils in all samples.
• The increase in the Si/Al ratio implied a decrease in the aluminum content. This process was carried out through the development of the allophane activation method by means of the alkaline fusion method followed by hydrothermal treatment, since desaluminization obtained an Si/Al ratio relative to the natural allophane. It is concluded that the higher the Si/Al ratio, the higher the activity of the allophane in contact with the oil.

• The operating temperature of the microactivity test based on the ASTM D3907 standard was 482 degrees Celsius for catalytic cracking, while according to thermal cracking, it was 420 based on the thermo gravimetry test as can be seen in Figures 5 and 6.

• The activity of natural and activated allophane was compared with the activity of the new FCC catalyst, determined by converting the mass–mass percentage of the crude feed and the products obtained in the catalytic cracking process. Identifying by gas chromatography with DHA application a lower API grade of 22.68 in all products were obtained with the different catalysts as can be seen in Table 21. The products obtained with the new catalyst FCC 1 and activated allophane 11 were highly paraninic, and also, this sample had a minimum aromatic content in all the products obtained from the microactivity test.

• The conversion obtained for the mass–mass percentage of the activated allophane had a considerable value in comparison to the natural allophane since the Si/Al ratio was greater for the reason that the numerical conversion value was greater in the activated allophane as can be observed in Table 27.

Table 27. Conversion rate of catalytic cracking of different samples.

| Shows                  | MATX, %M/M |
|------------------------|------------|
| Natural Allophane      | 5.60       |
| Activated Allophane 11 | 11.959     |
| Activated Allophane 15 | 9.81       |

• C8 to C15 carbon chains were identified in the different products obtained with the exception of activated allophane 11, which contained C9 to C15.

• The Navier–Stokes 3D equations allowed us to establish the dynamics of Newtonian and non-Newtonian fluids in this case of heavy crude oil, allowing us to establish the conditions of macroscopic fluid equilibrium; this equation was determined through the results of thermogravimetry tests with a 1:1 ratio of crude/catalyst or allophane (natural and activated).

Author Contributions: Conceptualization A.E.P.T. and P.F.H.M.; investigation, data analysis, interpretation, and writing.—Original manuscript preparation, review, and editing. Investigation E.H.J.C., translation D.A.H.C., review W.R., U.S. and J.B. All authors have read and agreed to the published version of the manuscript.

Funding: The research directorate (DI) of the Central University of Ecuador, financed projects PRY-004 “Technical and economic feasibility of industrialization of allophanes and their use as a catalyst for the FCC fluidized catalytic cracking process” and cif5-ce-fiq-2, “ALLOPHANIC NANOTECHNOLOGICAL ADDITIVE FOR ASPHALT”.

Acknowledgments: The research directorate (DI) of the Central University of Ecuador, as well as the group of the GIIP process research and Faculty Chemical Engineering, UCE.

Conflicts of Interest: The authors declare no conflict of interest.

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