Comparative study using different external sources of aluminum on the zeolites synthesis from rice husk ash

Marcos Antonio Klunk, Mohuli Das, Sudipta Dasgupta, Andrea Natale Impiombato, Nattan Roberto Caetano, Paulo Roberto Wander and Carlos Alberto Mendes Moraes

1 Department of Mechanical Engineering, University of Vale do Rio dos Sinos, Av. Unisinos 950, São Leopoldo, RS, Brazil
2 Indian Institute of Technology Bombay (IIT Bombay), Powai, Mumbai 400076, India
3 Department of Industrial Engineering, Alma Mater Studiorum University of Bologna, Viale del Risorgimento 2, 40136, Bologna, Italy
4 Department of Mechanical Engineering, Federal University of Santa Maria, Av. Roraima 1000, Santa Maria, RS, Brazil

E-mail: marcosak@edu.unisinos.br

Abstract

Rice husk is considered as a waste in the rice industry but is proficient in manufacturing different materials, such as zeolites, which is produced in large quantities all over the world, for example in Brazil. Zeolite is an adsorbent support material, which can be synthesized from rice husk ash (RHA) with external sources of aluminium (ESA). The scientific community has been conducting several measures to minimize the environmental impacts caused by greenhouse gases. Several mitigation processes are presently investigated, which includes carbon dioxide injections into adsorbent processes are presently investigated, which includes carbon dioxide injections into adsorbent materials (e.g. zeolites). The efficiency of this technology involves a zeolitic material with high crystallinity and high concentrations of SiO2 and Al2O3 (aluminosilicates). In the present work, zeolites have been synthesized from rice husk ash (SiO2 source) and external aluminium sources (Al2O3 - alumina, gibbsite and metakaolin) to fulfill that purpose. With the aid of XRF, XRD, SEM/EDS and FTIR techniques, the zeolitic material was characterized in two distinct crystalline phases: Mordenite and ZSM-5. The synthesis was carried out by the ideal addition of ESA (2.5 g) to RHA. According to the literature, the zeolitic materials formed by the mixture of Mordenite and ZSM-5 can be availed for gas separation and greenhouse gas storage.

1. Introduction

During rice production, large amounts of rice husks are released into the environment and these are generally used for the combustion, thereby generating rice husk ash (RHA). This byproduct is produced worldwide and causes an environmental problem such as air and water pollution [1]. On the other hand, the chemical analysis reveals that RHA contains 90%–99% of silica, which can be a cheap source to be used in several industrial sectors [2–4]. Several researchers have utilized silica obtained from RHA as a raw material for production in solar grade silicon (Si–GS) [5], silicon carbide (SiC) [6], silicon nitride ceramics (Si3N4) [7] and mullite (a fibrous alumina silicate mineral of low thermal expansion, formed within porcelain bodies during firing and in industry by calcining) [8–10].

Different methods of obtaining silica affect its structure and morphology and consequently influences its reactivity. The RHA is a residue rich in amorphous silica and is extremely active for the synthesis of zeolite in general [11–17].

Synthetic zeolites are classified by Si/Al ratio as the following: (i) low-silica zeolites (SiO2/Al2O3 ≤ 2); (ii) intermediate silica zeolites (2 ≤ SiO2/Al2O3 ≤ 5) and (iii) high-silica zeolites (SiO2/Al2O3 > 5) [18, 19]. X-ray fluorescence spectroscopy (XRF) reveals that Si/Al ratio in the silica of RHA is very high and ESA contributes to the reduction of the ratios, making it possible to synthesize zeolite with SiO2/Al2O3 > 5. The ESA used for the experiment were alumina [Al2O3], gibbsite [Al(OH)3] and metakaolin [Al2O3·2SiO2]. These additions assist to identify the suitable sources to approach the ideal ratio during synthesis of zeolites. The synthesized zeolites can
be used for the adsorption of carbon dioxide (CO₂) to mitigate the environmental impacts caused by greenhouse
gas emissions [20–24]. The wide application of zeolites for CO₂ adsorption is enabled due to larger pore cavities
compared to the molecular diameter of carbon dioxide [25–29]. The aim of the present work is to compare and
diagnose the additions of an external source of aluminium (ESA) for synthesis of zeolite from RHA.

2. Materials and methods

The materials and the methodology applied in this work consist to characterize the precursor material (RHA and
ESA) and the formed zeolites.

2.1. Rice husk ash

The rice husk arouses interest due to its composition rich in silica, availability, and cost, being able to add value
to this residue and for its utilization as a secondary source of materials [30, 31]. Rice husk is an abundant waste
material derived from agricultural production and has been used with great efficiency as an energy source
through burning. It is used as a fuel in rice processing because it is a renewable energy source with a reasonable
energy content of 12–18 MJ kg⁻¹ and has a high transport cost due to low packaging [4, 32].

Rice husk produces a black residue containing about 15% carbon and the remainder of silica on an average
during burning [33]. In some places RHAs are disposed of in landfills, causing air and water pollution [34–38].
However, the rice husk releases a large amount of silica and therefore, can be used as an alternative source of
silicon [39, 40].

2.2. Zeolites

In 1876, Alex Fredrick Cronstedt defined zeolite as a mineralogical structure having particular properties of ion
exchange and adsorption [41]. Zeolite is a natural or synthetic mineral containing defined crystalline structures
[42]. It consists of a tetrahedral structure (TO₄), where T represents different atoms such as silicon, aluminium,
germanium, iron, boron, phosphorus or cobalt. Predominantly, the major structures of zeolites represent
tetrahedral configuration of alumina (AlO₄)⁻³ and silica (SiO₄)⁻⁴ [43, 44]. The silicon and aluminium units
unite to form tetrahedral sheets, whereas hexagonal structures are constructed every six units oriented in the
same direction [45].

The zeolite’s cation exchange capacity is related to its Si/Al ratio [46]. There are approximately forty natural
occurrences of zeolites, and some of them are analcime, chabazite, clinoptilolite, erionite, faujasite, ferrierite,
heulandite, laumontite, mordenite and phillipsite [47, 48]. Natural zeolites have impurities that limit their
application, as a result people have begun to synthesize zeolites for academic as well as industrial purposes [46].
There are 200 types of synthetic zeolites, for example: A, X, Y, L, F, Mordenite, ZSM-5, ZSM-11 etc [42, 49].
Zeolites can be used to mitigate the environmental impacts caused by greenhouse gas emissions [20, 21]. These
synthetic zeolites have larger porosity compared to other types of zeolites, which provides them a wide variety of
applications.

Synthesis of high purity and crystallinity zeolitic material involves organic template [tetrapropylammonium bromide (TPAB), tetrapropyl ammonium hydroxide (TPAOH), cetyltrimethyl ammonium bromide (CTAB), dimethyl octadecyl [3- (trimethoxysilyl) propyl] ammonium chloride (TPO)]. This director has the function of defining a specific topography (atoms connectivity) that increases the crystallinity of the zeolitic material [50]. The high cost of manufacturing the zeolitic material is associated with the organic director as they are valuable reagents. In order to minimize economic costs in zeolite synthesis, researchers such as Dey et al (2013) [38], Huang and Wang (2011) [50], Cheng et al (2008) [51], Kim et al (2004) [52] and Cheng et al (2005) [53] do not use organic template. Research has shown that ZSM-5 zeolites synthesized without organic template have structures that allow the creation of active sites as well as a complex network of channels, which gives it different types of selectivity.

The generation of the Secondary Building Units (SBUs) were previously studied thoroughly and were
obtained by adjusting the variables that participated in the synthesis process such as temperature and time of
nucleation, concentration of alkaline treatment, pH of the zeolitic material after synthesis and ideal molar
quantities of the external sources of aluminium and silicon. The availability of Al³⁺ and Si⁴⁺ cations favour the
formation of the desired structure, acting as a director. The presence of Na⁺ cations, available through alkaline
attack, facilitated the formation of six-membered double ring structures. Consequently, silicon (SiO₄)⁻⁴ and
aluminum (AlO₄)⁻³ tetrahedra contributed to the increase in channel volume [53].

Geological carbon storage is a path that involves CO₂ capture from the exhaust gases stored in an
environment and henceforth, prevents it from entering the atmosphere again. These low carbon dioxide
emissions can be predicted by geochemical modeling [54–57]. One of the existing technologies involves CO₂
capture post-combustion, using adsorption as a selective process where the constituent molecules in a mixture
of gases adhere on the solid surface (zeolites) [26, 58–62]. The primary variables to be considered for adsorption are temperature, pressure and pore size [63]. The material selection should also be conducted after considering the economic criteria, not only regarding the costs of synthesis and choice of adsorbent material, but also the volume of adsorbent required. Henceforth, zeolites are produced by following a route of synthesis based on the RHA allied to an ESA [58–61].

2.3. Characterization of the rice husk ash and zeolitic material
A characterization step is an indispensable tool for understanding its properties and applications for a detailed study of a natural or synthetic material. Due to the limitations inherent in each one of the characterization techniques, it is essential to use various techniques for the characterization of a complete analysis. A proper understanding of the physical and chemical characteristics of rice husk ash and the synthesized zeolite is the first step for their application. The applied techniques in this work are pH, conductivity, moisture and calcination, identification of functional groups, morphology, chemical and mineralogical composition of the RHA and synthesized zeolites.

2.4. Synthesis of zeolites from rice husk ash
The proposed methodology was based on Wang et al (2018) [20] and the aim was to develop a synthesis process for the production of zeolites from rice husk ash. The methodology involves a few reactions in alkaline conditions (NaOH – 3.5 mol l⁻¹) with RHA. The External Sources of Aluminum (table 1) such as (i) alumina (AM); (ii) gibbsite (GT) and (iii) metakaolin (MK) was added in the reaction environment in order to obtain the Si/Al ratio feasible for the synthesis of zeolites and to guarantee their capacity of adsorbing CO₂ [20, 21].

The zeolites formed during the course of our present work are as follows: (i) ZRHA (Zeolite from Rice Husk Ash—without ESA); (ii) ZRHA-AM (Zeolite from Rice Husk Ash with Alumina); (iii) ZRHA-GT (Zeolite from Rice Husk Ash with Gibbsite) and (iv) ZRHA-MK (Zeolite from Rice Husk Ash with Metakaolin).

3. Results and discussion
The results obtained in this work represent the characterization of RHA as well as the zeolites formed in the synthesis process.

3.1. Characterization of ash and zeolites synthesized by the classical method
The first part of this study involves the characterization of the RHA and its respective synthesized zeolites. The aim of this stage was to compare the results of the ESA added to RHA in order to obtain the best SiO₂/Al₂O₃ ratio, thus directing towards the preparation of a zeolitic material for CO₂ adsorption.

3.1.1. Determination of pH and electrical conductivity
Table 2 shows the pH and electrical conductivity values of RHA and their respective zeolites.
According to the results, the resultant pH values for RHA samples were very close, ranging from 8.54 (RHA) to 9.31 (RHA + 3.0 g GT). In the study of Wang et al (2018) [20], the pH of RHA ranged from 8.0 to 12 depending on the characteristics of the ESA and the burning process of rice husk. The pH values of the aqueous solutions containing RHA and ESA are justified by the presence of carbonate, hydrogen carbonate, oxide or hydroxide anions which form compounds with K⁺, Ca²⁺, Mg²⁺ and Na⁺ present in the additions of alumina, gibbsite and metakaolin. Such compounds, when dissolved, cause alkalinity of the suspension. The pH of the zeolites varies between 9.70 and 9.54. This increase in pH related to initial ash has occurred due to the use of NaOH for the synthesis of zeolites by hydrothermal treatment.

The electrical conductivity values are related to the presence of certain elements in RHA and ESA. These dissociated compounds release their ions increasing the potential difference in the solution [64]. The values resulted in the ashes in the present study vary between 101.1 μS (RHA) and 157.7 μS (RHA + 3.0 g GT). This discrepancy is observed due to the easy dissociation of gibbsite, allowing the solubilization of a great number of ionic compounds. The electrical conductivity values for the zeolites (RHA + ESA) were much higher than the values of the precursor materials (RHA) due to the presence of exchangeable cations in the zeolitic structures.

### 3.1.2. Determination of moisture and calcination

Determination of moisture and calcination is frequently performed for RHA because both can indicate its better or worse performance in zeolite synthesis. The values of moisture and calcination are 0.4248% and 4.8368%, respectively. According to the results, the low moisture content in RHA (<3% per mass) corresponds to the retention of the combustion gases, which represents high temperature. The results of calcination are generally due to the presence of unburned coal (indicating the combustion inefficiency of a thermoelectric plant) and unstable mineral phases at high temperatures [65]. In this study, the calcination results indicate a low content and henceforth, the low grain size values of RHA (figure 1) contribute to a complete burn, resulting a great efficiency in the thermoelectric plant.

Comparing the results obtained in the studies of moisture and calcination from RHA, it can be observed that low calcination also presented low moisture content due to complete burning, thus reducing the ability to absorb water. Low moisture content and calcination positively influences the synthesis of zeolites, as it implies a great number of reactive phases during the synthesis [65].

### 3.1.3. Chemical composition

The potential application of RHA is defined by its chemical composition, which was determined by x-ray fluorescence, together with ESA (table 3). The existent compounds are derived from inorganic fractions in the ashes and ESA, so the results are presented in the oxides form. According to the results, there are large variations between the contents of the main ash and ESA components. The primary constituent of the RHA is silicon oxide (SiO₂) with 99.73% per mass, in which a SiO₂/Al₂O₃ ratio of 1108.

For the ESA, the main zeolite forming components are SiO₂ and Al₂O₃. The Fe₂O₃ compound is considered to be important because it is a limiting factor for obtaining the zeolitic material which is not reactive during the synthesis [46, 65].

### Table 2. pH and electrical conductivity values for RHA and their respective zeolites.

| Sample       | pH    | Electrical conductivity (μS) | Sample       | pH    | Electrical conductivity (μS) |
|--------------|-------|------------------------------|--------------|-------|------------------------------|
| RHA          | 8.54  | 101.1                        | ZRHA         | 9.20  | 304.8                        |
| RHA + 1.0 gAM| 8.78  | 120.7                        | ZRHA-AM1.0   | 9.24  | 954.7                        |
| RHA + 1.5 gAM| 8.80  | 121.0                        | ZRHA-AM1.5   | 9.31  | 955.2                        |
| RHA + 2.0 gAM| 8.85  | 123.4                        | ZRHA-AM2.0   | 9.45  | 957.5                        |
| RHA + 2.5 gAM| 8.93  | 125.8                        | ZRHA-AM2.5   | 9.50  | 959.8                        |
| RHA + 3.0 gAM| 8.99  | 130.1                        | ZRHA-AM3.0   | 9.54  | 968.4                        |
| RHA + 1.0 gGT| 8.81  | 124.4                        | ZRHA-GT1.0   | 9.11  | 938.3                        |
| RHA + 1.5 gGT| 8.98  | 131.0                        | ZRHA-GT1.5   | 9.24  | 940.7                        |
| RHA + 2.0 gGT| 9.09  | 139.9                        | ZRHA-GT2.0   | 9.37  | 947.3                        |
| RHA + 2.5 gGT| 9.18  | 144.2                        | ZRHA-GT2.5   | 9.39  | 959.9                        |
| RHA + 3.0 gGT| 9.31  | 157.7                        | ZRHA-GT3.0   | 9.42  | 962.1                        |
| RHA + 1.0 gMK| 8.62  | 119.8                        | ZRHA-MK1.0   | 9.07  | 927.7                        |
| RHA + 1.5 gMK| 8.69  | 125.5                        | ZRHA-MK1.5   | 9.19  | 931.8                        |
| RHA + 2.0 gMK| 8.72  | 134.6                        | ZRHA-MK2.0   | 9.25  | 940.2                        |
| RHA + 2.5 gMK| 8.82  | 141.4                        | ZRHA-MK2.5   | 9.39  | 949.9                        |
| RHA + 3.0 gMK| 8.92  | 150.8                        | ZRHA-MK3.0   | 9.41  | 954.9                        |
The contents of Ca, Mg and S oxides were lower than 5% for all samples. According to Ferret (2004) [46], these compounds damage zeolites synthesis. Calcium has a negative impact on the synthesis of zeolites due to the possible formation of calcium silicate hydrate during the hydrothermal treatment rather than the formation of zeolitic phases [66].

The SiO$_2$/Al$_2$O$_3$ ratios of the zeolites synthesized with an addition of 1.0; 1.5; 2.0; 2.5 and 3.0 g of alumina, gibbsite, and metakaolin, respectively, are shown in figure 2. According to the results, the zeolites synthesized with ESA presented discrepancies in the SiO$_2$/Al$_2$O$_3$ ratios. Due to the addition of ESA with alumina and gibbsite, the ratios vary from 23.04 to 22.20 and 44.34 to 42.20, respectively. Krisnandi et al (2017) [67] used different sources of silicon and aluminium for the synthesis of ZSM-5. The results reflect that the achieved SAR was approximately 20, which is in agreement with the result of the present research.

According to the values obtained from the x-ray fluorescence (table 3), alumina and gibbsite contribute 72.90% in Al$_2$O$_3$ and 49.71% in Al$_2$O$_3$ respectively.

Henceforth, there is a bias in the mordenite formation of both the external sources observed in XRD (figure 3). In the zeolitic material synthesized with ESA from metakaolin, the SiO$_2$/Al$_2$O$_3$ ratios vary from 88.81 to 86.30. This was observed due to the low mass percentage of aluminium (39.54 in Al$_2$O$_3$) and high amount of silicon (51.04 in SiO$_2$) in the metakaolin according to table 3.

The quantity of SiO$_2$/Al$_2$O$_3$ ratio contributed to the formation of ZSM-5 zeolites as analyzed by XRD (figure 3). In general, lower SiO$_2$/Al$_2$O$_3$ ratio results in higher amount of Al$^{3+}$ in the sample and consequently greater cation exchange capacity of the material. This phenomenon occurs due to generation of a negative charge when each silicon (Si) is replaced by an aluminium (Al), and this negative charge is further compensated by a cation [68, 69].

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**Table 3.** Chemical analysis of the compounds present in the RHA and ESA (% mass).

| Oxides    | RHA   | AM    | GT    | MK    |
|-----------|-------|-------|-------|-------|
| SiO$_2$   | 99.73 | 10.55 | 2.92  | 51.05 |
| Al$_2$O$_3$ | 0.09  | 72.90 | 49.71 | 39.54 |
| Fe$_2$O$_3$ | 0.02  | 2.82  | 21.85 | 2.91  |
| Na$_2$O   | —     | 1.10  | 0.94  | 0.09  |
| K$_2$O    | 0.65  | 5.18  | 0.51  | 0.62  |
| CaO       | —     | 0.91  | 0.22  | 2.80  |
| MgO       | —     | 0.77  | 0.45  | 0.97  |
| TiO$_2$   | —     | 0.44  | 2.98  | 3.58  |
| SO$_3$    | 0.06  | 2.82  | —     | —     |
| SiO$_2$/Al$_2$O$_3$ | 1108 | 0.14  | 0.06  | 1.29  |

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Figure 2. SiO$_2$/Al$_2$O$_3$ ratio obtained through the XRF of the zeolites synthesized according to the additions of ESA. Z1 (ZRHA-AM1.0), Z2 (ZRHA-AM1.5), Z3 (ZRHA-AM2.0), Z4 (ZRHA-AM2.5), Z5 (ZRHA-AM3.0), Z6 (ZRHA-GT1.0), Z7 (ZRHA-GT1.5), Z8 (ZRHA-GT2.0), Z9 (ZRHA-GT2.5), Z10 (ZRHA-GT3.0), Z11 (ZRHA-MK1.0), Z12 (ZRHA-MK1.5), Z13 (ZRHA-MK2.0), Z14 (ZRHA-MK2.5), Z15 (ZRHA-MK3.0).

Figure 3. X-ray (powder) diffraction of RHA (A) and zeolites formed from ESA: B) alumina; (C) gibbsite; (D) metakaolin. Crystalline phase as (1) cristobalite; (2) quartz; (3) mordenite; (4) kaolinite; (5) mullite; (6) ZSM-5.
The values of SiO$_2$/Al$_2$O$_3$ ratio cannot be considered to be absolute because the atoms detected by XRF may or may not be present within the crystalline structure of the synthesized zeolites. Therefore, the SiO$_2$/Al$_2$O$_3$ ratio calculated is derived from the sample and not necessarily from the crystal structure [68].
Comparing the quantity of SiO$_2$ in RHA and zeolites formed by ESA, it was observed that the SiO$_2$ content in the zeolitic products decreases in all samples. Hence, the filtrate which was obtained after the heating step in hydrothermal activation of the ashes and was not incorporated into the zeolitic material contains large amounts of silica. Therefore, this solution has the potential to be utilized for the synthesis of more products by containing this fundamental compound for the formation of a zeolite structure.

During calculation, the per cent yield for conversion of RHA to zeolitic material cannot be performed solely on the basis of XRF data. Therefore, part of the silica incorporated in the zeolitic material is not only the
synthesized zeolite structure but also includes remnant cristobalite and quartz in the final material. These crystalline phases are shown in XRD diffractograms (figure 3).

### 3.1.4. Mineralogical composition

X-ray (powder) diffraction allowed identification of the crystalline phases present in the RHA and zeolitic material. The samples selected to be analyzed by this technique were 2.5 g of ESA. The difference in the relative intensity of the peaks may indicate different proportions of the phases encountered. The discrepancies between the content of the compounds found in the various samples can be attributed to the different additions of ESA to RHA. Since the formation process of these materials is dependent on the temperature, cooling rate and purity of the aluminium sources, XRD analysis in RHA displayed that majority of the spectra of the material are in amorphous phase.

The samples selected for XRD were 2.5 g of ESA. The difference in relative intensity of the diffraction peaks for different samples may indicate different proportions of the phases acquired, maybe as a result of sample preparation in XRD. The differences between the quantity of the compounds found in different samples can be attributed to the different constituents of ESA in RHA because the formation of these materials is dependent on the temperature, cooling rate and purity of aluminium sources [70, 71]. The XRD analysis in RHA demonstrated that most of the material spectrum is in amorphous phase.

Analyzing the peaks in figure 3(A), cristobalite (21.91° 2θ) and quartz were found (27.04° 2θ and 36.63° 2θ), and the result is in accordance with the studies of Farooque et al (2009) [72], who also studied RHA with XRD. The presence of the cristobalite peak within the band between 15 and 30° 2θ along with a small amount of silica in the form of quartz justify the crystalline phase in RHA [73].

Quartz and cristobalite are present in the RHA precursor and do not melt under the conditions of combustion in thermoelectric power plants [72]. The presence of cristobalite and quartz favours the formation of zeolites by hydrothermal treatment. Analysis of x-ray (powder) diffraction to zeolitic materials synthesized from ESA are presented in figure 3(A)–(D). In additions of alumina and gibbsite, the diffractograms (figure 3(B) e 3(C)) show the formation of mordenite, kaolinite, mullite, quartz, and ZSM-5 (peaks with low intensity). These

![Figure 6. Energy dispersive spectroscopy of zeolites formed from alumina as ESA. The crystalline phase as cristobalite and quartz (B1) and (B2) mordenite and ZSM-5.](image-url)
results are in agreement with the research of Mignoni et al (2007) [74] and Shao et al (2002) [75] which dealt with synthesized mordenite with ESA. However, in the metakaolin additions, the peaks related to ZSM-5 are more evident and again the crystalline phases of kaolinite, mullite, cristobalite, and quartz also remain prevalent.

These results are in agreement with Kovo et al (2009) [76] and Zhang et al (2007) [77] which involved synthesized ZSM-5 zeolites with metakaolin.

The occurrence of the mullite and kaolinite phases are related to the reactions that occur between SiO2 (RHA present) and ESA with Al2O3 availability. Table 4 shows the chemical formulas of the crystalline phases present in the zeolites formed, as well as in the precursor material of the formation of the zeolite.
In general, quartz and cristobalite cannot be dissolved during the hydrothermal process and remain in the zeolites. These two phases were found, in varying amounts in all the samples.

As shown in figures 3(B) and (C), the mordenite and ZSM-5 zeolites were formed from the additions of alumina and gibbsite. The mordenite zeolite has high thermal stability and acidity and can be used as an adsorbent in the separation of greenhouse gases like CO\textsubscript{2} \cite{78, 79}.

ESA additions which have precursor material such as metakaolin (figure 3(D)) synthesized ZSM-5 (Zeolite Socony Mobil-5) belonging to the MFI (Mobil Five) family, also known as pentasil. This zeolite has many industrial applications and the most important is the capture and storage of CO\textsubscript{2}, due to its high selectivity in catalytic reactions and for the high degree of thermal and acid stability \cite{20, 21}.

Observing the diffractograms of the zeolites, formation of kaolinite is verified in all the samples that were submitted to ESA. This occurred due to the presence of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} in the alumina, gibbsite, and metakaolin according to table 3.

As previously mentioned, aluminium being a structural element of zeolites, influences the formation of these materials quantitatively. It is noteworthy that identification of the phases in the zeolite samples from RHA using the mineralogical characterization by XRD technique served as a comparative analysis of different ESA. Si and Al present in the ESA are dissolved in different proportions during the hydrothermal synthesis. As a result, RHA + ESA will have different Si/Al ratios which will result in discrepant zeolites using the same activation conditions.

The amorphous phase content of aluminium in ESA will determine the formation of zeolites during hydrothermal treatment \cite{69}. Hence, differences in amorphous/crystalline phase contents in the samples may have influenced the amount and type of zeolite synthesized by conventional hydrothermal treatment shown in this study.

### 3.1.5. Morphology
The scanning electron microscopy technique was utilized in the present work to complement the other characterization techniques. In figures 4(A) and (B) are the SEM/EDS demonstrations from RHA. This sample...
has a typical appearance characterized by the presence of angular shapes of different diameters and irregular particles of varying sizes (figure 4(A)). The physical properties of silica present in RHA samples are responsible for the shape of irregular-sized particles, and this characteristic is also observed in particles that have undergone rapid cooling [80]. The combustion conditions of RHAs in the thermoelectric power plants determine the morphology of the particles. When RHA burning takes place in pulverized form, the resulting ash contains predominantly irregular shaped angular particles [81].
The angular shape represented by these materials is the result of surface tension acting during the burning of RHA at high temperatures in the mills to minimize surface free energy [82]. According to the figure 4(A), RHA (from burning in the pulverized form) presents morphology and characteristics similar to other studies [33, 34, 83, 84]. The micrographs of these samples are shown with respect to 1000 × magnification. In general, RHA is formed by clusters of particles of different shapes and sizes except being spherical. The spongy appearance of the particles occurs due to the high calcination losses (4.8368%). This morphology is a result of the heterogeneity of RHA because they are constituted of particles with variable sizes and irregular shapes. Figure 4(B) shows energy dispersive spectroscopy with the appearance of peaks related to silicon and oxygen, confirming the crystalline phase of cristobalite and quartz according to XRD (figure 3(A)).

After the hydrothermal treatment of the RHAs, the synthesized zeolites have a cluster of agglomerated particles of similar diameter and are covered by particles of similar shapes. This aspect is related to the precipitation of the zeolitic material on the surface of the unreacted ash particles after the synthesis [70, 84]. Figures 5, 7 and 9 represent the micrographs of the zeolites formed by ESA from alumina, gibbsite, and metakaolin.

According to EDS technique, the presence of the chemical elements Ca, Na, K, Al, Si, and O₂ acts as evidence for the formation of zeolite called mordenite (Figures 6 B2 and 8 B2). On the other hand, in figure 10 B2, evidence of the formation of zeolite ZSM-5 composed of the chemical elements Na, Al, Si, O₂ has been displayed [85–88].

The utilization of ESA in the process of zeolite synthesis has a direct influence on the crystal morphology and crystalline network composition.

3.1.6. Fourier–transform infrared spectroscopy—FTIR

The sample for FTIR analysis was prepared by mixing KBr pellets with RHA and ESA. The resulting spectra are shown in figures 11(A)–(C), and 11(D). The FTIR spectra presented in figure 11(A) corresponds to RHA. The 900 cm⁻¹ preliminary absorption band occurs due to the asymmetric stretching vibration of Si–O–Si, whereas
the peak at 468 cm\(^{-1}\) vibration represents Si–O bending vibrations according to the researchers Pongdong \textit{et al} 2015 [89] and Flanigen and Khatami (1974) [90].

Figures 11 (B) and (C) correspond to FTIR spectra of zeolites formed from ESA (alumina and gibbsite, respectively). These two samples reveal the typical vibrational bands of mordenite, which agree with the previous reports [91]. The FTIR spectra of mordenite exhibit two stretching vibrational peaks at 3605 cm\(^{-1}\) and 3400 cm\(^{-1}\) associated with the terminal silanol groups (Si–O–H) and the bridging Si-OH-Al groups, respectively [92].

\textbf{Figure 11.} Fourier-transform infrared spectroscopy of RHA (A) and zeolites formed from ESA: (B) alumina; (C) gibbsite; (D) metakaolin.
A band observed around 1663 cm$^{-1}$ is bending vibrational H–OH. The presence of a band at 1230 cm$^{-1}$ is assigned to -OH vibrations. 800 cm$^{-1}$ is derived from Al–O–Al bending vibration due to external symmetric stretching. Also, the band at about 550 cm$^{-1}$ corresponds to the coupling vibration of Al–O and Si–O while 468 cm$^{-1}$ vibrations are associated with Si–O bending vibrations [93].

FTIR spectra of zeolite ZSM-5 formed from ESA (metakaolin) is shown in figure 11(D). The presence of a band at 3400 cm$^{-1}$ was related to hydrogen bonding stretching vibration due to the existence of adsorbed water. Bands at 800 and 1000 cm$^{-1}$ were related to the internal asymmetric stretching vibration of Si–O–Si or Si–O–Al, and the bands at 450, 550 and 1230 cm$^{-1}$ were characteristic of ZSM-5 structure [94]. Among them, the band at 550 cm$^{-1}$ is related to a structure of the double five-membered rings of the pintails zeolites [95]. On the other hand, the bands at 2955 and 2840 cm$^{-1}$ were attributed to C–H asymmetric and symmetric stretching. Finally, the peak at 1457 cm$^{-1}$ probably occurred due to CH$_2$ deformation [96].

4. Conclusions

RHA with the addition of ESA was adequate to obtain zeolitic material by hydrothermal treatment. The zeolitic materials presented different SiO$_2$/Al$_2$O$_3$ ratios in accordance with the ESA, indicating that the zeolitization process was favourable for obtaining Mordenite and ZSM-5 zeolites. In the study of mineralogical composition, the synthesized zeolites presented similar diffractograms, with peaks characteristic of each crystalline phase, indicating an analogous mineralogical composition. Inorganic phases such as Cristobalite, Quartz, Kaolinite, Mordenite, and ZSM-5 were obtained by addition of ESA. The zeolitic material with precursor alumina and gibbsite presented four crystalline phases: Mordenite, Cristobalite, Quartz, and Kaolinite. The presence of Zeolite Socony Mobil-5 (ZSM-5) is observed to be differential in the diffractograms for zeolite synthesized with metakaolin precursor. The chemical composition of the zeolitic material using XRF was of fundamental importance in determining the SiO$_2$/Al$_2$O$_3$ ratio. Through this technique, it was possible to identify ideal ESA additions for the synthesis of zeolites from RHA, which was 2.5 g. The external sources of gibbsite and metakaolin had a slight increase in the SiO$_2$/Al$_2$O$_3$ ratios for 3.0 g. This behaviour was not observed for addition of ESA to alumina. Henceforth, we need to investigate the quantities of alumina that can be added without increasing the SiO$_2$/Al$_2$O$_3$ ratios, and also avoid values which are close to the precursor material consisting of RHA, thus making the zeolite synthesis less efficient.

The results of the morphology of both RHA and zeolites using SEM/EDS techniques complemented the results of XRD, XRF, and FTIR according to the composition of minerals formed in each crystalline phase of the synthesized zeolites. The resulting zeolitic materials displayed mixtures of zeolite phases of Mordenite and ZSM-5, which according to the literature can be used for the separation of gases and storage of greenhouse gases.

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ORCID iDs

Marcos Antonio Klunk © https://orcid.org/0000-0002-7495-8030

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