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# Synthesis of Zeolites Prepared from Coal Bottom Ash: Influence of Time, Temperature and NaOH Concentration

**Jonas Valente Matsinhe[1,2], Domingos Lusitaneo Pier Macuvele[1,3], Eliana Suzi Wakassugui Dos Santos[1], Jarina Costa Moreira[1], Miguel Meque Uamusse[2], Leidiani Muller[1], Geraldo Jorge Mayer Martins[1], Humberto Gracher Riella[1]**

[1] *Universidade Federal de Santa Catarina, Centro de Tecnologia, Departamento de Engenharia Química e Engenharia de Alimentos*
[2] *Universidade Eduardo Mondlane, Faculdade de Engenharias, Departamento de Engenharia Química – Moçambique*
[3] *Universidade Pedagogica, Faculdade de Ciencias, Lichonga - Moçambique*
* Corresponding author email: jvmatsinhe@gmail.com

**ABSTRACT**

Nowadays, the main application of coal mine in the world is to produce energy through thermoelectric power plants. Energy generation is always associated with the production of enormous amounts of ashes, both bottom and fly ashes. The main objective of this work is to study the effect of time, temperate and concentration on Synthetic zeolites produced from utilizing minerals of coal bottom ash. However, for the factor significance analysis, factorial planning of two levels and three factors was used, where eight experiments were obtained, and the results of FTIR transmittance showed favorable variation in time and temperature, and the variation of the NaOH concentration was not significant. It was concluded that the concentration of NaOH only influences the zeolites formation when combined with the crystallization time.

***Keywords***: Coal bottom ash; synthesized zeolites; thermoelectric power plants

## 1. INTRODUCTION

Most of the energy consumed in the world is mainly obtained through fossil fuels (coal, oil and natural gas), with a small contribution of biomass, hydropower, nuclear and wind energy. According to the BP statistical review of world energy in 2015, coal is the most abundant of fossil fuels, with proven reserves of around 890 million tons, which considered the most popular non-renewable energy resources, but in the long term, it is the most important world energy reserve. In terms of contribution in the world energy matrix, according to the national energy balance (2015), coal is currently responsible for about 8.8% of world energy consumption and 41.5% of all electricity generated. Although renewable sources, such as biomass, solar and wind, will occupy a larger share from energy matrix in the future. Coal will continue to be the main input for electricity generation, especially in developing countries, for many decades. One of the main environmental problems caused by thermoelectric power plants is production of tons of ashes during power generation productions. Eventually most of the produced ashes are being deposited in landfills and consequently contaminating soils and groundwater (Singh & Siddique, 2016). Many techniques widely used for recovering higher value materials from the ash, different metals can be utilized and considered as potential sources (Blissett & Rowson 2012). However, processes that turn these ashes into higher value materials are becoming necessary to reduce environmental impacts. In this perspective, this work presents an application study of using coal bottom ashes in the NaY zeolites synthesis and to evaluate the influence of time, temperature and concentration of crystallization, in specific area in zeolites..

Among the ashes and zeolites there are similarities on their composition, since several authors report that the coal bottom ash have in the amorphous phase aluminum silicates in mass compositions higher than 70%, as shown in table 1, and these are elements precursors of synthetic zeolites. Although bottom ash includes in the composition elements that by their nature make zeolite difficult to form (iron case), but because of the high aluminum silicates content, these ashes become attractive sources in the synthesis of zeolites.

**Table 1**: Different values of aluminum silicates present in bottom ash

| **Autores** | **$SiO_2$ (%)** | **$Al_2O_3$ (%)** | **$Al_2O_3.SiO_2$ (%)** |
|---|---|---|---|
| Gothe (1990) | 56.30 | 32.6 | 88.90 |
| Pozzobom (1997) | 55.98 | 26.73 | 82.71 |
| Kniess (2001) | 54.04 | 25.19 | 79.23 |
| Matsinhe (2012) | 54.00 | 25.10 | 79.10 |

Zeolites are crystalline hydrated aluminum silicates with elements of group I and II of the periodic table. Its structure is based on infinite three-dimensional networks of tetrahedral of $[SiO_4]^{4-}$ and $[Al_2O_4]^{3-}$ joined by the vertices by oxygen. These networks form a large amount of open and empty spaces, which are responsible for the definition of numerous special zeolite properties, among which specific area is the highlighted (Junior et al, 2012). The substitution of $Si^{4+}$ by $Al^{3+}$ in the tetrahedral generates considerable freedom of movement, allowing reversible dehydration and high ion exchange capacity when the pores and channels are accessed by cations.

## 2. METHODOLOGY

According to the International Zeolites Association, IZA (2015), among several factors, the formation of the zeolitic phase is influenced by time, crystallization temperature and the alkalinity of the reaction mixture. Crystallization Time: is an important parameter to be considered in the synthesis of zeolites, because, the crystallinity increases with time. As the desired zeolites are generally metastable phases, which can undergo further dissolution, while a more stable phase is formed, it is necessary to know the crystallization kinetics, to synthesize pure crystalline phases. For this, time needs to be optimized. Crystallization Temperature: is the fundamental parameter for formation of the crystalline structure. In the synthesis of zeolites, the crystallization temperature has a strong effect on the formation of the zeolites. Higher temperatures usually lead to the production of denser phases, while lower temperatures form more open structures. The crystallization kinetics can also modified with the temperature variation used, particularly the nucleation period, which becomes shorter at elevated temperature. Alkalinity: the control of crystallization during the synthesis of a zeolite depends very much on the alkalinity of the medium. The increase in alkalinity will decrease the induction and nucleation period and increase the crystallization of the zeolite. In addition, a change in alkalinity may also affect particle size, such as the morphology of zeolites.

For the synthesis of zeolites, bottom ash from mineral coal burning was used as a direct source of silicon and aluminum, but since the Si / Al ratio is not sufficient for formation of FAU (NaY) zeolite structure, a pure source of aluminum was added. In the Figure 2 shown the flowchart describing the synthetic process.

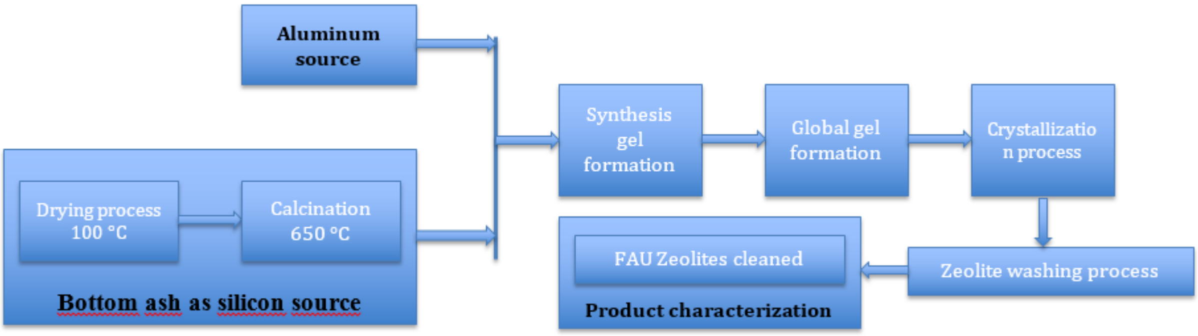


**Figure 1:** Flowchart of zeolite synthesis from coal bottom ash

The silicon source undergoes two previous processes, drying and calcination, and then, in the prepared aluminum source solution, 22.72 g of ash solution (37.0 g of ash, 8.09 g of $Na_2O$ and 62.4g of water) and the solution was left under moderate agitation until complete homogenization, then kept at 25 ° C for 24 hours. And the aluminum source was prepared by dissolving in 19.95 mL of ultra-pure water in 4.07 g of NaOH under constant stirring until complete dissolution, then 2.09 g of $Na_2Al_2O_4$ (sodium aluminate) was added. Tables 2 and 3 show, coding variables and factorial planning, respectively, the values of the maximum and minimum levels were found in IZA (2015). However, with the planning done it was used as response variable the specific area determined by BET methodology.

**Table 1:** Variables codifications (level -1 and +1)

| | | Factors | | |
|---|---|---|---|---|
| | | Time | Temperature | [NaOH] |
| Levels | - | 24 h | 80 ºC | 5,0 M |
| | + | 48 h | 100 ºC | 7,0 M |

**Table 2:** Planning of experiments for syntheses de zeolites

| Experiments | Samples | Factors | | |
|---|---|---|---|---|
| | | Time | Temperature | [NaOH] |
| 1 | CAZ1 | - | - | - |
| 2 | CAZ2 | + | - | - |
| 3 | CAZ3 | - | + | - |
| 4 | CAZ4 | + | + | - |
| 5 | CAZ5 | - | - | + |
| 6 | CAZ6 | + | - | + |
| 7 | CAZ7 | - | + | + |
| 8 | CAZ8 | + | + | + |

## 3. RESULT AND DISCUSSION

The results of chemical analysis by X-ray fluorescence spectrometry of the ashes are presented in Table 4. Almost 80% of the composition of this material presents as $SiO_2$ (57.30%) and $Al_2O_3$ (23.70%) as main oxides, this characteristic being expected since these are the main constituents of the coal bottom ash.

**Table 4:** Chemical analysis of coal bottom ash

| Elements | Coal bottom ash |
|---|---|
| | Composition w/w (%) |
| $SiO_2$ | 57.30 |
| $Al_2O_3$ | 23.70 |
| $Fe_2O_3$ | 7.65 |
| MnO | 0.05 |
| MgO | 0.71 |
| $TiO_2$ | 1.20 |
| CaO | 1.71 |
| $Na_2O$ | 0.50 |
| $K_2O$ | 2.97 |
| $P_2O_5$ | 0.06 |
| Fire loss | 4.15 |

The results observed in the chemical analysis were confirmed by the XRD of Figure 2, of the same ash. However, the observed amount of aluminum silicates present is sufficient for these ashes to be converted into NaY zeolites.

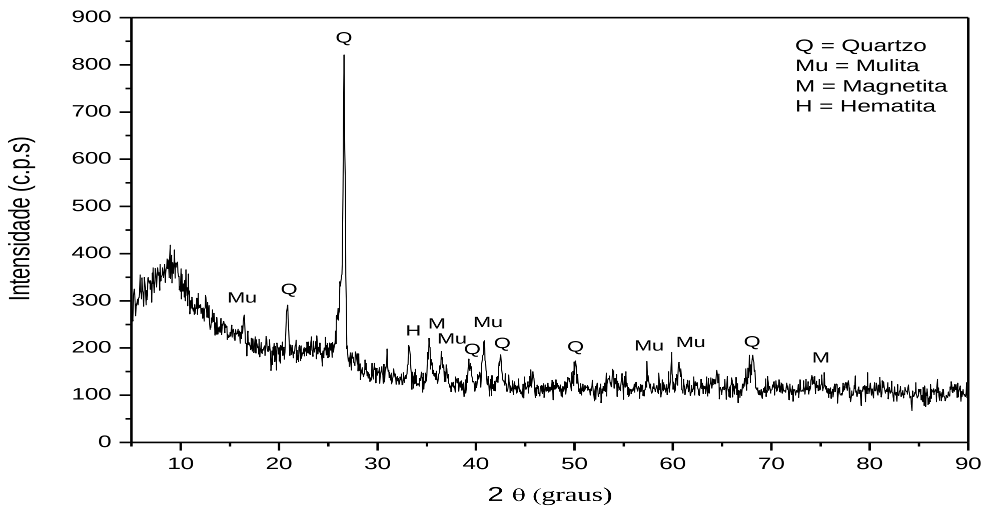


**Figure 2:** Mineralogical analysis of coal bottom ash

The specific area were observed in the BET methodology, and Table 5 briefly shows the values read with a duplicate.

**Table 5:** Results of specific area of zeolite synthetized from coal bottom ash

| Exp. | Samples | Factors | | | Results | |
|---|---|---|---|---|---|---|
| | | Time | Temperature | [NaOH] | Zeolites specific area ($m^2/g$) | |
| 1 | CAZ1 | - | - | - | 72.5 | 72.6 |
| 2 | CAZ2 | + | - | - | 60.4 | 64.2 |
| 3 | CAZ3 | - | + | - | 70.3 | 70.1 |
| 4 | CAZ4 | + | + | - | 72.5 | 72.7 |
| 5 | CAZ5 | - | - | + | 65.1 | 63.5 |
| 6 | CAZ6 | + | - | + | 68.3 | 67.6 |
| 7 | CAZ7 | - | + | + | 75.0 | 72.7 |
| 8 | CAZ8 | + | + | + | 70.2 | 69.4 |

Statistical planning was able to identify the effects of factors to increase the specific area, however, through the Pareto diagram it is noted that the NaOH concentration has no significant effect on the specific area, its combination with other favorable factors and Statistically significant for the increase of the specific area, as shown in figure 3.

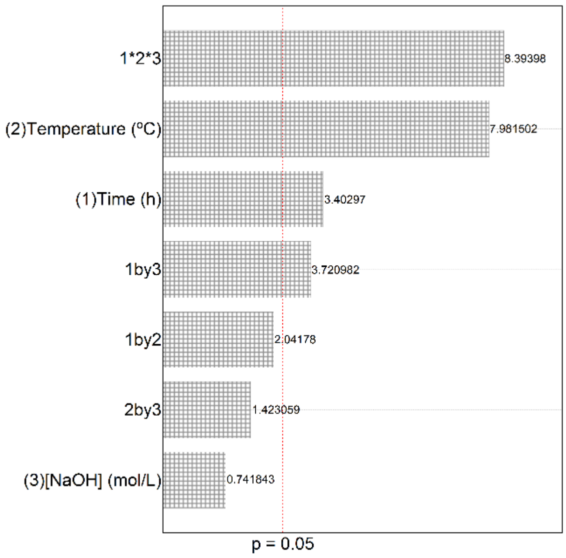


**Figure 3:** Pareto diagram for variables effects for zeolites synthetization from coal bottom ashes

The combination of all factors possesses in terms of magnitude greater significant effect of all. This shows that the NaOH concentration, although not having a significant effect, somehow has characteristics that influence the specific area and formation of zeolites. The contour curves figure 4, clearly show the NaOH concentration behavior by varying the temperature. The specific area increases only with increasing temperature, thus showing the statistical significance of temperature. By observing the data it is noted that variables such as time and temperature exclusively influence the specific area, however, the combined effects are not significant as shown in figure 4.

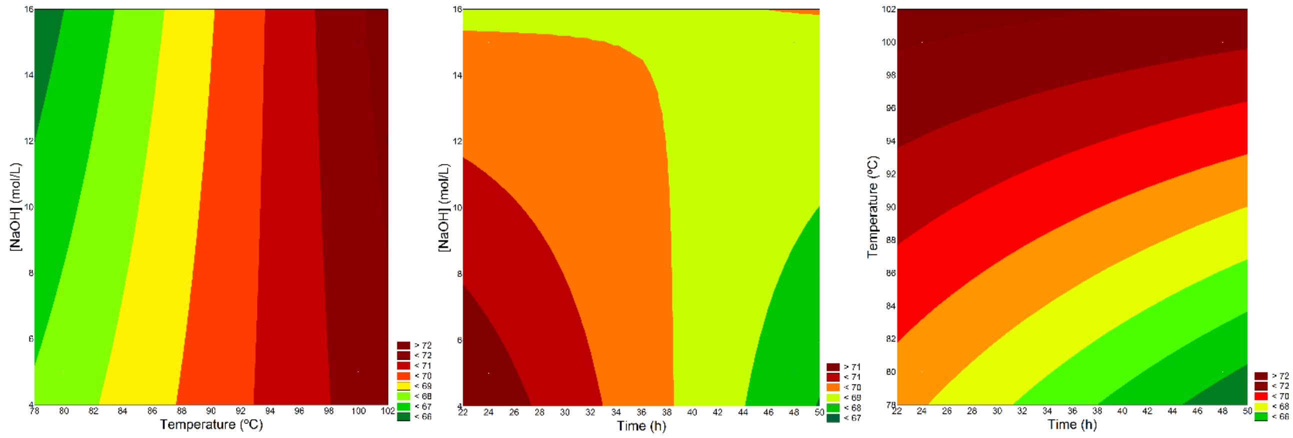


**Figure 4:** Surface contour of specific area in zeolites synthesized from coal ash

As it will be noted, the effect of NaOH concentration on zeolite formation is not significant when analyzed separately, on the contrary, when combined with the crystallization time, becomes significant. This behavior shows that the variation of the solution acoustic concentration must be related to the variation of time

## 4. CONCLUSIONS

The bottom ashes from coal industries are attractive sources of silicon and aluminum, for use as raw material in the synthesis of zeolites, since they have approximately 70% of $SiO_2$ and $Al_2O_3$, which is satisfactory enough for creation and formation of zeolite structure. The experimental design was adequate for the study (r2 = 0.95) and through it was concluded that the time, temperature, time combination and concentration of NaOH, and combination of all variables (time, temperature, NaOH) significantly influence the formation of zeolites from mineral coal bottom ash. The NaOH concentration alone does not influence the formation of zeolites from coal ash.

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