



## Full Length Article

# Biodiesel production using coal fly ash-derived sodalite as a heterogeneous catalyst



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## ABSTRACT

This study aimed to synthesized zeolites via a hydrothermal process in an alkaline medium using coal fly ashes as an alternative source of silicon. The zeolites were evaluated for their crystallinity, morphology, and surface area. The characterization of the sample revealed that the zeolite type sodalite was synthesized, and quartz and mullite were identified as by-products. The microstructure of the powders showed clusters with specific surface areas of approximately  $10 \text{ m}^2/\text{g}$ . The synthesized sodalite was used as a catalyst for transesterification of soy oil to obtain a maximum conversion of 95.5 wt% at  $65 \text{ }^\circ\text{C}$  with a 4 wt% catalyst concentration, a 12:1 methanol-to-oil molar ratio, and a reaction time of 2 h. The mechanistic pathway for sodalite catalyzed transesterification and the possible formation of active sites was proposed.

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## 1. Introduction

Biodiesel is composed of mono alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats and is an excellent alternative to petroleum diesel [1–3]. It presents important characteristics such as non-toxicity, biodegradability, a high energy content, and a sulfur-free composition [4,5].

Biodiesel is currently produced by a homogeneous base catalyzed by triglycerides, which produces fatty acid methyl esters (FAMES). Basic catalysts such as potassium hydroxide (KOH) can produce yields of 97–99% in 0.5–1 h [6,7]. However, the homogeneous base catalysis process is very sensitive to high free fatty acid (FFA) and water contents, which can lead to soap formation and lower biodiesel yields [7–9].

To avoid saponification, acid catalysts such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) can simultaneously catalyze both esterification and transesterification reactions [7,10]. Therefore, biodiesel can be produced directly from low-cost oils, such as used cooking oil, which are generally associated with high FFA and water concentrations [7]. However, the use of an acid catalyst transesterification is much slower than that of the basic catalyst reaction and requires excessive quantities of methanol. Furthermore, there are high costs related to both waste treatment and the necessary stainless steel equipment [6,7].

A heterogeneous catalytic process may be employed for efficient transesterification reactions. Some advantages of heterogeneous catalysis are the ease with which catalysts are separated from the solution and the consequent ability to reuse the catalyst in subsequent studies [8,11]. Various heterogeneous catalysts for transesterification and esterification reactions have been studied, including niobium oxide ( $\text{Nb}_2\text{O}_5$ ) [8],  $\text{Sr}_3\text{Al}_2\text{O}_6$  nanocomposite [11],  $\text{TiO}_2$  nanotubes [12,13], pre-treated silica ( $\text{SiO}_2\cdot\text{HF}$ ) [14], and others [3,8,15].

Zeolites are microporous crystalline aluminosilicates that possess molecular shape selective properties. The synthesis is settled by aluminum and silicon precursors, which are the structural elements of zeolites [16]. Furthermore, pure chemicals—even many industrial waste materials—are suitable educts for zeolite formation. Models of the use of adequate industrial wastes in zeolite chemistry would be of interest for waste management and environmental protection, leading to cheaper production of zeolites under the premise of the insertion of waste materials [17]. Coal fly ash is the most abundant by-product from coal-based thermal power plants [16]. Since coal fly ash is composed largely of silica-aluminum, it can be easily converted into zeolite via a hydrothermal treatment in an alkaline solution [18]. Such a treatment process can lead to the formation of various types of zeolites at different conditions of temperature, concentrations of alkaline reagent, reaction time, and solution/fly ash ratio [16].

Zeolites have shown promising results as catalysts in the transesterification of refined and waste oils [5,7,8,10,19,20]. Suppes et al. [20] carried out the transesterification of soy oil with NaX

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and ETS-10 zeolites and obtained a conversion rate of 82.0% with NaX at 60 °C in 24 h. Ramos et al. [5] studied three different zeolites (mordenite, beta, and X) and obtained 95.1% methyl esters at 60 °C in 7 h with zeolite X. However, heterogeneous transesterification has never been performed by a coal fly ash-derived zeolite, despite reaction time reduction being an important pathway to achieving viability and alkaline transesterification substitution.

Based on these considerations, the objectives of this study were to synthesize zeolites from coal fly ash via a hydrothermal method, characterize the zeolites morphologically, and investigate their use as a highly effective catalyst for the transesterification process.

## 2. Materials and methods

### 2.1. Materials

The primary raw material, coal fly ash samples, were collected from a Brazilian thermal power plant (Candiota Thermal Power Station) located in Rio Grande do Sul state. The ashes studied were generated from the combustion of the Candiota Mine coal in a pulverized-bed until reaching 1400 °C on a large-scale unit. Table 1 lists the physico-chemical properties of the coal fly ash samples used in this investigation. The contents were determined via X-ray Fluorescence analysis (XRF-1800, Shimadzu). Results reveal that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and iron oxides were the primary constituents of the coal fly ash samples. The content of SiO<sub>2</sub> was above 60 wt%, indicating that the coal fly ash samples were suitable for synthesizing zeolites.

Solvents and other reagents were analytical grade (Merck or similar). The chromatographic standards were acquired from Sigma-Aldrich. The gases used in the chromatographic analyses (H<sub>2</sub>, N<sub>2</sub> and synthetic air with a purity exceeding 99.999%) were purchased from White Martins. Edible soybean oil was purchased in a local market from Liza<sup>®</sup> (acid number = 0.05 mg KOH g<sup>-1</sup>).

### 2.2. Zeolite synthesis from coal fly ash

The synthesis of zeolite using coal fly ash as an alternative source of silicon was performed using a method adapted from that of Petkowicz et al. [21]. The synthesis was conducted as follows: 0.15 g of NaOH was added to 16 mL of deionized water. This solution (referred to as solution A) was then divided into two equal portions and poured into polypropylene bottles; these solutions were referred to as solutions B and C. To solution B, 1.65 g of aluminate sodium (NaAlO<sub>2</sub>) was added and stirred until complete dissolution. To solution C, 1.17 g of NaOH, 1.3 mL of deionized water, and 0.89 g of SiO<sub>2</sub> (coal fly ash) were added and stirred until com-

plete dissolution. Then, the silicate solution C was poured into the aluminate solution B, forming a sticky gel that was stirred for 15 min up to complete homogenization. The gel that was formed was left to rest for 6 days (i.e., the aging period). The crystallization temperature was 100 °C for 24 h. Thereafter, the mixture was washed with deionized water until a pH of 9 was achieved. Finally, the solid material was dried at 100 °C for 24 h. Fig. 1 shows the detailed synthesis process of zeolite from coal fly ash. The Si/Al ratio for the sample was calculated to be 3.

### 2.3. Characterization of zeolite

The morphology of the sample was analyzed by Scanning Electron Microscopy (SEM) using a JEOL JSM 6060 instrument. The specific area was measured by adsorption–desorption isotherms (N<sub>2</sub>) at 77 K using the BET (Brunauer, Emmett, and Teller) method. The analysis was performed using a Quantachrome Nova 1000e equipment. The X-ray Diffraction (XRD) analyses were carried out using a PHILIPS X-ray diffractometer (model X'PERT MDP) with Ni-filtered Cu K $\alpha$  radiation at 15.418 nm in the 2 $\theta$  range from 5 to 45°.

### 2.4. Biodiesel production by heterogeneous transesterification

Transesterification reactions were carried out in a 100 mL flask equipped with a condenser. The soybean oil with the measured weight was transferred to the flask and heated to 65 °C with continuous stirring at 300 rpm. Next, methanol and the catalyst were added to the oil, initializing the time of reaction. The total reaction time was 2 h. Different molar ratios of methanol and oil were tested (6:1, 9:1 and 12:1), and the amount of catalyst used was 1, 2, 3, and 4% of the weight of the oil. At the end of the reaction, the reaction mixture was transferred to a separatory funnel to promote the separation of the glycerol and biodiesel phases. The glycerol phase was recovered—along with the catalyst—and was stored for later reuse. The biodiesel phase was purified with water preheated at 55 °C and stored for analysis.

### 2.5. Characterization of biodiesel

The biodiesel conversion was determined according to method EN 14103 for analyzing the ester content. This analysis was conducted in a gas chromatograph (GC 2014; Shimadzu) using a flame ionization detector (FID) equipped with a Rtx-wax polyethylene glycol (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) column. Hexane was used as solvent, and the carrier was gas nitrogen at a flow rate of 1 mL/min. A solution of ethyl palmitate (10 mg/mL) was used as internal standard. The temperature program was as follows: 120 °C for 2 min, heating up to 230 °C at a rate of 5 °C/min and holding at 230 °C for 2 min. The injector and the detector were set for 250 °C; the injection volume was 1  $\mu$ L.

## 3. Results and discussion

### 3.1. Characterization of the zeolite

Fig. 2 shows the result of X-ray diffraction for the coal fly ash. Based on the presented XRD patterns, the coal fly ash is composed predominantly of quartz and mullite, and apparently small amounts of muscovite. These results are consistent with the findings reported in the literature [22,23]. The formation of mullite is related to the combustion of coal at temperatures above 1050 °C. The coal that created the ash used in this work was burned at 1400 °C; so the presence of mullite was expected.

**Table 1**  
Composition of coal fly ash by XRF.

Components	wt%
SiO <sub>2</sub>	68.43
Al <sub>2</sub> O <sub>3</sub>	14.78
Fe <sub>2</sub> O <sub>3</sub>	7.91
CaO	3.80
K <sub>2</sub> O	2.51
TiO <sub>2</sub>	1.16
SO <sub>3</sub>	0.57
MgO	0.32
ZrO <sub>2</sub>	0.10
MnO	0.07
P <sub>2</sub> O <sub>5</sub>	0.07
SrO	0.05
Rb <sub>2</sub> O	0.05
ZnO	0.02
Y <sub>2</sub> O <sub>3</sub>	0.01

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