

Kinetic Study of the Catalytic Pyrolysis of Elephant Grass Using Ti-MCM-41

Maria do Socorro Braga Fontes^{a*}, Dulce Maria de Araújo Melo^b, Joana Maria de Farias Barros^c,
Renata Martins Braga^d, Gicélia Rodrigues^e

^aPrograma de Pós-Graduação em Ciência e Engenharia de Materiais – PPGCEM, Centro de Tecnologia – CT, Universidade Federal do Rio Grande do Norte – UFRN, Natal, RN, Brazil

^bDepartamento de Química, Universidade Federal do Rio Grande do Norte – UFRN, Natal, RN, Brazil

^cDepartamento de Química, Universidade Federal de Campina Grande – UFCG, Cuité, PB, Brazil

^dDepartamento de Engenharia de Energias Renováveis – DEER, Centro de Energias Alternativas e Renováveis – CEAR, Universidade Federal da Paraíba – UFPB, João Pessoa, PB, Brazil

^ePrograma de Pós Graduação em Engenharia Química – PPgEQ, Centro de Tecnologia – CT, Universidade Federal do Rio Grande do Norte – UFRN, Natal, RN, Brasil

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This work aimed to study the kinetics of thermal and catalytic pyrolysis using Ti-MCM-41 as catalyst in order to assess the catalytic pyrolysis efficiency compared to thermal pyrolysis of elephant grass. Ti-MCM-41 molecular sieve was synthesized by hydrothermal method from hydrogel with the following molar composition: 1.00 CTMABr: 4.00 SiO₂:X TiO₂: 1 + X Na₂O: 200.00 H₂O, which structure template used was cetyltrimethylammonium bromide (CTMABr). The materials synthesized were characterized by X-ray diffraction, IR spectroscopy, thermogravimetric analysis and specific area by the BET method, for subsequent application in the biomass pyrolysis process. The kinetic models proposed by Vyazovkin and Flynn-Wall were used to determine the apparent activation energy involved in the thermal and catalytic pyrolysis of elephant grass and the results showed that the catalyst used was effective in reducing the apparent activation energy involved in the thermal decomposition of elephant grass.

Keywords: elephant grass, thermogravimetry, Ti-MCM-41, kinetics, catalytic pyrolysis

1. Introduction

In recent years, intensive research has been carried out for the development of fuels from biomass, either for environmental (conversion of biomass into energy with lower environmental impacts) or economic reasons (alternatives to fossil fuels), requiring greater knowledge on the kinetic parameters involved in thermal conversion reactions for better control of the products obtained.

Among the techniques used for biomass thermal conversion, pyrolysis is considered the most promising due to the greater process flexibility, which allows obtaining liquid, solid or gas¹. Thermogravimetric analysis (TG / DTG) has been an essential tool for modeling the pyrolysis kinetics, based on the principle that the reaction velocity depends on temperature (T), conversion (α) and time (t). Several mathematical models have been proposed for the identification of kinetic parameters such as activation energy, reaction order and conversion¹.

The use of lignocellulosic materials in thermal processes (pyrolysis and / or gasification) has proven to be advantageous, given that these materials are renewable energy sources that can be converted into bio-oil and various products of industrial interest^{2,3}, and among these materials, elephant grass stands out, which is lignocellulosic biomass easy to grow and abundant in Brazil. It consists

mainly of cellulose, hemicellulose, lignin and small amounts of extractives and minerals⁴. The proportions of EG components play an important role in the distribution of pyrolysis products. Elephant grass has significant potential as a renewable energy source for fuel conversion of greater calorific power⁵. In this context, this study aimed at assessing the apparent activation energy involved in the holocellulose decomposition (cellulose + hemicellulose) of elephant grass (*Pennisetum purpureum*) through catalytic and conventional pyrolysis using Ti-MCM-41 as catalyst.

2. Experimental Procedure

2.1. Catalyst synthesis

Ti-MCM-41 molecular sieve was hydrothermally synthesized using experimental procedure adapted from literature syntheses described in Braga⁶ to obtain gel with the following molar composition: 1.00 CTMABr: 4.00 SiO₂: xTiO₂: 1 + x Na₂O: 200.00 H₂O. The “x” value was set so that the Si / Ti molar ratio remains equal to 50. After gel preparation, the material was transferred to a Teflon container with stainless steel autoclave and heated in an oven at 100°C for 120 hours (5 days). The content was washed with distilled water and then with a 2% HCl solution in

*e-mail: socorro.fontes@yahoo.com.br

ethanol for the partial removal of surfactant. Finally, the solid resulting from the crystallization process was oven-dried for 12 hours and calcined at 550°C for 2 hours.

2.2. Biomass

The biomass selected for this study was elephant grass (EG) (*Pennisetum purpureum* Schum) from the Laboratory of Biomass and Biofuels at UFRN. The biomass was submitted to drying in the sun, ground and crushed in a Wille-type mill and sifted in sieve with mesh of 0.8-1.0 mm.

About 20 mg of biomass was used, which was submitted to thermal pyrolysis and for the catalytic pyrolysis, a mechanical mixture containing 70% by weight of elephant grass plus 30% of catalyst was used.

2.3. Ti-MCM-41 characterization

Ti-MCM-41 was submitted to different characterization methods to evaluate its properties for application in the catalytic pyrolysis of EG. X-ray diffractogram of the catalyst synthesized was obtained using a Shimadzu X-ray diffractometer, model XRD-7000, with CuK α monochromatic radiation ($\lambda = 1.5406 \text{ \AA}$) obtained by 30 kV, in 30 mA filament current. The morphological characterization of the material synthesized was determined using N₂ adsorption/desorption isotherms, in QuantaChrome equipment, Model NOVA-2000. To determine the specific area, the BET method was used and for pore size distribution⁷, the Barret-Joyner-Halenda (BJH) model was used. The micrographs performed in this work were obtained in JEOL scanning electron microscope model JSM-6360 with the aim of observing the morphology, particle size and homogeneity of samples.

2.4. Determination of the kinetic parameters

Many mathematical methods have been proposed to obtain kinetic parameters from TGA experiments. In this work, two models were selected, Flynn and Wall and Vyazovkin in order to compare the results obtained in the determination of the kinetic parameters.

ASTME 1641 norm is based on the method proposed by Flynn and Wall⁸ using the Least Squares method to determine the estimated activation energy (E_a) by means of Equation 1.

$$Ea = -\left(\frac{R}{b}\right) \times (\partial \log \beta) / (\partial (1/T)) \quad (1)$$

Where β is the heating rate, T is the absolute temperature (K), b is an interaction variable, R is the universal gas constant and Ea is the activation energy (J mol^{-1}). The Model-free Kinetics method is based on the theory of Vyazovkin⁹, which applies isoconversional techniques, in which for each conversion α , $\ln \beta / T_{\alpha}^2$ was graphically represented as a function $1/T_{\alpha}$, also providing a series of lines with slope $-E_a/R$, so that this theory is based on Equation (2).

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{RK_0}{E_a g(\alpha)} \right] - \frac{E_a}{R} \frac{1}{T_x} \quad (2)$$

Where α is the conversion degree, K_0 is the pre-exponential factor (s^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$) and T is the temperature. Thermogravimetric analyses simulating

the thermal pyrolysis were performed in a thermobalance, model DP-QA500 from Union Instruments, using nitrogen atmosphere at flow rate of $50 \text{ ml} \cdot \text{min}^{-1}$ in the temperature range from 30 to 900°C and heating rates of 5, 10 and $20^\circ \text{C min}^{-1}$.

3. Results and Discussion

The X-ray diffractogram of calcined MCM-41 and Ti-MCM-41, assessing the structural properties of these samples, is shown in Figure 1. The presence of three typical peaks was observed, one of high intensity attributed to the reflection line of the plane (100) and other two, of less intensity, attributed to reflections of planes (110) and (200), characteristic of the hexagonal mesoporous structure. The introduction of titanium into the MCM-41 structure caused a decrease in the X-ray intensity of peaks, indicating a change in the structural arrangement in relation to that found in the MCM-41 structure¹⁰.

The morphology of the mesoporous material is formed by the agglomeration of particles with irregular and rounded shapes, as can be seen in Figure 2 through scanning electron microscopy.

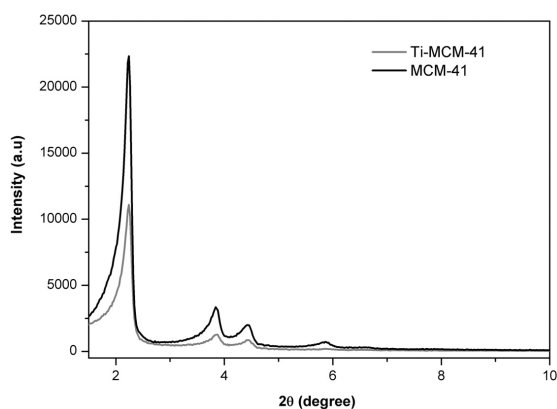


Figure 1. X-ray diffractogram of calcined MCM-41 and Ti-MCM-41.

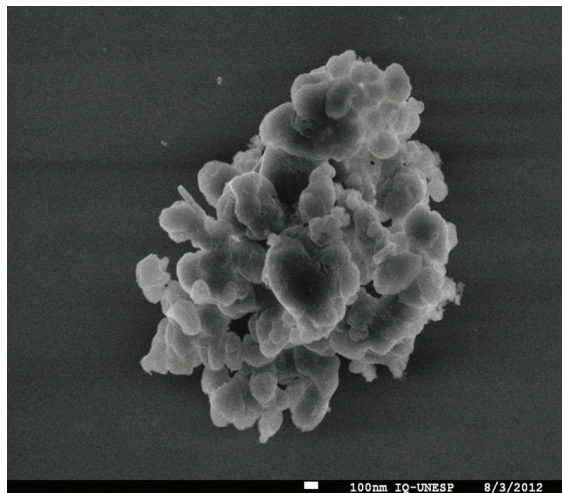


Figure 2. Scanning electron microscopy of calcined Ti-MCM-41.

The thickness of the silica wall that forms the hexagonal structure of MCM-41 was obtained by the difference of the lattice parameter a_0 , obtained by X-ray diffraction, and the pore diameter d_p that was obtained by BJH. Table 1 shows that the presence of titanium in the MCM-41 structure caused an increase in the pore diameter and consequently a slight reduction in the wall thickness when compared to pure MCM-41; According to literature, increasing titanium content in the synthesis mixture results in an increase in the lattice parameter (a_0) and this change is probably due to the greater length of the Ti–O bond (1.80 Å) when compared to the Si–O bond (1.61 Å)¹¹. Other factors that influence the structural parameters are differences in ionic radius of Ti⁴⁺ (0.68 Å) and Si⁴⁺ (0.41 Å) as can be seen in Table 2, the length of the Ti–O–Si bond differs from that of O–Si bond, certainly leading to deformation of its structure. In addition, the replacement of Si⁴⁺ by Ti⁴⁺ can block the action of the structure template, changing its ionic strength, preventing the formation of the tubular mesoporous structure. This could result in the formation of pores partially broken as can be seen by the decreased specific areas¹².

Figures 3a and b illustrate, respectively, TG and DTG curves obtained from the catalytic and thermal pyrolysis of Ti-MCM-41/Pennisetum purpureum and

Table 1. Crystallographic parameters obtained by X-ray diffraction and specific area by the BET method for calcined MCM-41 and Ti-MCM-41.

Samples	S_{BET} (m ² /g)	a_0 (nm)	d_p (nm)	$W=a_0-d_p$ (nm)
MCM-41	998	5.060	3.208	1.852
Ti-MCM-41	645	5.107	3.389	1.718

a_0 - Cell parameter (calculated from $a_0 = 2 d_{100} / \sqrt{3}$ (nm)). d_p - pore diameter (BJH method at the adsorption step); W - wall thickness.

Table 2. Si–O and Ti–O bond energy.

Bond	Bond energy (kJ mol ⁻¹)
Si–O	217.04
Ti–O	458.56

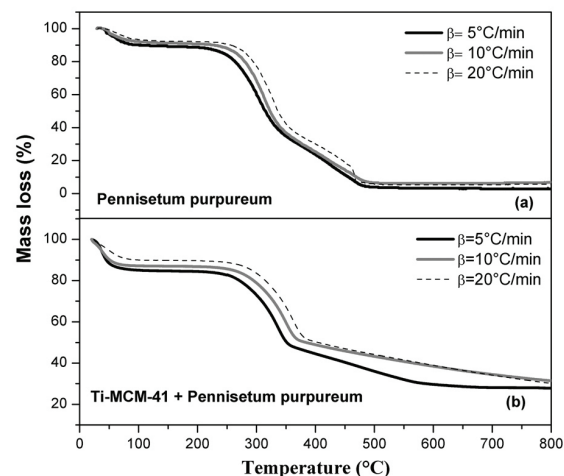


Figure 3. TG curves of Pennisetum purpureum + Ti-MCM-41 (a) and pure Pennisetum purpureum (b).

pure Pennisetum purpureum, at heating rates of 5, 10 and 20°C min⁻¹. According to the DTG curves, Figures 4a and b, the initial and final temperatures of thermal events involved in the decomposition of the EG biomass could be determined. Three mass losses were observed, the first at temperatures below 200°C, relative to moisture loss corresponding to approximately 8% of mass loss. In the second temperature range, from 200 to 395°C, mass loss of about 77% was represented by the most volatile matter of biomass attributed mainly to cellulose, hemicellulose and part of lignin decomposition, and the third mass loss is continuously developed overlapping the other events, being more pronounced at temperatures above 400°C. The last event is related to lignin decomposition, which has polyaromatic structure thermally more resistant than hemicellulose and cellulose¹³. Comparing the curves, it was observed that both samples exhibited pronounced mass loss at temperatures between 187 and 380°C, which represents the highest percentage of biomass volatile compounds; thus, this temperature range has been selected for kinetic studies.

Figures 5a and b shows the conversion curves *versus* temperature for the thermal and catalytic pyrolysis of the biomass. The kinetic study determines the decomposed fraction (α) as a function of the reaction time (t) in processes in which the temperature is kept constant or in processes in which the temperature varies linearly with time. In TG, the decomposition reaction (α) was defined by Equation 3¹⁴.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (3)$$

Where: α is the conversion, m_t is the sample mass that varies with time (t), m_o is the initial sample mass and m_f is the final sample mass.

In the Model-free Kinetics, each $\ln \beta/T\alpha^2$ conversion was graphically represented as a function of $1/T\alpha$, providing a series of straight lines with slope $-Ea/R$ ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The Flynn and Wall method graphically represented the logarithm of the heating rate ($\log \beta$) *versus* inverse of temperature corresponding to conversion ($1/T\alpha$) from the three curves.

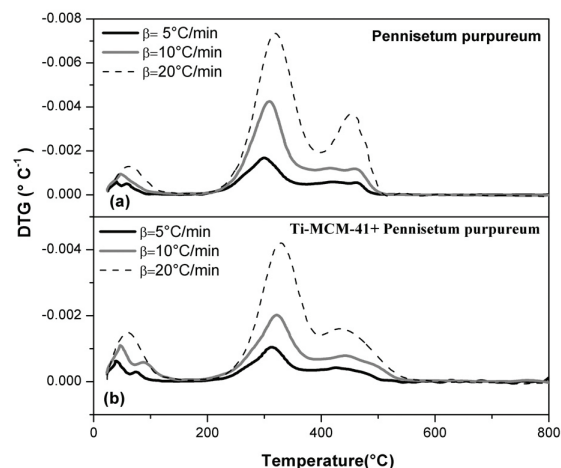


Figure 4. DTG curves of Pennisetum purpureum + Ti-MCM-41 (a) and pure Pennisetum purpureum (b).

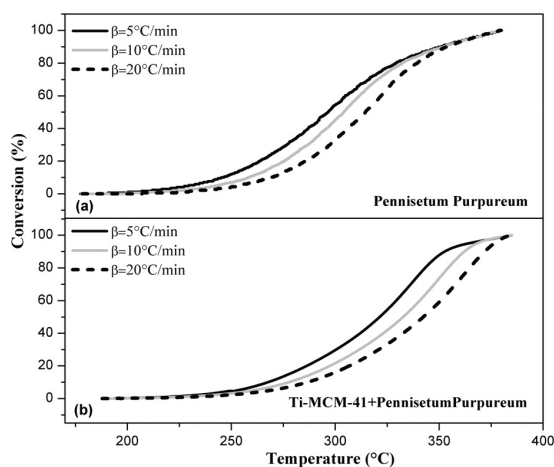


Figure 5. Conversion and pyrolysis curves of *Pennisetum purpureum* + Ti-MCM-41 (a) and pure *Pennisetum purpureum* (b).

Table 3 shows the data of the apparent activation energy at conversions of 5 to 80%, obtained by Model-free Kinetics and Flynn and Wall models, observing a decrease in the apparent activation energy for biomass pyrolysis in the presence of the catalyst, evidencing that the mesoporous

Table 3. Apparent activation energy of biomass decomposition.

Sample	E_a (kJ mol ⁻¹) Flynn and Wall	E_a (kJ mol ⁻¹) Model-free kinetic
CE	220.4	229.5
CE + Ti-MCM-41	163.5	169.6

Ti-MCM-41 acted as catalyst for the pyrolysis of elephant grass.

4. Conclusion

It was observed through the catalyst characterization that the addition of titanium did not change the MCM-41 structure and morphology. Thermal analysis is a good tool to investigate the kinetic behavior of the biomass during thermal conversion processes. The apparent activation energy values for the methods applied were very close, indicating that the Model-free kinetics and ASTM methods are both adequate to determine the kinetic parameters.

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