

# Effect of the Al-MCM-41 catalyst on the catalytic pyrolysis of atmospheric petroleum residue (ATR)

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**Abstract** Thermogravimetry (TG) was used in this study to evaluate thermal and catalytic pyrolysis of Atmospheric Petroleum Residue (ATR) which can be found in the state of Rio Grande do Norte/Brazil, after a process of atmospheric distillation of petroleum. The utilized sample in the process of catalytic pyrolysis was Al-MCM-41, a mesoporous material. The procedures for obtaining the thermogravimetric curves were performed in a thermobalance with heating rates of 5, 10, and 20 °C min<sup>-1</sup>. From TG, the activation energy was determined using the Flynn–Wall kinetic method, which decreased from 161 kJ mol<sup>-1</sup>, for the pure ATR, to 71 kJ mol<sup>-1</sup>, in the presence of the Al-MCM-41, showing the efficiency of the catalyst in the pyrolysis of Atmospheric Petroleum Residue.

**Keywords** Atmospheric petroleum residue · Al-MCM-41 · Thermogravimetry · Flynn–Wall kinetic model · Activation energy

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## Introduction

The petroleum refinement process usually starts by distillation units at atmospheric pressure. Different boiling temperatures separate the hydrocarbons and the distillation residue are called atmospheric residue (ATR), a quite heavy residue. This heavy end of an atmospheric distillation is also subjected to thermal treatments to obtain lighter fraction. The residue at the bottom of the distillation column can still be reused in another process, the vacuum distillation, generating new fractions with high economic potential, since the ATR has a low commercial value [1, 2].

The ATR, a fraction of high molecular weight, is made up of many compounds, its heaviest being the asphalthene, which is the main component of coke on thermal decomposition, in the search of products with lower molecular weight. In addition to ATR the other compounds obtained from atmospheric distillation are naphtha, kerosene, diesel, and gasoil, all of them with a high economic value [3].

With the increased demand for light olefins and the lack of feedstock from the conventional source, catalytic pyrolysis has attracted great interest in recent years. Compared with conventional thermal pyrolysis, catalytic pyrolysis not only can reduce reaction temperature and energy cost, but also can allows one to flexibly adjust product distribution. Catalytic pyrolysis can also produce light olefins from a wide range of lower quality feedstock's, such as heavy oils [4].

The hexagonal mesoporous structures with high surface area create possibilities to generate the surface acidity, which is necessary to catalyze organic reactions in the petroleum industry. Studies involving the incorporation of aluminum in the structure of mesoporous materials can be visualized in other major works [5, 6]. The presence of the hydroxyl groups associated with a tetracoordinated metal, such as, aluminum, within the framework of MCM-41

favors the Bronsted acidity, improving the catalytic activity of mesoporous materials, since the MCM-41 has no short range organization (since its walls are amorphous) [7].

Thermogravimetry was used to study thermal and catalytic behaviors of the ATR, for it is the ideal technique as measuring the substance's loss of mass as a function of the temperature. The utilized catalyst was Al-MCM-41 (Si/Al = 50), which has a hexagonal array of mesopores, with pore diameter ranging from 2 to 10 nm, as well as a fine thermal stability, high specific area values, and high pore volume, as described in the literature [8].

Thermogravimetry (TG/DTG) was used to evaluate thermal and catalytic pyrolysis of Petroleum Atmospheric Residue (ATR). In this study, the kinetics of the process was monitored by TG, using integral dynamic curves at multiple heating rates, and the activation energy was estimated from the Flynn–Wall kinetic model [9, 10].

## Experimental section

### Synthesis

The Al-MCM-41 material was synthesized through the hydrothermal method, using a gel with molar composition: CTMABr:2 NaOH:4 SiO<sub>2</sub>:200 H<sub>2</sub>O:x Al<sub>2</sub>O<sub>3</sub>, where the value of “x” was adjusted to that of the molar ratio Si/Al, which was equal to 50. CTMABr represents the cetyltrimethylammonium bromide, which is a surfactant, and which was used as a template for the sample; NaOH was used as a source of sodium; SiO<sub>2</sub> (Silica gel) corresponded to the source of silicon; H<sub>2</sub>O as the solvent and Al<sub>2</sub>O<sub>3</sub> (pseudoboehemita) was utilized as a source of aluminum.

The first solution was prepared by mixing silica gel, sodium hydroxide, a source of aluminum, and the solvent, keeping the mixture stirred for 2 h at 60 °C. The second mixture containing the template and the solvent were kept under stirring for 30 min. Then to the first solution was added the second, and the mixture remained under agitation for 30 min.

Then, this mixture was placed in a Teflon stainless steel autoclave and was afterward kept over a period of 5 days at a temperature of 100 °C. The pH of the gels is around 14. Corrections were made daily in the pH range 9–10 with a solution of acetic acid up to 30%. After the hydrothermal synthesis, the material was filtered and washed with 100 mL of distilled water to remove possible ion bromine and sodium waste. After this procedure, each material was placed to dry at 100 °C for 4 h.

### Characterizations

To study the catalytic activity of the material, a sample of ATR was used. The kinetic parameters for pyrolysis of the

ATR alone and with a catalyst (ATR/Al-MCM-41) were determined by Thermogravimetry (TG/DTG) model 851, Mettler Toledo Instruments, in the temperature range 25–880 °C, with heating rates of 5, 10, and 20 °C min<sup>-1</sup> and atmosphere of helium flowing at 25 mL min<sup>-1</sup>.

Applying the Flynn–Wall multiple heating rate model, the values of activation energy for the process were determined. In all the tests, were used alumina crucibles and a sample of approximately 20 mg of ATR for the thermal pyrolysis. As for the catalytic pyrolysis, an amount of 70% of ATR with 30% of the catalyst was analyzed.

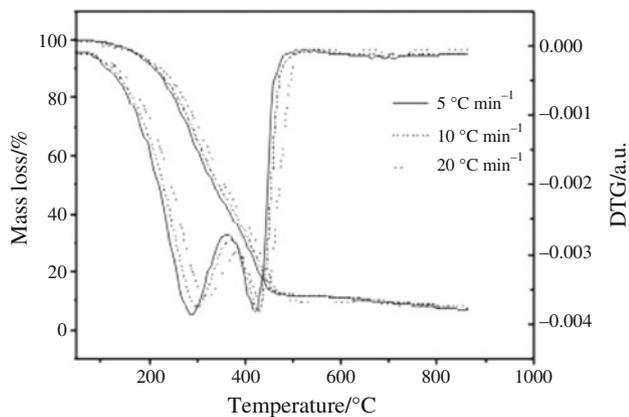
## Results and discussion

The kinetic study of the thermal pyrolysis of the materials through thermogravimetry (TG) has been a useful tool for calculating the kinetic parameters involved in the process. Some factors are decisive for these calculation parameters, such as the experimental conditions (mass sample, type of sample support, heating rate, and atmosphere) and the calculation method employed. Once the calculated parameters are dependent on the calculation method used, integral methods were chosen in this study, based on Flynn–Wall method [11, 12].

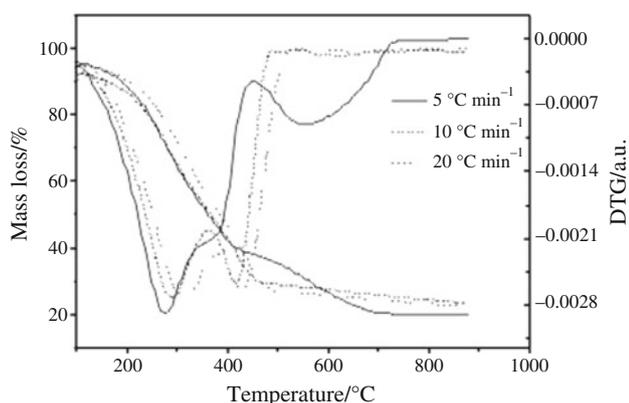
The velocity of the residue of catalytic cracking depends on the parameters: conversion ( $\alpha$ ), temperature ( $T$ ), and time of reaction ( $t$ ). In each process, the reaction velocity is given as a function of conversion  $f(\alpha)$  and can be determined from experimental data. The effect of heating rate ( $\beta$ ) in TG curves is the most widely studied. Usually, with the steady increase of ( $\beta$ ), there also occurs an increase of the thermodecomposition temperature with higher temperature values. The detection of intermediate compounds from TG curves also depends on the heating rate used, as well as, the nature of the sample [13].

Figures 1 and 2 present the mass loss versus temperature of ATR and mixture Al-MCM-41/ATR at three different heating rates, using helium flowing at a rate of 25 mL min<sup>-1</sup>. Each sample has a typical mass loss region.

The DTG curves show, with more clarity, two events that occur in bands of different temperatures. The first loss is attributed to the distillation of light materials, and the second to the cracking of hydrocarbons of high molecular weight. The mass losses for the thermal and catalytic cracking were in the range of 25–800 °C, and using the catalyst, the losses occurred at lower temperatures, thus evidencing the catalytic effect for the process of catalytic pyrolysis. Considering the region of cracking, the maximum temperatures in the losses of mass occurred in the range of 420–440 °C for ATR and 350–430 °C for ATR/Al-MCM-41. This difference of temperature between the two samples evidenced the catalytic effect of the mesoporous material



**Fig. 1** TG and DTG curves for pyrolysis of ATR without catalyst



**Fig. 2** TG and DTG curves for pyrolysis of ATR with catalyst

Al-MCM-41 on the process of ATR pyrolysis. Table 1 contains values of temperatures and percentages of mass loss of the obtained TG curves.

It was furthermore observed that with the increase of the heating rate was detected an increase of the pyrolysis temperature to higher values, and that the percentage values of mass loss tended to decrease; thus, it was assumed that the reaction occurred more rapidly and that there was no a complete cracking of the residue. Using the catalyst (Al-MCM-41), it was observed that a larger amount of

**Table 1** Values of temperatures and percentages of mass loss

| Sample        | Heat rate/°C min <sup>-1</sup> | Temperatures/°C | Mass losses/% |
|---------------|--------------------------------|-----------------|---------------|
| ATR           | 5                              | 70–490          | 93.16         |
|               | 10                             | 77–515          | 92.27         |
|               | 20                             | 80–530          | 92.61         |
| ATR/Al-MCM-41 | 5                              | 25–725          | 80.16         |
|               | 10                             | 115–485         | 76.72         |
|               | 20                             | 118–532         | 77.63         |

material was left in the crucible after the pyrolysis, and this could be because it increases the velocity of the reaction, but that it is not consumed during the reaction, its function being that of providing an alternative path for the reaction that has a lower activation energy [14].

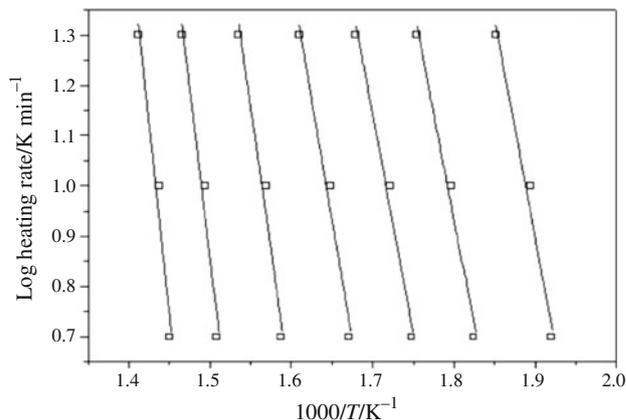
To calculate the activation energy of catalytic pyrolysis through Flynn–Wall, method Eq. 1, was used:

$$E_a \cong -18.2 \frac{\partial \log \beta}{\partial (1/T)} \tag{1}$$

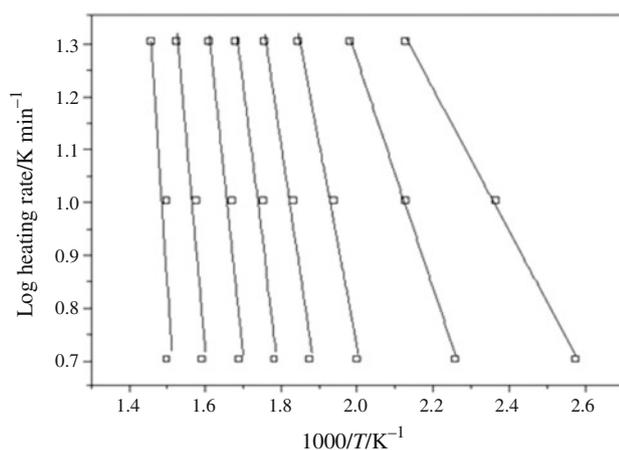
where  $\beta$  is the heating rate,  $T$  is the absolute temperature (K), and  $E_a$  is the activation energy (kJ mol<sup>-1</sup>). Therefore Figs. 3 and 4 present a plot  $\log \beta$  versus  $1,000/T$  to several conversion degrees of the process, which must be a straight line with the angular coefficient equal to the  $\partial \log \beta / \partial (1/T)$ , which permits calculation of  $E_a$  via Eq. 1. The linearity function for the thermal degradation rates confirms that the adopted kinetic model can be used to evaluate the residue pyrolysis [15].

The use of a solid catalyst for residue of petroleum catalysis requires information concerning the kinetic parameters, and mainly the energy of activation relating to the process. Reliable methods for determination of the activation energy using dynamic integral TG curves at several heating rates have been proposed by Flynn–Wall.

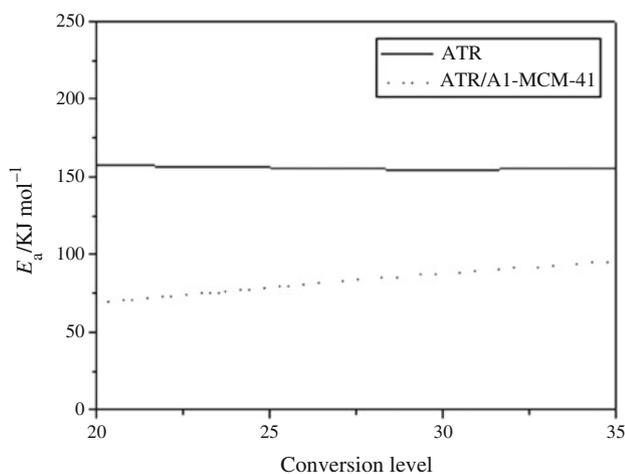
Thus, it was possible to calculate the apparent activation energy relating to the pyrolysis of a residue using the slope of the logarithmic heating rate curve as a function of reciprocal temperature. It could be stated that Flynn–Wall method work well in practically any conversion grade. Figure 5 presents the apparent activation energy observed for the pyrolysis of ATR, which was 161 kJ mol<sup>-1</sup>, compared with that of 71 kJ mol<sup>-1</sup> for ATR/Al-MCM-41, evidencing that the mesoporous Al-MCM-41 acted as catalyst for the pyrolysis of the Atmospheric Residue with the higher conversion level of pyrolysis, the apparent



**Fig. 3** Curves for determination of the apparent activation energy using the Flynn–Wall kinetic method for ATR without catalyst



**Fig. 4** Curves for determination of the apparent activation energy using the Flynn-Wall kinetic method for ATR mixed with Al-MCM-41 catalyst



**Fig. 5** Apparent activation energy versus conversion level

activation energies tend to have higher values due to the cracking of heavier compounds that occur in these regions.

## Conclusions

The sample was successfully synthesized, according to the results obtained through physicochemical characterizations, realizing show the formation of a mesoporous structure. The catalyst activity on the pyrolysis of residues was evidenced by a decrease of the activation energy of the process when the Al-MCM-41 was used. Thermogravimetry was the main technique utilized, which can be used in a satisfactory way to monitor the effective participation of the Al-MCM-41 catalyst on the process. The linearity function for the pyrolysis rates confirms that the adopted kinetic model can be used to evaluate the thermal and

catalytic pyrolysis in the ATR degradation. It is also noteworthy to remark that the current study proved to be singularly interesting because no mention has been made in previous in studies of residues, such as ATR, about and the results of the application of the mesoporous catalyst (Al-MCM-41) over the residue (ATR), as well as in kinetic study of a catalytic pyrolysis over the above mentioned sample.

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