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OIL SLUDGE ACTIVATION ENERGY ANALYSIS FOR THERMO-CONVERSION

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Abstract. *The thermo-conversion of oil sludge has been presented as a promising alternative for petroleum industrial residues treatment. The composition, characteristics, and energetic analysis of a material are crucial to determine the right conversion process. This study focuses on the thermo-kinetic analysis of oil sludge, bottom sediments in oil fuel storage tanks, through the dependence of the activation energy with the conversion degree. The ASTM 1641-04 method, a model-free kinetics, was applied to thermogravimetric (TGA) data to calculate the effective activation energy (E_a) during a pyrolysis process. It also includes the proximate and ultimate analysis of the oil sludge. Three different heat rates were used (5, 10, 20 ºC/min) in a nitrogen atmosphere. The material presents a high viscosity (between 2.74 and 5.19 Pa.s) and high ash content (40.36%). The results obtained from the TGA showed that the pyrolytic breakdown pathway is independent of the heating rate and can be described through a simple first-order kinetic reaction (f (a) = 1-a). The final mean activation energy was 102.97 kJ/mol. The calculated pre-exponential factor using this value equals $8.7.10^{15}min^{-1}$.*

Keywords: *Oil sludge, Activation Energy, thermo-conversion*

1. INTRODUCTION

In the oil refinery industry, one of the biggest challenges is the proper disposal of oily sludge. The oil sludge is a recalcitrant material in the form of a stable water/oil emulsion with solids, hydrocarbons, and heavy metals (Mazlova & Meshcheryakov, 1999). This kind of residue is formed in different phases of the oil industry, such as crude oil extraction, transportation, storage and refining (Roldán-Carrillo et al., 2012). Besides the recalcitrant characteristic of the material, it is also highly toxic, the volatiles fumes may cause skin and eyes irritation, as well as, cause respiratory problems. If placed directly in the environment can cause growth problems in plants, pollute subterranean water and affect microbiological fauna(Gong et al., 2018).

In 2018, approximately 94.7 million barrels of oil were produced daily worldwide, of which 2.7 million were produced in Brazil alone (ANP, 2019). A considerable amount of oily sludge can be generated from the oil refining industry during the stages of oil exploration, production, transportation, storage, and refining. Approximately one ton of oil sludge is generated for every 500 tons of processed oil (0.2%) (Hu et al., 2013). It is estimated that global oil sludge production surpasses 60 million tons a year (Li et al., 2020). In this paper it is analyzed the oil sludge formed by the sediments formed in fuel oil storage tanks, which is the main oily sludge produced in the Gabriel Passos refinery, representing 34.7% of the total amount of oil sludge produced.

Thermochemical treatments for oil sludge are still considered new treatments, although gasification is considered a clean energy conversion technology. With low environmental impact, which can use various types of materials such as biomass, industrial, urban or agricultural waste as fuel to obtain a fuel gas rich in hydrogen, carbon monoxide, in addition to the possibility of synthesis of chemical compounds such as methanol (Hu et al., 2020). Another advantage is the low operating costs and high possibility of commercialization of synthesis gas obtained during the gasification process, as a basis for power generation (Aydin et al., 2018).

The thermochemical processes depend on the changes promoted by temperature on the physical and chemical properties of the fuel (solid, liquid or gaseous). These changes can be physical (inter-molecular), when there is no intra-molecular break, presenting a phase change (to solid, liquid, or gas), and can be chemical, when the intra-molecular break occurs and leads to the formation of different intra-molecular bounds (Vyazovkin, 2015).

The measure of the reaction rates as a function of temperature is crucial to infer the thermo-kinetic behavior of materials subject to temperature variations, since is crucial to separate the contributions coming from physical and chemical phenomena in a heterogeneous system or process (Torres-García et al., 2020).

Due to the complex nature of reactions, it is necessary to evaluate the thermal kinetic behavior of the thermochemical process to make it commercially feasible (Ali et al., 2021). This paper presents a kinetic analysis of oil sludge samples in order to determine the activation energy and pré-exponential factor of the devolatilization process of this material.

2. EXPERIMENTAL PROCEDURE

2.1 Sample and characterization

The oil sludge samples were supplied by Petrobras, from Gabriel Passos refinery, from bottom sediments in crude oil storage tanks. The samples did not suffer any pretreatment due to the unknown characteristics of the material.

The proximate analysis of the oil sludge was performed according to the ASTM D3172 standard, using a TGA LECO 701. The moisture, volatiles, fixed carbon and ashes were obtained at 100°C, 650°C, 900°C and 750°C, respectively, the temperature was constant until a constant weight was obtained. The ultimate analysis was performed using a Perkin-Elmer CHNS Analyzer, where the oxygen is calculated based on difference, the results from the proximate and ultimate analysis can be observed in Table1.

Table 1. Oil sludge proximate and ultimate analysis

Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)	Oxygen (%)
35,76	3,83	0,00	2,98	57,44
Fixed Carbon (%)	**Volatile (%)**	**Ash (%)**	**Moisture (%)**	
7,99	44,57	40,36	7,08	

The oil sludge at room temperature is a high viscosity liquid, with a paste consistency, measured using a Brookfield viscometer. Two samples have their viscosity measured from 50°C to 80°C, as presented in Figure 1. At 80°C, both samples reach nearly the same viscosity value, between 2.74 and 5.19 Pa.s. This data in this section is presented by Santiago (2020).
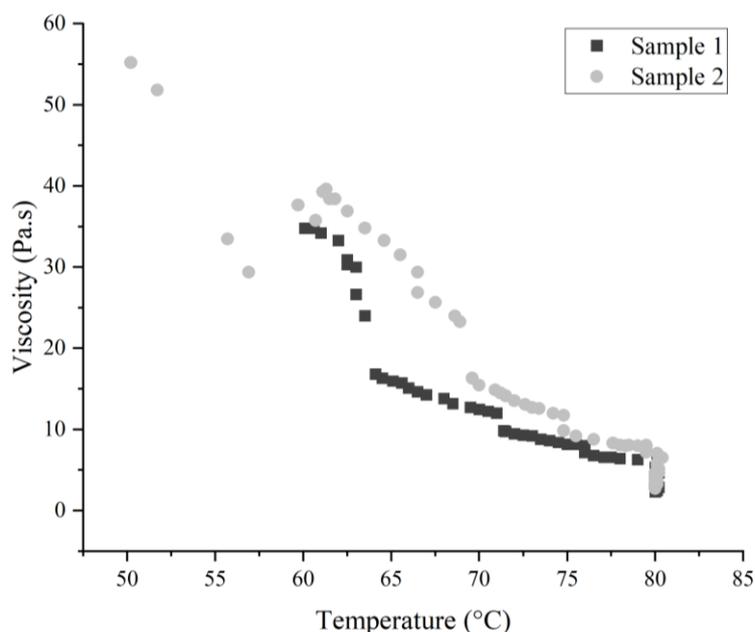

Figure 1. Oil sludge viscosity test with temperature increase

A Thermogravimetric Analyzer (TA) Mettler TOLEDO TC11 was used to obtain the weight loss with the temperature, at different heating rates. In this study, the heating rates used were 5, 10 and 20°C/min. The mass weight loss curve can be observed in Figure 2.
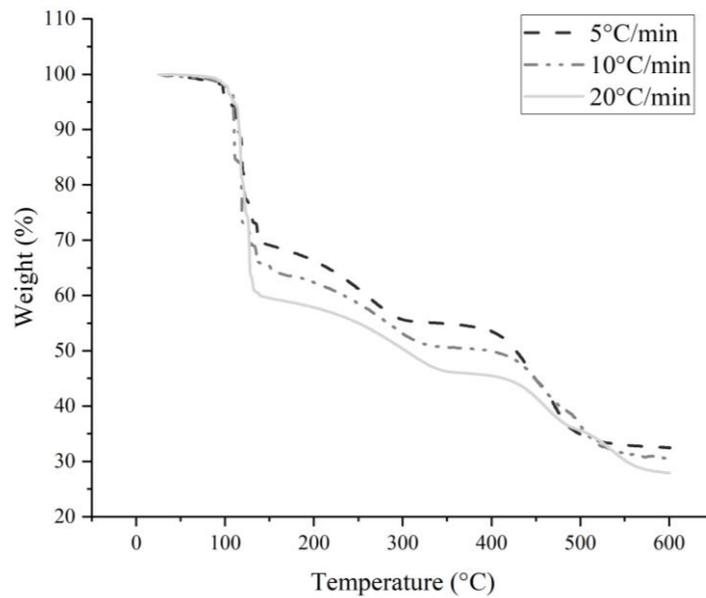
Figure 2. Weight loss with temperature

Based on the paper developed by Barneto et al. (2014) that compares the thermal degradation profiles of crude oil and oil sludge, and considers, under thermogravimetric conditions, the same pattern of fraction for both materials, being the same: benzene-ligroin ($\leq$180°C), kerosene-gas oil (180-300°C), paraffins-base oils (300-400°C), condensed aromatics (400-550°C) and asphaltenes (550-600°C). Based on these fractions the oil sludge sample shows a higher concentration of benzene-ligroin (43%), condensed aromatics (resins) (18%) and kerosene-gas oil (10%), respectively. It also can be noticed that the higher heating rate the higher the initial weight loss, but the curve behavior is virtually the same.

2.2 Non-isothermal kinetics method

A non-isothermal kinetics method was applied to determine the material activation energy and the pre-exponential factor, described in the ASTM 1641-04, based on Flynn and Wall method (Flynn, 1983; ASTM, 2007). The primary reaction rate in solid particles can be described as a k coefficient multiplied by the reagent's concentration as in Eq. 1.

$$rate = k.f(reagents\_concentration)$$, (1)

All the kinetic studies, isothermal and non-isothermal, must be done based on Eq. 2, which can be rewritten as Eq. 3 (Arrhenius Equation).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{\left(\frac{-E_\alpha}{RT}\right)}f(\alpha)$$, (2)

$$k = Ae^{\left(\frac{-E_\alpha}{RT}\right)}$$, (3)

Where the degree of conversion, namely α, which values range from 0 to 1 ($0 \leq \alpha \leq 1$), is a parameter that describes the reaction progress from the initial state to the final state. It can be determined experimentally as a function of the overall change in a physical property that accompanies a process(Vyazovkin et al., 2014). The t is the time (min), T is the absolute temperature (K), A is the pre-exponential factor (min^{-1}), E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol.K), and $f(\alpha)$ is a function of the reaction model, which describes the dependence of the global reaction rate on the conversion. Eq. 4 defines the degree of conversion α as the material loss divided by the total weight loss as T or t tends to infinity.

$$\alpha = \frac{(m_0-m)}{(m_0-m_\infty)}$$, (4)

In Eq (4), m_0 is the initial sample weight, m is the weight of the material at the time t and m_∞ is the final weight. Therefore, in non-isothermal conditions, the explicit time dependence of the kinetic rate equation can be approached by using the heating rate (β). Considering a linear heating rate, $d\alpha/dT$ can be written as a β function (Eq. 5).

$$\frac{d\alpha}{dT} = \frac{1}{\beta}\left(\frac{d\alpha}{dt}\right),$$
(5)

Combining Eq. 1 and Eq. 5, an expression as Eq. 6 is obtained.

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{\left(\frac{-E\alpha}{RT}\right)}f(\alpha),$$
(6)

Equation 6 expresses the global reaction rate ($d\alpha/dT$) dependence on the temperature (T) and the conversion degree (α). Assuming that A, f (α), and E_a are independent of T and that A and E_a are independent of α, Eq. 6 can be integrated from T_0 to T, and since T_0 is negligible, the final logarithmic form of the expression is Eq. 7, which, based on Doyle's approximation, can be write in the form of Eq. 8.

$$LogF(\alpha) = Log\left(\frac{AE}{R}\right) - Log\beta + Log\, p\left(\frac{E\alpha}{RT}\right),$$
(7)

$$Log\,\beta = c - \left(p\left(\frac{E}{RT}\right)\frac{E\alpha}{R}\right)\left(\frac{1}{T}\right),$$
(8)

Where $-(p(E/RT)\cdot E_\alpha/R) = \Delta\log\beta/\Delta(1/T)$ equals the slope of the curve that correlates the logarithm of the heating rate and the reciprocal of the absolute temperature. The Activation energy then can be calculated based on Eq. 9, with the slope of the curve, and the values from $p\ (E/RT)$, determined by Flynn and Wall (1965).

$$E_\alpha = -R\left(\frac{\Delta Log\beta}{\Delta\left(\frac{1}{T}\right)}\right)/p\left(\frac{E}{RT}\right),$$
(9)

After the activation energy determination, the pre-exponential factor is determined by Eq.10.

$$A = -\left(\frac{\beta}{E_\alpha}\right)R\,ln(f(\alpha))10^\alpha,$$
(10)

Where f (α) is a conversion function, on thermochemical conversion the main used model is reaction order dependent, described by Eq. 11, where n represents the reaction order. In order to simplify the model considered the reaction order as 1.

$$f(\alpha) = (1 - \alpha)^n,$$
(11)

3. RESULTS OF THE KINETIC ANALYSIS

The thermal behavior between 25°C and 600°C, displayed in Figure 1, show a higher mass variation in the range of 100°C to 550°C, representing 63% of the total sample weight and 92% of the weight loss, with the portion relative to temperatures below 100°C being related to the moisture present in the material. These results can be related to the high content of volatiles in the material (approximately 75% af), that are consumed in lower temperatures.

Based on the thermogravimetric data obtained, initially it was calculated the mass conversion from room temperature to 600°C, which represents the temperature for which the mass value becomes virtually constant. Figure 3 displays the weight conversion until 600°C. The conversion values and referent temperatures are the main starter of the kinetic analysis calculation, from which, using ASTM method presented, it was possible to construct the graphic shown in Figure 4.

Fig 4 results show the fitted straight lines formed by reciprocal temperature and the heating rate logarithm various conversion points, varying from 5% to 90%. The lines show a low negative slope, becoming positive in some cases. These results show low activation energies, since the higher the slope module, the higher the material activation energy, as can be observed in Eq. 8, which shows that the curve slope and the activation energy are directly proportional.
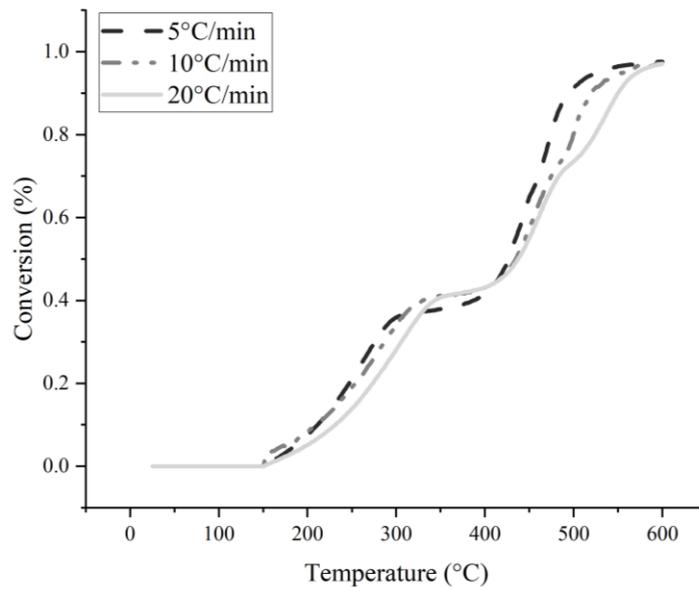
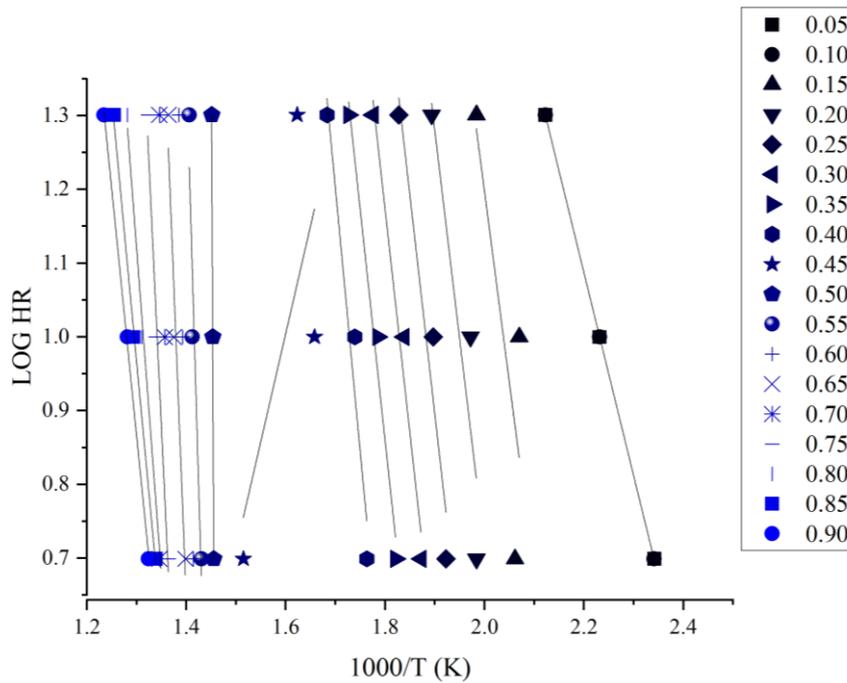Figure 3. Oil sludge conversion with temperature for different heating rates

Figure 4. Logarithm of heating rate vs. reciprocal absolute temperature for different conversion points.

Based on the results shown in Figure 4 it is possible to calculate the activation energy, using Eq. 8. As can be seen in Figure 4 some of the curves show a very small negative slope value, even becoming positive, as the curve that represents the conversion degree of 0.45. This would result in negative activation energy, therefore some of the conversion levels were not considered for the E_a calculation, as shown in Figure 5.
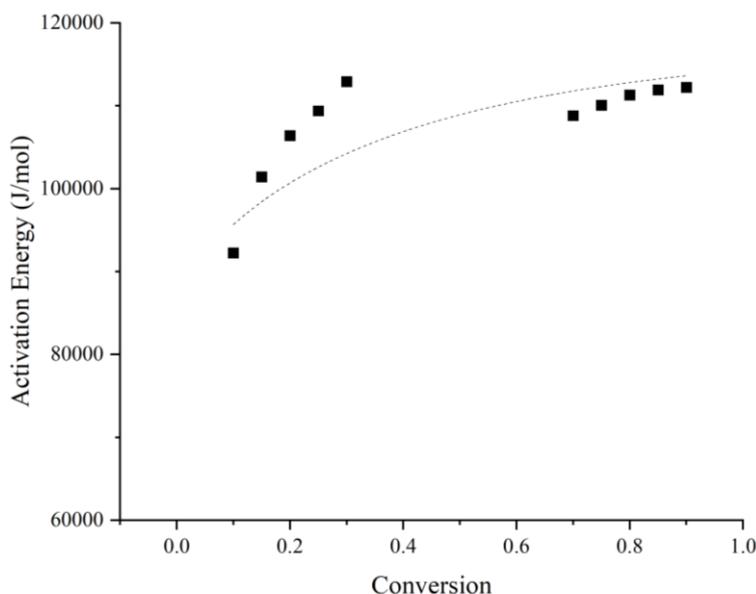
Figure 5. Activation Energy dependency on the conversion level

As presented in Figure 5, the activation energy range from 45.8 to 130 kJ/mol, with a mean value of 104.06 kJ/mol, for this result the pre-exponential factor is $4.89.10^{12}$ min^{-1}. When compared to data shown by different authors such as Cheng et al. (2019) and Shie et al. (2000), the results presented in this paper are within the range for oily sludge activation energy. Cheng et al. (2019) show a range from 103.1 to 120.2 kJ/mol and Shie et al. (2000) from 69.9 to 123.2kJ/mol.

4. CONCLUSIONS

Oil sludge, obtained from sediments formed in oil fuel storage tanks bottom, is a major residue issue in the petroleum industry, due to its high pollution potential. In this study, the thermogravimetric degradation of oil sludge was analyzed to determine the weight loss behavior, aiming at calculating its activation energy and pre-exponential factor. These characteristics are very important to find the thermo-kinetic behavior of materials exposed to temperature variations.

The TG analysis show that the decomposition of dried oil sludge under a nitrogen atmosphere is a multi-step procedure with intricate reaction mechanisms. Heating rates have a significant effect on weight loss, mainly in the initial temperatures (100-150°C). The results show a mean activation energy of 104.06 kJ/mol, and for this result, the pre-exponential factor was $4.89.10^{12}$ min^{-1}, being consistent with data from the literature.

5. ACKNOWLEDGEMENTS

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