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Kinetics of batch microwave drying of drill cuttings contaminated with an olefin-based fluid

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Abstract

Drilling is one of the phases of oil and gas production. During this phase, drill cuttings are created and transported from the well to the surface by the circulation of fluids. Usually these fluids are synthetic-based and the drill cuttings must be treated before being disposed in order to prevent potential environmental impacts.

The microwave drying technology is a promising alternative to the treatment of drill cuttings contaminated with synthetic-based fluids. In microwave ovens, the heat is generated by direct transformation of electromagnetic radiation into thermal energy, within the material to be dried, which results in higher energy efficiency and lower drying time, when compared to other thermal desorption techniques.

Therefore, this work presents the study of the drying of drill cuttings contaminated with an olefin-based fluid in a batch scale microwave oven, the Milestone NEOS GR. Three process variables were considered in the study: initial internal olefin mass fraction, applied power and specific energy. The residual content of olefin was evaluated in each experimental test and some dielectric properties of samples with different olefin concentrations were measured. Then, the drying kinetics was investigated through the modeling of data using a semi-empirical drying equation, which included the dielectric loss tangent as parameter.

Introduction

During the drilling operation of oil and gas wells, rock fragments, also known as drill cuttings, are created by the action of the drill and are continuously removed due to the circulation of the drilling fluid. This fluid is injected into the drill pipe and returns to the surface through the annular space between the well wall and the drill pipe. At the surface, the mixture of fluid and drill cuttings is redirected to a solids control system that has several kinds of equipment responsible for promoting separation of the drilling fluid and cuttings, thus allowing the reuse of recovered fluid[1].

The drilling fluid has other fundamental functions besides acting as a carrier of the cuttings. Among the functions of the fluid are: the stabilization of rock formations and lubrication of the drilling pipe[2]. Accordingly, it can be stated that the development and selection of drilling fluids are of great importance to the oil industry.

In wells of great depth and complexity, synthetic-based drilling fluids are used. This type of non-aqueous fluid guarantees the stability required for the drilling operation but contaminates the rock fragments generated by the drill activity. Therefore, prior to the disposal of drill cuttings carried by synthetic-based fluids, it is necessary to treat these solids since these fluids have compounds of low biodegradability and substantial toxicity[3].

In 2010, the United States Environmental Protection Agency (US EPA) stipulated that the organic content of synthetic fluid present in discarded solids on offshore platforms may not exceed 6.9% by mass[4].

Nowadays, an equipment is used by Petrobras by the end of the solid control system[5]. It has as main functions the recovery of drilling fluid and the decontamination of drill cuttings at organic contents lower than the limit defined by US EPA. However, the organic content of synthetic fluid achieved by this equipment is very close to the environmental limit defined by law, which makes the search for new alternatives necessary since there is a tendency of increasing demands on the limits imposed for the disposal of cuttings contaminated with synthetic fluids.

One of the options for the treatment of drill cuttings currently studied is microwave drying. Recent research results indicate that this technology is a promising alternative in the decontamination of cuttings[6,7].

Once microwaves promote selective heating at a molecular level, this technique presents advantages when compared to conventional heating methods, especially considering the time variable[7]. In addition, the decontamination levels achieved by this technique are higher than those achieved by the technique currently used.

The objective of the present work was to study the drying of cuttings in a bench-scale microwave oven, the Milestone NEOS-GR, in order to verify the kinetics of the treatment method for drill cuttings contaminated by an olefin-based drilling fluid.

Microwave drying

Microwave irradiation is a fast method of heating materials, both domestically and industrially. Microwaves have several advantages over conventional heating, such as non-contact heating (reduction of surface overheating), energy transfer

instead of heat transfer (penetrating radiation), heating selectivity of materials, volumetric heating and reduced time of operation[8].

In order to observe microwave heating, at least one component present in the mixture must be polar or ionic. Thereby, these components have the ability to reorient rapidly in response to the constant change in the electromagnetic field of microwave radiation[8].

The dielectric properties of materials determine the absorption of the electromagnetic energy, the conversion efficiency of the electromagnetic energy into thermal energy and the heating uniformity in the material volume. As a result, they allow the understanding of the behavior of a material during the microwave assisted heating process. Consequently, the measurement of dielectric properties of the material is essential to evaluate the applicability of the microwave technology[8].

The dielectric property studied and measured in this work was the dielectric loss tangent ($tan\ \delta$). This property indicates the ability of a given material to convert electromagnetic energy into heat[8]. A material is considered absorbent (has the capacity to absorb the electromagnetic energy and convert it into thermal energy) for loss tangents greater than 0.1.

The specific energy (EE) was another variable considered in this work. It is an important parameter in processes that use microwave, being defined as amount of energy supplied per unit of mass. In batch processes, it is calculated according to Equation 1:

$$EE\left(\frac{kWh}{kg}\right)=\frac{P(kW)\ t(h)}{m(kg)} \tag{1}$$

In which P is the power applied, t is the heating time and m is the mass of material fed into the process.

Microwave drying kinetics

Several mathematical models are proposed in previous works for the study of microwave drying kinetics of materials. One of the most used models in the analysis of drying curves of microwave assisted processes is the Page model[9], correspondent to Equation 2:

$$\frac{X-X_{eq}}{X_i-X_{eq}}=exp\left(-k\ t^n\right) \tag{2}$$

in which X is the mean moisture of the material at time t, X_{eq} is the mean moisture of the material at equilibrium, X_i is the initial mean moisture of the material, k represents the drying constant at time t and n is a parameter that is correlated to the shape of the curve.

Both parameters k and n are functions of the process variables: composition and mass of material, microwave working frequency, applied power, among others. The higher the value of the parameter k, the higher the drying rate under the conditions used. Otherwise, the dimensionless parameter n indicates the effects of the experimental conditions in three ways: if the behavior is purely exponential (n is equal to 1), when drying is faster than the exponential curve (n is greater than 1) and when the drying is slower than the exponential behavior (n is lower than 1)[10].

Although this model is widely used for the study of microwave drying curves, it can be observed that there are no variables directly connected to dielectric properties. Therefore, a new kinetic model was proposed in this work for the kinetic analysis of the microwave drying process[11], presented in Equation 3:

$$\frac{X}{X_i}=exp\left(-k\ tan\delta\ EE^n\right) \tag{3}$$

The dielectric loss tangent ($tan\delta$) was considered constant for each one of the initial olefinic concentrations on a wet basis, corresponding to the tangent loss measurement of each sample before the drying process at the 2.4 GHz frequency, which is the operating frequency of the microwave used in this work. The loss tangent is the variable that represents the influence of the microwaves on the drying process.

The power and mass variables were also included into the equation since their influence is important to the microwave drying process. They are inserted in the specific energy term (EE). The units considered for the variables of power, mass and time were respectively: kilowatt (kW), kilogram (kg) and hour (h). These units were selected in order to maintain the same units adopted in Equation 1.

Predictive kinetic models that include the dielectric properties of materials are fundamental not only for a better understanding of the mechanisms involved in drying, but also for the design of systems that apply microwaves. The detailed research of the process, seeking to ally economic and technical factors, besides the cooperation with the industry, are essential for the success of the microwave drying as an alternative for the treatment of materials.

Materials and methods

Microwave drying experiments

The Figure 3.4 is a representation of the experimental batch scale unit used for the drying of drill cuttings in this work. It consists of the following items: (1) Milestone microwave furnace, model NEOS-GR, with adjustable power up to 900 W, frequency of 2.45 GHz and internal cavity dimensions of 24 x 29 x 26.5 cm (L x W x H); (2) furnace control panel; (3) chiller, for cooling the recirculated liquid in the condenser; (4) vacuum pump, for the removal of vapors from the microwave cavity; (5) refractory porcelain container where contaminated cuttings are allocated; (6) glass dome; (7) connecting glassware; (8) condenser and (9) separatory funnel.

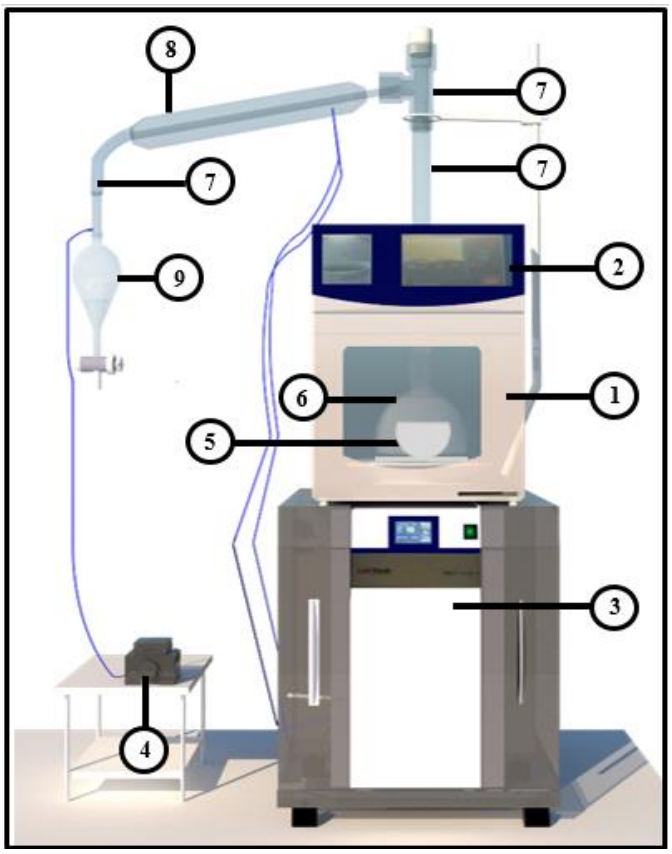


Figure 1: Experimental batch scale microwave unit used for drying tests.

The retort method was used before and after each drying test, in order to quantify the internal olefin content in the cuttings. For this, a 50 mL Fann retort was used. In this test, a sample of contaminated gravel is heated until all of the fluid is evaporated. The vapors are condensed and collected in a graduated cylinder in order to measure the concentration of the aqueous and organic phases on a wet basis[12].

The cuttings contained residual organic phase and moisture content. Hence, these solids were subjected to an isopropyl alcohol extraction process in Soxhlet extractors to remove the organic phase during 48h. Then, they were oven dried at 105° C during 24 h for removal of water and residual isopropyl alcohol. Thus, cuttings free of moisture and organic phase were obtained.

The drilling fluid used to contaminate the clean cuttings was a synthetic fluid with an internal olefin as organic base. It has approximately the following mass composition: 33% internal olefin, 33% water and 34% additives.

Samples of clean drill cuttings were quartered and subsequently mixed with drilling fluid in order to achieve the following mass contents of olefin: 7.5, 10 and 12.5%. In each sample, the water content was also the same of olefin content. Accordingly, the mass content of 7.5% corresponds to a sample containing 7.5% of water and 7.5% of internal olefin on a wet basis.

In the microwave drying procedure, a fixed mass of 250 g of contaminated drill cuttings was used in each of the tests. These samples were placed in a porcelain container and inserted into the furnace, being positioned in the center of the cavity (Figure 1). Both the time and power were set on the control panel. Subsequently, the vacuum pump was turned on and the experiment started.

The selected powers were 250, 500 and 750 W. Regarding the duration of drying, tests were carried out at different time intervals until the organic content reached 1% by mass on a wet basis.

At the end of each experiment, the recipient with the cuttings was reserved. Up to 2 h after the end of the test, time which was sufficient for the vapor still trapped in the sample to be released, the retort of the material was performed.

Dielectric properties measurements

The dielectric properties of the cuttings and drilling fluids at room temperature were measured by the coaxial probe method on the Fieldfox Keysight N9913A RF analyzer using the high performance N1501A probe (Figure 2). The frequency range used in the measurements was 2 to 3 GHz.

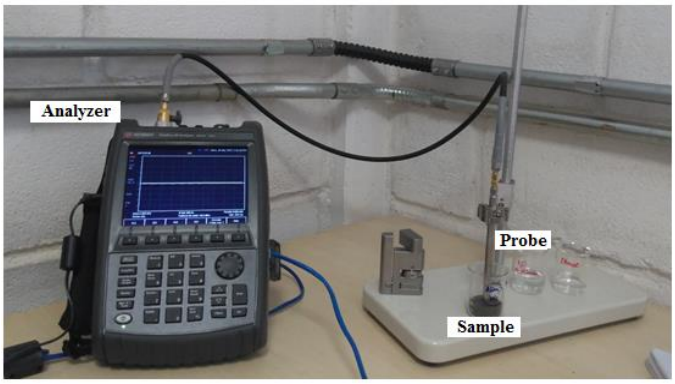


Figure 2: System used for the measurement of dielectric properties at room temperature.

The contaminated cuttings samples were prepared and placed in 100 mL beakers. Samples with the same organic and water mass contents were used in comparison to the drying tests: 7.5, 10 and 12.5%. Again, the mass content of 7.5% corresponds to a sample containing 7.5% of water and 7.5% of internal olefin on a wet basis.

The probe was inserted into the previously prepared sample. The position of the probe for measurements was different for liquids and solids, meeting the guidelines of the equipment manufacturer's manual[13,14].

Measurements were made in four different positions in the same sample, in order to obtain the mean values of dielectric loss tangent ($tan\delta$) at the microwave operating frequency, 2.45 GHz.

Kinetic model

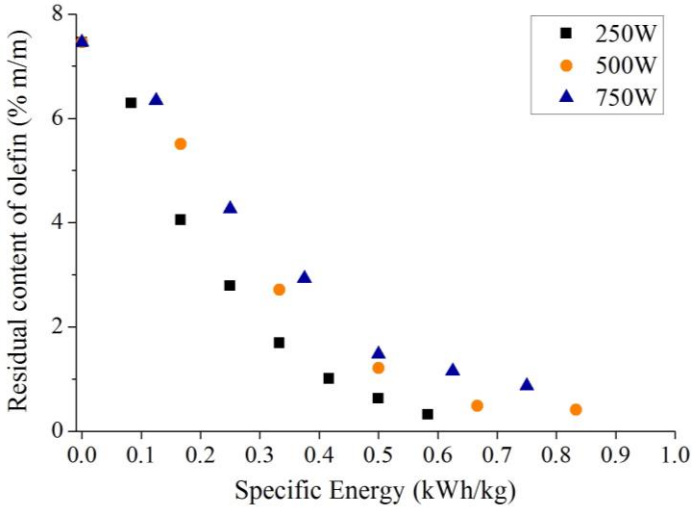
The proposed kinetic model was validated based on the results of the drying kinetic tests and the measured dielectric properties. The adjustments obtained for the experimental

results were executed by the Gauss-Newton method, according to the model proposed in Equation 3. It is worth mentioning that in this model the value of the dielectric loss tangent was considered constant in relation to the initial organic content of the sample of each test (7.5, 10 and 12.5% by mass on a wet basis).

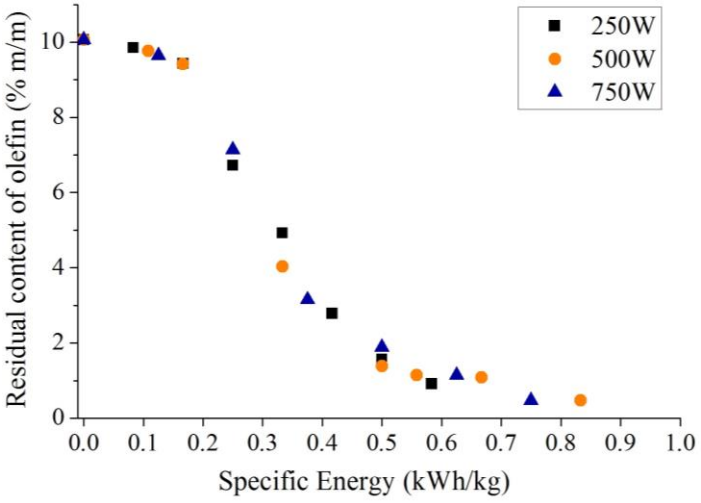
Results and discussion

Microwave drying experiments

The results obtained for the residual internal olefin mass content as a function of the specific energy (EE) and power in the drying tests are presented in Figure 3, for each one of the initial organic content adopted (7.5, 10 and 12.5% by mass, respectively).



(a)



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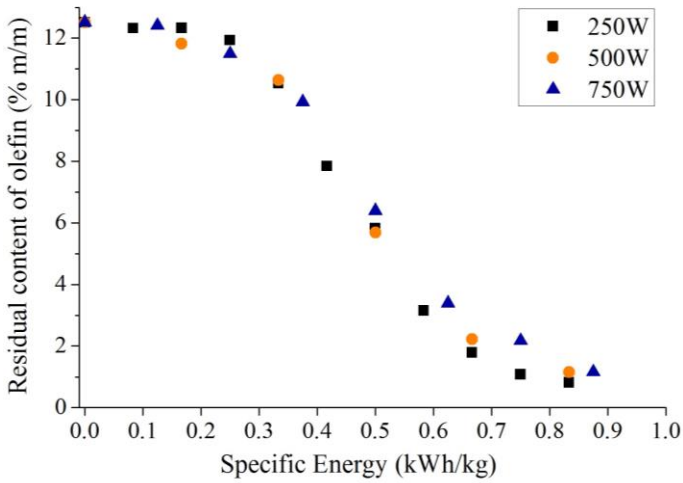


(c)

Figure 3: Residual content of olefin in samples of 250 g with initial olefin contents of (a) 7.5%; (b) 10% and (c) 12.5% (m/m) in function of the specific energy for different powers.

As expected, the higher the specific energy, the greater the removal of olefin. Although the time interval until the range of the 1% content was lower for higher powers, with the application of lower power a greater decontamination was obtained when considering the residual content of olefin in relation to the specific energy. In other words, it is possible to note that a lower specific energy is required for a given level of organic phase removal at lower heating rates (lower power). This trend can be observed in Figure 3 and is in agreement with the literature[6,15].

In the curves of Figure 3 (b) and (c), the drying of the drill cuttings shows a behavior that differs from that observed in Figure 3 (a): the existence of a stationary region of low decontamination of olefin in the tests of lower specific energy, which becomes more evident with the increase of the initial organic content of the cuttings.

It is believed that, in this stationary region, the internal olefin has not reached its boiling temperature range and the small decontamination in this period is due to the drag by the water vapor.

Table 1 contains the results for the most extreme points in each series, that is, the tests of the highest drying time for each applied power and initial olefin content, with their respective specific energy. It is important to emphasize that in all tests the initial sample mass was fixed (250 g).

The best result obtained from the drying experiments presented in Table 1 was for the test with lower initial olefin content (7.5%) and lower applied power (250 W), in a longer drying time (35 min). The residual moisture content of internal olefin reached was 0.32% by mass on a wet basis. This was also one of the tests of lower energy expenditure, with an specific energy of 0.58 kWh / kg.

On the other hand, the worst results are related to the tests in which cuttings had the highest initial organic content

(12.5%), in the powers of 500 W and 750 W. The residual olefinic contents reached were, respectively, 1.15 and 1.16%.

Table 1: Residual contents for the most extreme points of each series of experiments, with their respective initial content of olefin, applied power, time and specific energy.

Initial content of olefin (% m/m)	Power (W)	Time (min)	Specific Energy (kWh/kg)	Residual content of olefin (% m/m)
7.5	250	35	0.58	0.32
7.5	500	25	0.83	0.41
7.5	750	15	0.75	0.87
10	250	35	0.58	0.91
10	500	25	0.83	0.47
10	750	15	0.75	0.57
12.5	250	50	0.83	0.81
12.5	500	25	0.83	1.15
12.5	750	17.5	0.88	1.16

Thereby, the next section addresses the measurements of dielectric properties which, together with the drying tests results, are fundamental for the evaluation of the kinetic model proposed in this work.

Dielectric properties

In Table 4.5 are the dielectric properties of drill cuttings with different organic and water contents at a temperature of 27º C and frequency of 2.45 GHz.

Table 2: Dielectric properties of contaminated drill cuttings with different olefin and water contents, at a temperature of 27º C in the frequency of 2.45 GHz.

Content of olefin (% m/m)	Water content (% m/m)	Loss tangent (tan δ)
0	0	0.234
7.5	7.54	0.296
10	9.71	0.312
12.5	12.39	0.350

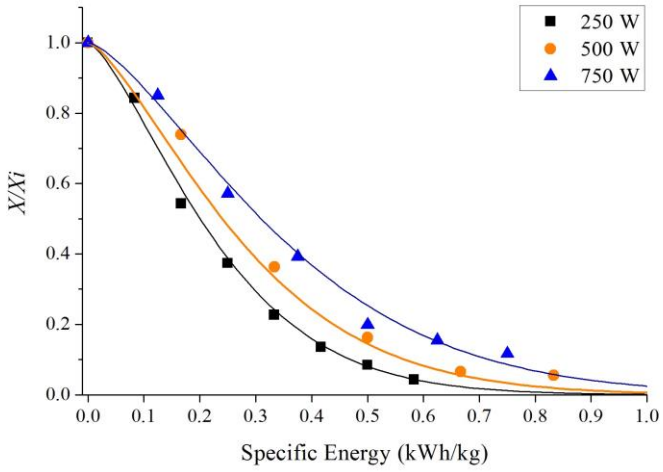
It is observed that, even without the presence of fluid, the cuttings used in this work are a material that has the capacity to heat under the application of a frequency of 2.45 GHz based on the value obtained for the dielectric loss tangent of the first sample presented in Table 2 (value greater than 0.1). Moreover, as the concentration of fluid increases, the dielectric loss tangent increases.

As observed in the drying results presented in the previous section, the values obtained for the loss tangent also confirm that the material undergoes heating under the application of microwaves

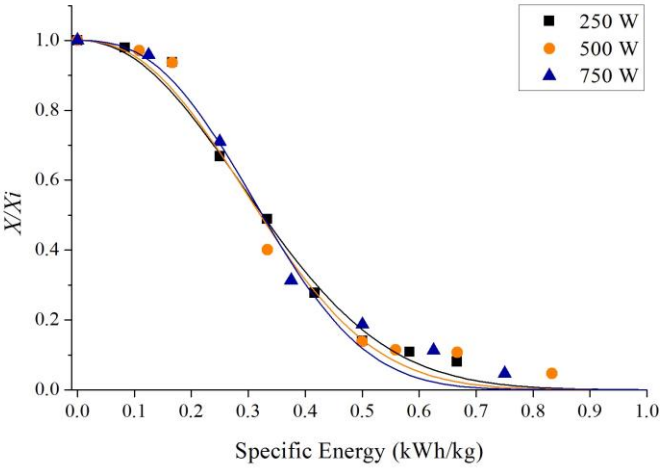
Kinetic model

The results were analyzed according to the kinetic model present in Equation 3. It is important to remember that the values of the loss tangent used in the model are relative to the samples before the beginning of the drying process, for the initial content of olefin and water of each test, in accordance to the data presented in Table 2.

Figure 4 contains the nonlinear adjustments obtained for the kinetic curves of different initial olefin content and powers.



(a)



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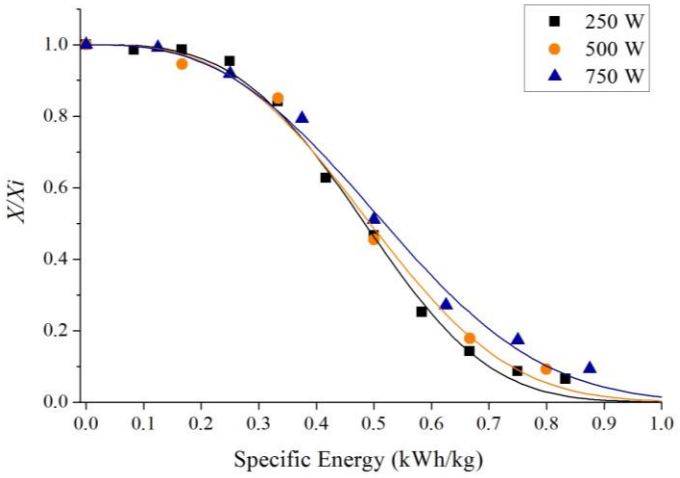

(c)

Figure 4: Adjustments of the kinetic model for each power applied as a function of the specific energy in the following initial contents of olefin: (a) 7.5%, (b) 10% and (c) 12.5%.

All the curves present in Figure 4 have the specific energy variable in the abscissa axis and the relative olefin content in the ordinate axis. The relative olefin content is equivalent to the division of the residual olefin content of each test by the initial olefin content of the sample.

The numerical values obtained for the constants of the proposed kinetic model can be found in Table 3. The coefficient of determination of the non-linear regressions are also in this table.

Table 3: Results for the regression parameters of the proposed model.

Initial content of olefin (% m/m)	Power (W)	k (kg/kWh)^n	n	R^2
7.5	250	22.58	1.41	0.998
7.5	500	17.22	1.40	0.997
7.5	750	12.50	1.43	0.994
10	250	21.65	2.60	0.993
10	500	16.37	2.33	0.984
10	750	12.48	2.17	0.987
12.5	250	19.80	3.25	0.996
12.5	500	15.03	2.97	0.994
12.5	750	10.98	2.75	0.994

By the dimensional analysis, the parameter k has the following dimensions: (kg/kWh)^n. Therefore, according to these units, this parameter can be related to the drying rate of the process for a given sample mass and applied power. Since the initial mass of all tests was fixed (250 g), the value of this parameter must be closely related to the applied power intensity.

In Table 3, for the same power values, the k value of the curves is approximately equal, even if in these tests the initial contents of olefin are different. In other words, the drying rates in the experiments of the same power value are approximately the same in the studied olefin content range. This proximity of values to the parameter k as a function of the power is of great importance, since both the prediction and the control of the drying process could be facilitated by establishing a mathematical expression that allows to relate the power to the drying rate.

Another important point to highlight is that, for experiments with the same initial olefin content, the k-parameter values decrease with the increase of the applied power. In other words, the final decontamination is influenced negatively by the power. This trend is consistent with the experimental results obtained during the drying tests. The data previously presented showed that, for the same specific energy and a higher power, a lower level of organic decontamination was achieved.

In turn, the parameter n is related to the shape of the curves present in Figure 4 and is dimensionless. According to the data presented in Table 3, the values of n are approximately equal for experiments of the same initial olefinic contamination. Thus, the shape of the curve is more dependent on the initial olefin content than on the applied power. Such assertion can be confirmed from the observation of the similarity of the curves present in Figure 4 when an initial olefin content is fixed.

Conclusions

Based on the results obtained in the drying experiments presented in this study, it can be concluded that the drill cuttings, by the end of the process, have residual contents of internal olefin that meet the current environmental legislation. In addition, the microwave drying tests achieved higher decontamination yields when compared to the current technology used, the vertical filtering centrifuge. Since there is a tendency of increasing demands on the limits imposed for the disposal of cuttings contaminated with non-aqueous fluids, the results achieved by the use of microwave make it a feasible alternative. The lowest value obtained for the residual organic content on a wet basis was 0.32% by mass and specific energy of 0.58 kWh / kg.

For a constant value of specific energy, higher power results in higher heating rates which, in turn, decreases the removal efficiency of the organic phase. Moreover, the specific energy influences the olefin drying process in a positive way: the higher the specific energy, the greater the removal when considering a fixed initial content of olefin.

The dielectric loss tangent of the drill cuttings is directly proportional to the drilling fluid content. Besides that, the value of the loss tangent (greater than 0.1) ensures that the material is

heated under the application of microwaves even without the presence of the fluid.

Finally, the proposed kinetic model was coherent in the analysis of the microwave drying kinetics within the selected operational range. The regressions resulted in coefficients of determination between 0.984 and 0.998. Furthermore, the results obtained for the parameters of this model and its interpretation confirmed the trends observed in the results of the drying tests.

Acknowledgements

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