DECONTAMINATION OF DRILLED CUTTINGS BY MICROWAVE DRYING: KINETICS ASPECTS

\(^{a}\) Pereira, M. S.; \(^{a}\) dos Santos, J. M.; \(^{a}\) Barrozo, M. A. S.; \(^{a}\) Ataíde, C. H.\(^{1}\); \(^{b}\) Martins, A. L.

\(^{a}\) School of Chemical Engineering, Federal University of Uberlândia, Uberlândia – MG, Brazil

\(^{b}\) CENPES/PETROBRAS, Rio de Janeiro, Brazil

ABSTRACT

The discharge of cuttings contaminated with drilling fluid is one of the great problems faced by the oil industry nowadays. The search for alternative treatments for this residue is an imperative. In exploration areas of Brazil and the Gulf of Mexico, when synthetic fluids based on n-paraffin are used in drilling wells, the legal limit of hydrocarbons in drilled cuttings discharged offshore is 6.9% by mass. Presently, several technologies are being studied to ameliorate the problem, among them, the microwave drying technique. Based on these new research developments, this work investigates kinetic aspects of the use of microwave drying in the decontamination of drilled cuttings. The results show that the microwave drying of cuttings tends to occur in three phases. In Phase 1, the removal of moisture is much higher than that of the n-paraffin. In Phase 2, there is a significant removal of moisture and organic phase. In Phase 3, the residual moisture content is constant, whereas the organic phase remains removed. The extension of Phases 1 and 2 may increase the efficiency of the process. This can be achieved by lowering the applied power, increasing the cutting mass, and decreasing the control temperature of the system.

KEYWORDS

kinetic of drying; microwave drying; drilled cuttings; drilling fluid

---

\(^{1}\) To whom all correspondence should be addressed.
Address: School of Chemical Engineering, Federal University of Uberlândia, Av. João Naves de Ávila, 2121, Campus Santa Mônica, Bloco 1K, Uberlândia-MG, Brazil.
ZIP Code: 38408-100 | Telephone: +55343230-9400/ext. 764 | e-mail: chataide@feq.ufu.br
doi:10.5419/bjpg2015-0001
1. INTRODUCTION

The contamination of drilled cuttings by drilling fluid are generated constantly during drilling activities. Drilling fluids are used to maintain hydrostatic stability of the wells, to lubricate the column, to cool the bit, to keep the cuttings generated in suspension, and to carry these cuttings to the surface. Drilling fluids are classified basically into two categories: aqueous and non-aqueous. Among the non-aqueous are the oil-based and synthetic fluids (ASME Shale Shaker Committee, 2005).

Increasingly stringent environmental laws have stimulated researches on the decontamination of drilled cuttings. A primary separation of drilling fluid and drilled cuttings is done through the solids control system, involving the use of different equipments. However, the cuttings from this system still contains about 20% of fluid by mass. Therefore, an additional treatment is necessary to adjust the level of n-paraffin in the cuttings to comply with the current legislation. In areas in Brazil and the Gulf of Mexico, when synthetic fluids based on n-paraffin are used in drilling wells, the legal limit of hydrocarbons in drilled cuttings discharged offshore is 6.9% by mass (Pereira et al., 2014). The use of microwave heating as a promising alternative for cuttings decontamination has appeared in the last years (Robinson et al., 2009, 2010, 2012), motivating the present work.

In conventional heating systems the energy is transferred through conduction, convection, and radiation, or a combination of them. In microwave heating, energy is supplied directly to materials by molecular interaction with the electromagnetic field generated. Therefore, the elements or components of the material are heated individually and instantaneously, overcoming the limits imposed by material heat and mass transfer properties (Metaxas and Meredith, 1983).

A material can be characterized based on its dielectric properties. The two main ones are: dielectric constant (or relative permittivity) and dielectric loss factor. The first one is a measure of how much energy is stored in the material, whilst the second measures the dissipation of this energy as heat (Meredith, 1998; Clark et al., 2000). At 25°C and 2.45 GHz, the dielectric constant of distilled water and n-paraffin is about 77 and 2, respectively. Water is a material that heats up quickly in a microwave field, while the n-paraffin has little interaction with this (Meredith, 1998).

Microwave energy can penetrate the material directly through molecular interaction with the electromagnetic field, and provide a quick heating process at improved heating efficiencies, if compared with conventional techniques (Hu et al., 2013). When using a microwave for treating a mixture of materials with different dielectric properties, a selective heating could occur (Chan & Chen, 2002; Shang et al., 2006). This behavior should be observed in the microwave drying of drilled cuttings, since water is a dielectric material and n-paraffin is a transparent material.

In microwave drying systems, although the heating is differentiated (individual and instantaneous), the kinetics of microwave drying can be determined in the same way as in conventional systems (Tahmasebi et al., 2013). An important parameter to be considered in drying processes is the equilibrium moisture content. This is the moisture content at which the material is neither gaining or losing moisture. This, however, is a dynamic equilibrium and changes with relative humidity and temperature of the air drying (Mujumdar, 2006). In microwave drying, the equilibrium moisture is usually close to zero, because the microwave directly heats the water.

Li et al. (2011) have shown that the kinetics drying of water in the microwave process is similar to conventional kinetics drying. However, the drying rate achieved in a microwave oven is much higher than that achieved in conventional dryers (Giri & Prasad, 2007). It is expected that the n-paraffin also follows a conventional kinetics, but with different drying rates for water.

Mathematical models for drying kinetics are used increasingly in design, optimization, and control of industrial dryers. Numerous models for the description of the drying process are reported in literature to include theoretical, semi-theoretical, and empirical models. Many investigators have successfully used different thin layer equations available in the literature to explain the drying of a wide variety of products (Cai & Chen, 2008; Jayas et al., 1990; Midilli et al., 2002; Basunia & Abe, 2001; Yaldiz & Ertekin, 2001; Panchariya et al., 2002; Togrul & Pehlivan, 2003; Madhiyanon et al., 2009).
Empirical models are helpful in designing new, or in improving existing, drying systems. Thin-layer equations can contribute to the understanding of the heat and mass transfer phenomena, the computer simulations in the design of new processes, and the improvement of existing commercial drying operations (Pillai, 2013).

This work investigates the mechanism of removal of moisture and n-paraffin from contaminated cuttings using microwave drying. The knowledge of kinetics is important to guide the search for optimal operating conditions to the decontamination of drilled cuttings. The results show that water and n-paraffin follow a conventional kinetics of drying, but with different drying rates. Thus, microwave drying of cuttings is characterized by the combination of both kinetics of drying, which leads to a heating in three phases. From these data, some hypotheses have been investigated on the microwave drying process of cuttings.

2. MATERIALS AND METHODS

The material used in this work consists of drilled cuttings contaminated with synthetic drilling fluid collected at Petrobras onshore drilling rigs in Bahia, Brazil. The contents of n-paraffin and water in this material by mass are 8.3% and 9.8%, respectively. The drilling fluid used is a synthetic fluid called BRMUL— an emulsion of water in n-paraffin at the ratio of 45/55, respectively. Additives are put into the fluid to ensure the stability of properties such as density and viscosity. The specific mass of the drilling fluid used is 1.2 g/cm³. This is a yield-pseudoplastic fluid and exhibits time-dependent flow behavior. The cuttings’ Sauter mean diameter of the solids, measured by sieving, is 238 µm. The size distribution shows how large the range of the size particles is. The roundness of the particles indicates that most of the cuttings have a nearly circular projection (Pereira et al., 2014).

Dielectric constant and dielectric loss factor of the drilling fluid were measured at 2.45 GHz using a coaxial probe (85070E from Agilent) attached to a network analyzer. The data were compared with the properties of water and pure n-paraffin, as shown in Figure 1. The fluid dielectric properties showed intermediate values between water and pure n-paraffin. This is quite understandable, since the drilling fluid is a mixture of both.

The data from n-paraffin confirm that it is a material substantially transparent to the action of microwaves. Therefore, the drilling fluid heating by microwaves takes place mainly by heating its aqueous phase. Furthermore, it was observed that the properties of water have considerable sensitivity to temperature, which was not observed in the drilling fluid and pure n-paraffin behavior, at least within the studied temperature range.

![Figure 1. Dielectric properties of drilling fluid: Dielectric constant (a) and dielectric loss factor (b).](image-url)
The experimental unit consists of a microwave oven. The oven’s cavity had the following dimensions: 100 x 60 x 35 cm. There were 6 microwave sources with 1 kW of power each, working frequency of 2.45 GHz, an exhaustion system with a 1.5 HP suction fan, a condenser, and a data acquisition system. The microwave sources could be turned on and off separately, generating applied powers ranging from 1 to 6 kW. The steam temperature inside the experimental unit was monitored by a thermal resistance sensor (PT 100) and, to avoid degradation of the oil base, the temperature was controlled. The unit was sealed to exclude external air, even if there was suction (exhaustion). Figure 2 illustrates the experimental unit with its afore mentioned main components.

The unit control system allowed setting a reference temperature for the generated vapors. In the experiments, this temperature was 120°C and it was maintained at this level by an on-off control system. The operation of the microwave oven was automated and the parameters that can be modified by the operator were control temperature and heating time. The heating time corresponds to the total amount of time that the sample was exposed to the microwaves (time the sources were on). Because there were intervals where the sources were off, the heating time is less than the total operating time.

The retort method (API, 2005) was applied to measure the level of n-paraffin and water in the drilling fluid and in the dried cuttings. For this, a retort FANN of 50ml was used. This is a method used largely by oil industries and all concentrations are calculated by mass. The results obtained on a wet basis were converted to a dry basis.

Tests involving microwave drying of drilled cuttings were carried out. The vapors heating curves and the residual n-paraffin and moisture contents were evaluated. Ten experiments were conducted with drying times equal to 24 (Test 1), 36 (Test 2), 42 (Test 3), 48 (Test 4), 54 (Test 5), 60 (Test 6), 66 (Test 7), 72 (Test 8), 78 (Test 9), and 84 (Test 10) minutes. The parameters kept constant were: applied power (3 kW), mass of cuttings (6 kg), and control temperature (120°C). The heating curve of each test was monitored.

At the end of each experiment, the residual n-paraffin and moisture contents were evaluated in terms of moisture ratio (MR), as described by Equation 1:

\[
MR = \frac{X - X_e}{X_0 - X_e}
\]

(1)

Where, \(X\) is the moisture content at a specific time, \(X_0\) is the initial moisture content, and \(X_e\) is the equilibrium moisture. Generally, the kinetic models are used to describe the removal of moisture, but, in this study, they were also used to describe the removal of organic phase, because it is
the highest goal of cuttings decontamination. In this case, the n-paraffin ratio (NR) is expressed by Equation 2:

$$NR = \frac{Y - Y_e}{Y_0 - Y_e}$$  \hspace{1cm} (2)

Where, $Y$ is the n-paraffin content at a specific time, $Y_0$ is the initial n-paraffin content, and $Y_e$ is the equilibrium n-paraffin content. The equilibrium moisture content ($X_e$) was calculated from the results and the equilibrium n-paraffin content ($Y_e$) was assumed to be zero.

Among the several kinetic models reported in the literature two of them were chosen to describe water and n-paraffin removal: Page’s semi-empirical model and Henderson-Pabis index model. The parameters for these models were determined using a statistical software package for non-linear regression analysis of the n-paraffin and moisture ratio against drying time. These models, described in Table 1, were adopted based on the literature (Yu et al., 2011; Pillai, 2013; Tahmasebi et al., 2013), which showed good results for these models applied in the microwave drying of different materials. The parameters of the Page model are $n$ (dimensionless) and $k$ (s$^{-n}$), and the ones of the Henderson-Pabis model are $a$ (dimensionless) and $k$ (s$^{-1}$). In both cases, $k$ is the drying rate.

### Table 1. The equations of Page and Henderson-Pabis models.

<table>
<thead>
<tr>
<th>Models</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Page</td>
<td>$x = \exp(-kt^n)$</td>
</tr>
<tr>
<td>Henderson-Pabis</td>
<td>$x = a\exp(-kt)$</td>
</tr>
</tbody>
</table>

$x =$ MR or NR; $t =$ heating time.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Heating curves

The large difference between the boiling point of water and n-paraffin, as well as in their dielectric properties, indicates that the drying of these two substances occurs at different rates and starts at different temperatures. These features should influence the heating curve of microwave drying of drill cuttings investigated in this work. The boiling point of water is 100°C (1 atm) and it is highly dielectric, thus, it reacts instantaneously to the action of microwaves. The boiling point of n-paraffin is around 298°C (1 atm) and it has low dielectric constant, thus, it reacts slowly to the action of microwaves.

Figure 3 shows the heating curve of Test 1 and also the average heating curve of the others experiments. The control temperature adopted in the tests was 120°C, however, in Test 1, corresponding to 24 minutes of drying, this temperature was not reached.

All others experiments led to a period with control of the vapors’ temperatures. The main difference in these cases is the time of temperature control. The path until set point was reached had little variation between the tests, with an average standard deviation of 5°C.

The heating until the control temperature is achieved seems to take place in three distinct phases. The first, Phase 1, up to 10 minutes; the second, Phase 2, between 10 and 25 minutes; and the third one, Phase 3, from 25 minutes. Phase 1 is characterized by quickly heating. The level of drilling fluid removal during this period has not been studied, so it is not possible to affirm that fluid evaporation takes place in this phase.

However, a change in the heating curve slope from 10 minutes is significant, indicating a change in the drying process at this point. Since the slope decreased, it is understood that the drying rate increased. After 25 minutes, another change of slope could be observed on the heating curves indicating changes on the evaporation of drilling fluid.

These three stages are described as follows: the water begins to evaporate before the n-paraffin because it has a lower boiling point and a higher dielectric constant (Phase 1). Then, the n-paraffin
starts to evaporate along with the water, but at different rates (Phase 2). Finally, all water is removed and the n-paraffin remains evaporated until reaching the equilibrium (Phase 3). Thus, it is understood that water and n-paraffin are removed with different drying rates, and the combination of these two rates leads to a heating in three phases. In Phase 1, only water evaporates; in Phase 2, water and n-paraffin evaporate at different rates; and, in Phase 3, only n-paraffin is removed.

3.2 Kinetics aspects

The drying curves for microwave drying, in terms of moisture and n-paraffin, are shown in Figure 4. The observed behavior is similar to that showed in the literature (Shang et al. 2006), in which the cuttings decontamination using the microwave drying technique was studied with a few grams of cuttings and using an oil-based fluid. It is noteworthy that the removal of moisture is much
more intense than the removal of n-paraffin. The equilibrium moisture is reached in, approximately, 35 minutes. The water removal is practically invariable (falling drying rate), whereas the removal of the organic phase continues to increase significantly up to 80 minutes.

The drying curves of both water and n-paraffin show a conventional shape (exponential fall). Nonetheless, the water drying curve is much shallower, indicating that water removal is more intense in the first minutes if compared to the n-paraffin removal. This behavior is in accordance with dielectric properties and boiling point of water and n-paraffin, which are significantly different.

Considering the results on a wet basis, the time required to reduce the level of n-paraffin, under the legal limit established for offshore disposal of cuttings (6.9%), is less than 24 minutes. At 65 minutes, levels below 2% could be reached.

### 3.3 Kinetics models

Kinetic models are used to describe conventional drying. These models will be employed in this work to describe the microwave drying of water and n-paraffin. The n-paraffin ratio (NR) and the moisture ratio (MR), obtained from Equations 1 and 2, were adjusted according to kinetics drying models of Page and Henderson-Pabis. The parameters are shown in Table 2, as well as the correlation coefficient and p-value.

From the data presented in Table 2, considering only the correlation coefficient, the Page model is the one that best fits the moisture and the n-paraffin ratio. However, a more detailed analysis, taking into account the p-value, shows that Page model should not be used to describe the moisture removal. For a significance level of 5%, the parameter $k$ for the moisture ratio should not be considered (p-value > 0.05). Therefore, the Page model is the one that best describes organic phase removal while the Henderson-Pabis model is the

| Table 2. Parameters of kinetics drying models for n-paraffin and moisture ratio. |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
|                                  | n-paraffin ratio |          | Moisture ratio |          |
|                                  | Parameters | p-value  | Parameters | p-value  |
| Page                            | $k$        | 0.0033 ± 0.0013 | 0.1287 | 0.0042 ± 0.0025 | 0.0379 |
|                                 | $n$        | 1.4709 ± 0.1035 | 0.0000 | 1.8780 ± 0.1850 | 0.0000 |
|                                  | $R^2$      | 0.9933 |          | 0.9996 |
| Henderson-Pabis                 | $k$        | 0.0221 ± 0.0016 | 0.0000 | 0.0782 ± 0.0048 | 0.0000 |
|                                 | $a$        | 1.0554 ± 0.0559 | 0.0000 | 1.0026 ± 0.0230 | 0.0000 |
|                                  | $R^2$      | 0.9780 |          | 0.9974 |

Figure 5. Experimental moisture along with n-paraffin ratio and models adjustment.
one that best describes water removal. The moisture drying rate \( (k) \) obtained by the Henderson-Pabis model is almost three times higher than n-paraffin drying rate. This is a result of water being a highly dielectric component while n-paraffin is a slightly dielectric component.

Figure 5 shows the experimental n-paraffin (a) and moisture (b) ratio, and the models adjustments for both responses.

Notably, moisture and n-paraffin are removed at different rates. In 24 minutes the moisture ratio decreases from 1 to 0.2, while n-paraffin ratio decreases from 1 to 0.65. This disparity could be attributed to the large difference between the dielectric properties of these substances. From 35 minutes, the removal of the organic phase takes place, while the moisture ratio remains constant and equal to zero. Therefore, the equilibrium moisture of the system was achieved and the residual water cannot be removed anymore by the method applied. Nevertheless, it is observed that n-paraffin remains removed.

3.4 Discussion

The results showed that the removal of the organic phase keeps increasing with time of drying, though residual moisture content keeps constant. Yet, the n-paraffin has a low dielectric constant, being a material that has little interaction with microwaves. Therefore, it does not heat itself efficiently. In microwave drying of cuttings, the n-paraffin seems to be initially heated through conduction by the heated water. Moreover, the cuttings are also heated and should have a role in the heating of the organic phase.

Since the heated water seems to be the main source for heat in the organic phase, the permanence of the drying in Phases 1 and 2 (where the effective removal of water occurs) should increase drying efficiency. Phase 1 can be prolonged by slowing the heating rate during this period, which can be done in two ways: by increasing the mass of material or decreasing the power applied, as shown by Pereira (2013). For Phase 2, it is expected that a slow removal of water is promoted during this period by controlling the vapor temperatures at the start of this phase. Thus, the control of the vapor temperatures would be done in Phase 2, and the system would take more time up to enter Phase 3.

4. CONCLUSIONS

Based on the results presented, one can infer that the microwave treatment of drilled cuttings contaminated by synthetic fluid takes place in three phases. These phases are a result of the combination of n-paraffin and moisture drying kinetics. In Phase 1, there is no removal of organic phase. In Phase 2, both moisture and n-paraffin are removed, but the drying rate of water is greater. In Phase 3, the level of n-paraffin removal continues to rise while the level of moisture removal remains constant. In addition, both water and n-paraffin follow a classical kinetic behavior; however, their drying rates are significantly different. Their combination leads to heating in three phases, as explained above. The microwave drying process can be optimized extending Phases 1 and 2 (periods in which dewatering takes place). To extend Phase 1, lower power should be applied or a larger mass of cuttings should be adopted. To extend Phase 2, the control of vapor temperatures should be carried out.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided by PETROBRAS and CAPES.

5. REFERENCES


[http://dx.doi.org/10.1016/j.seppur.2005.08.012](http://dx.doi.org/10.1016/j.seppur.2005.08.012)

[http://dx.doi.org/10.1016/j.cherd.2013.06.013](http://dx.doi.org/10.1016/j.cherd.2013.06.013)

[http://dx.doi.org/10.1016/S0260-8774(02)00329-1](http://dx.doi.org/10.1016/S0260-8774(02)00329-1)

[http://dx.doi.org/10.1081/DRT-100103936](http://dx.doi.org/10.1081/DRT-100103936)