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Water content of a Brazilian refinery oil sludge and its influence on pyrolysis enthalpy by thermal analysis

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Abstract Residual oil sludges represent an environmental problem in the oil industry and need a proper destination in order to allow sustainable industrial processes when exploring natural resources. In the present paper, the influence of the water content on the oil sludge pyrolysis process was studied by thermal analysis. A method using thermogravimetry on calcined mass basis was developed to estimate the water content of oil sludges. The water present in the sludge vaporizes during the first thermal processing stage, interfering in the initial process of the organic components pyrolysis and increasing the total oil sludge pyrolysis enthalpy. By quantitative differential thermal analysis (DTA) it can be seen that the water content of the sludge may significantly affect the thermal balance of its industrial pyrolysis process.

Keywords Calcined mass basis · Oil sludge · Pyrolysis · TG/DTG/DTA · Water content

Introduction

Increasing efforts have been done to improve the management of industrial wastes. In oil refineries the generation of sludges from many processing steps is significant and they are classified as dangerous (Class 1) by the Brazilian Society of Standard Methods (NBR 10004), due to their high oil content. Recent studies [1–3] have shown that oil sludges may be converted thermally to lower molecular mass products with higher economic value. Usually thermogravimetry (TG) has been used to study this processes in the presence of some additives such as inorganic salts, oxides and catalyzers, aiming the highest conversion during sludge pyrolysis. Thermal analysis has proven to be extremely useful for the characterization of sludges and to obtain their thermal processing properties [4–8].

The pyrolysis and combustion of crude oils and oil shales has also been evaluated and studied by thermal analysis [9–12]. Pyrolysis studies are used to evaluate distillation or thermal cracking processes of their organic fractions [11, 13, 14]. Combustion studies are very useful to evaluate their use as energy sources for many applications, included in situ partial combustion processes, to increase heavy crude oil recovery from underground reservoirs [9].

Differently from crude oils, oil sludges may have high water contents, because they are a mixture of residual organic products stored with wastewater. One of the parameters that may or not allow the economical viability of its thermal conversion process, is the water content present in the oil sludge, which demands a high energy for its release during sludge pyrolysis. For the water content estimation, a procedure by thermogravimetry on calcined mass basis [15] was developed, by using the comparison of the analysis between a sludge sample and that of the product obtained after its lyophilization process. The procedure was also applied to the oil sludge after a natural partial dehydration process during its storage. By quantitative differential thermal analysis (DTA) [16] and using as reference the fusion enthalpy of a very pure standard indium sample, determined in the same operating conditions, it can be seen that the energy demand of the dewatering step during pyrolysis is significantly reduced from 1144 kJ/kg to 595 kJ/kg in the case of the partially dehydrated sludge, which shows how the water content of the

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Experimental

Materials

A Brazilian Refinery oil sludge sample (OS) was analyzed. A sample of this sludge was lyophilized at −40 °C and at 10^{-4} Torr vacuum pressure, which are internal laboratory standard operating conditions the authors use for lyophilization of oil sludge samples. The lyophilized sludge (LS) is a reference sample of same organic composition without water, to be used in the method to estimate the OS water content.

A part of OS sample, after being stored for 6 months, presented a separation of a water phase, by a natural de-emulsification process. The remaining sludge phase, denominated partially dehydrated sludge (PDS), differs from the original OS sample only in water content. It was used in the present paper as an example to show how, by using the developed method, one can analyze how much water can be separated by natural de-emulsification process. Before analysis, all samples were manually homogenized.

Thermal analysis

The thermogravimetric curves were obtained using a simultaneous thermogravimetry and differential thermal analysis TG/DTA TA Instruments equipment, model SDT2960. Prior to the experiments, temperature, base line and mass calibration runs were performed according to the suggested procedures of the manufacturer. The analyses were performed from 25 °C to 1000 °C. Duplicate analyses have shown maximum differences of 0.1% total mass loss, within this temperature range. A flow of 100 mL/min of nitrogen gas was used to assure the purge of released gases during the thermal analyses. A heating rate of 10 °C/min was used, which is a usual heating rate used for crude oil fractions pyrolysis thermal analyses [11, 14].

Fundamentals

The curves plotted by the software of a thermal analysis instrument are usually obtained on the basis of the sample initial mass (Mi). The TG curve plotted by the equipment used in the present paper shows, by default, the residual mass of a sample as a percentage of Mi, as a function of temperature. Thus, the residual calcined mass of the sample (Mc) at the end of the analysis (1000 °C) is a percentage of Mi. In the present case, DTG curve points represent percentual mass changing rates of Mi and DTA curve points, the difference between sample and reference temperatures ($T_s - T_{ref}$) divided by Mi.

When two samples (1 and 2) have different initial compositions, their TG, DTG and DTA curves, based on respective Mi_1 and Mi_2 initial masses, cannot be directly compared. However, if their respective calcined masses Mc_1 and Mc_2 have the same composition, thermal analysis curves obtained on respective calcined mass basis can be used to correctly compare the experimental data.

In this paper, for example, as all samples have the same calcined mass composition, OS and PDS samples, which have different water contents, were compared with the lyophilized sludge. By using the plotting tools of the equipment Universal Analysis software, the following procedure was used to obtain the corresponding TG, DTG and DTA curves on respective calcined mass basis:

I. From the TG curves based on respective initial sample mass basis, Mc_1 and Mc_2 at 1000 °C are measured (X_1% and X_2%). (*Note*: $Mi_1 = Mi_2 = 100\%$)
II. Then, all TG, DTG and DTA curve points on respective initial sample mass basis of both samples are divided respectively by $X_1/100$ and $X_2/100$.

The above procedure results in new TG_1 and TG_2 curves on respective Mc basis, where the new numerical values of the calcined masses of both samples is the same (100%) and those of the initial masses on calcined mass basis are, respectively $(100/X_1)$% and $100/X_2)$%.

Multiplying TG and DTG curves of samples 1 and 2 on respective calcined mass basis by $X_1/100$, one transforms all curves on sample 1 initial mass basis. This regenerates initial sample 1 thermal analysis curves on its initial mass basis and also allows one to obtain sample 2 thermal analysis curves on a same Mi_1 basis, as well as to proceed the quantitative comparison of both cases on an easier basis.

When sample 2 is a part of sample 1, its new initial mass on Mi_1 basis TG plot represents its content in sample 1 composition. As will be shown, this procedure was applied to compare the thermal analysis data of original sludge (OS) and the same sludge after its partial dehydration process and that of the lyophilized one to measure the water content of OS, which was lost during its lyophilization process and that of the partially dehydrated sample, in a same plot.

Results and discussion

Figure 1 shows TG and DTG curves of the original, partially dehydrated and lyophilized sludge on respective initial mass basis. The mass losses of these curves cannot be directly compared, because the initial composition of the samples is not the same (they differ on respective water content).

As the final composition after pyrolysis of the samples at 1000 °C is the same, Fig. 2 shows the corresponding TG and DTG curves on respective calcined mass, which allows a same basis of comparison. To have an easier and same composition basis, Fig. 3 shows respective TG and DTG curves on the original sludge initial mass basis.

From Figs. 2 and 3 it can be seen that, on any of these two same basis of comparison, after the initial water loss step of the original and partially dehydrated sludges, their DTG curves are practically the same than that of the lyophilized sludge one, indicating that during the continuous mass loss up to 950 °C, practically the same pyrolysis steps are occurring in the three cases. The mass losses occurring from 250 °C to 550 °C, may probably due to the presence of heavy gas oil residues, residual aromatics, resins and asphaltene [11, 13] and the mass losses at higher temperatures, to residues from atmospheric and vacuum distillation [13].

From Fig. 1, it can be seen that the residual calcined mass of the lyophilized sludge (LS) at 1000 °C ($M_{c,\ LS}$) is equal to 43.21% of its respective initial mass ($M_{i,\ LS}$), at the beginning of the analysis, which value is 100%, because this lyophilized sludge TG curve was plotted on $M_{i,\ LS}$ basis. From these data, one can calculate that the mass ratio $M_{i,\ LS}/M_{c,\ LS}$ is equal to 100/43.21 = 2.314. Note that independently of any basis on which the TG curve of the lyophilized sludge is plotted, this $M_{i,\ LS}/M_{c,\ LS}$ mass ratio will always be equal to 2.314. Thus, as in Fig. 2 the value of $M_{c,\ LS}$ is 100%, because its TG curve is plotted on $M_{c,\ LS}$ basis, the value of $M_{i,\ LS}$ is 231.4%.

From Fig. 1 it can also be seen that the mass ratio $M_{i,\ OS}/M_{c,\ OS}$, between initial and calcined masses of the original sludge (OS), is equal to 100/24.59 = 4.067. Thus, as in Fig. 2 original sludge TG curve is plotted on its calcined mass basis, the values of $M_{c,\ OS}$ and $M_{i,\ OS}$, on $M_{c,\ OS}$ basis, are respectively be 100% and 406.7%.

For the partially dehydrated sludge (PDS) sample, from Fig. 1 it can be seen that $M_{i,\ PDS}/M_{c,\ PDS}$ mass ratio is equal to 100/30.12 = 3.320 and in Fig. 2, $M_{c,\ PDS}$ and $M_{i,\ PDS}$ values, are respectively equal to 100% and 332.0%.

As calcined masses of OS, PDS and LS samples have the same composition, which is considered equal to a 100% reference mass in all cases in Fig. 2, this means that the initial masses of the original, partially hydrated and lyophilized oil sludges are proportional, respectively to 406.7%, 332.0% and 231.4%.

Figure 3 shows the TG curves of the three samples, plotted this time on a same OS initial mass basis. As the previous mass proportion has to be the same on any same basis of comparison, one can see that the initial masses of OS, PDS and LS samples are respectively equal to 100%, 81.64% and 56.91% of $M_{i,\ OS}$. On this basis it is more easy to deduce that the OS contains (100 − 56.91) = 43.2% of water and that PDS water content is equal to (81.64 − 56.91) × 100/56.91 = 30.3%.

The above results show that is possible to reduce the initial 43.19% of original sludge (OS) water content to 30.3% in the partially dehydrated sludge by a natural partial dehydration process during storage.

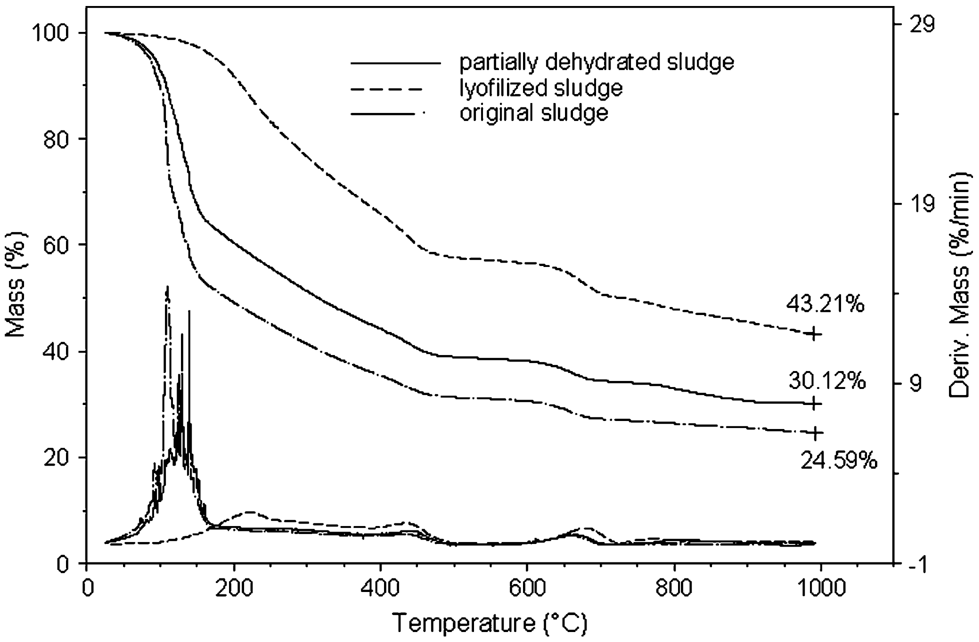


Fig. 1 TG and DTG curves of the refinery sludge samples with different water contents on respective initial mass basis

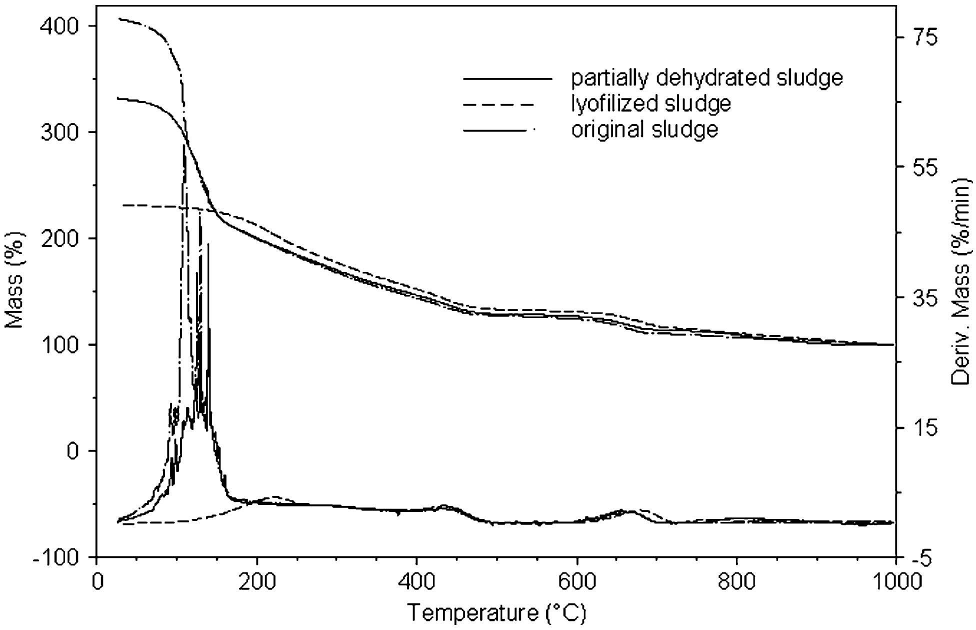


Fig. 2 TG and DTG curves of the refinery sludge samples with different water contents on respective calcined mass basis

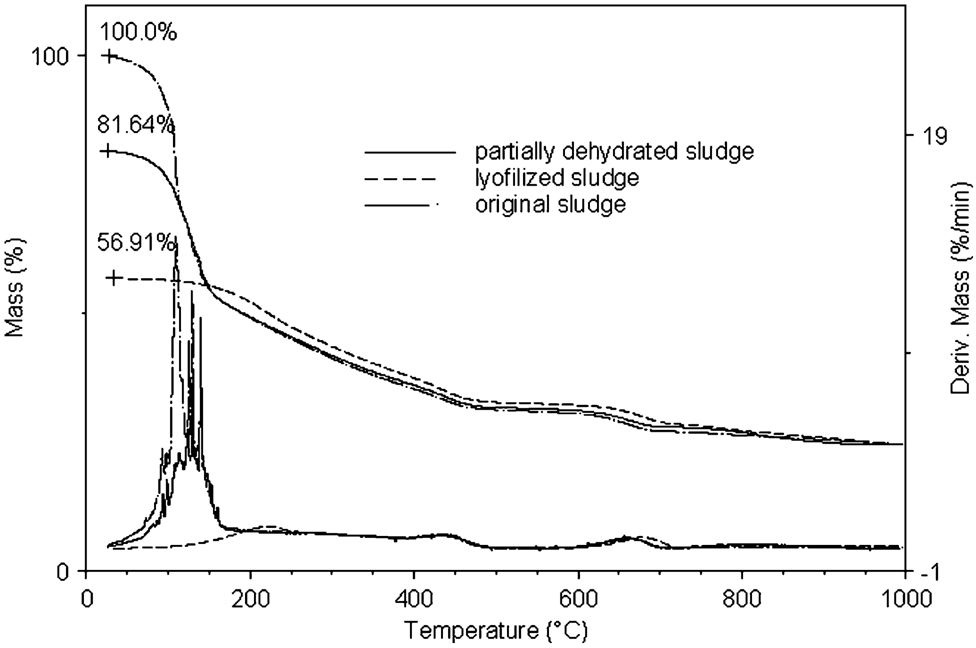


Fig. 3 TG and DTG curves of the refinery sludge samples with different water contents on original sludge initial mass basis

The water contents obtained for the original sludge (OS) by Karl Fischer determination were 38.01 and 45.44 mass%. These results are compatible with those obtained by the developed thermal analysis method as shown in the Fig. 1.

By quantitative differential thermal analysis (DTA) [16] and using the heat of fusion a pure standard indium sample, to obtain a conversion factor f_{In}, at the same operating conditions (10 °C min^{-1} and 100 mL min^{-1} N_2 flow) within the temperature range of water loss, it can be seen from Fig. 4, that the energy consumption during the first step of significant mass loss (mainly due to water loss), is significantly reduced from 1144 kJ/kg to 595 kJ/kg in the case of the partially dehydrated sludge. This confirms that significant water content was naturally eliminated from the original OS phase during the long-term storage.

The enthalpies of the three following pyrolysis steps, high temperature organics cracking, resin and coke formation [11], which occur between 350 °C and 950 °C as shown in Fig. 5, are due to the heavier organic components decomposition and transformation steps. For this temperature range, they were estimated by using a conversion factor f_{Al}, based on a pure aluminum standard fusion DTA peak area and respective heat of fusion.

Fig. 4 DTA curves of standard Indium sample and of OS and PDS samples, at the temperature range where the volatilization of water and of the lighter organics occur (original curves were shifted and sludge curves are on OS initial mass basis)

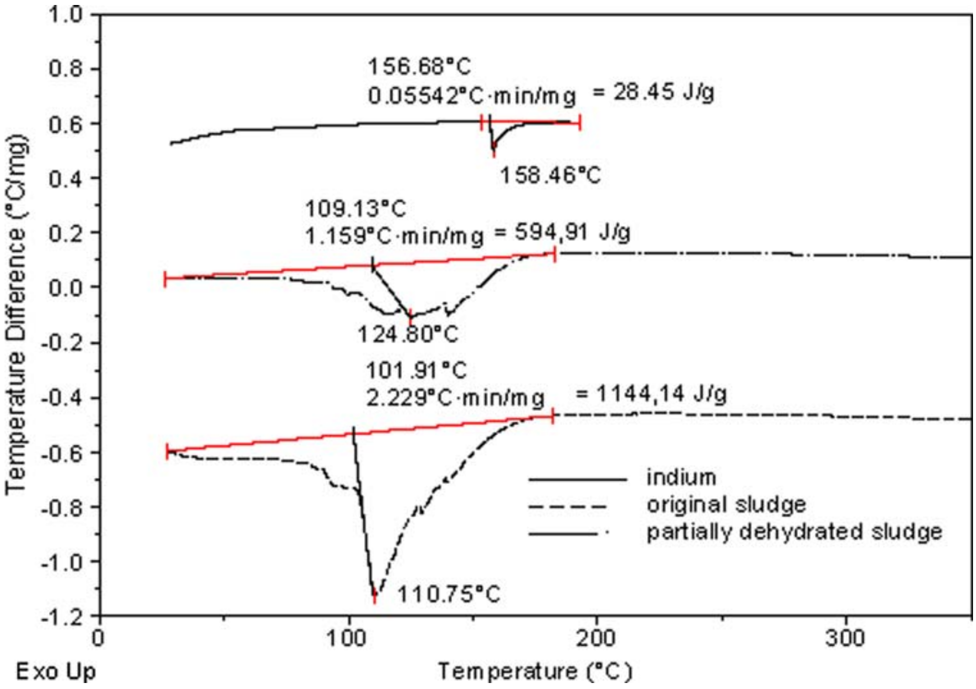
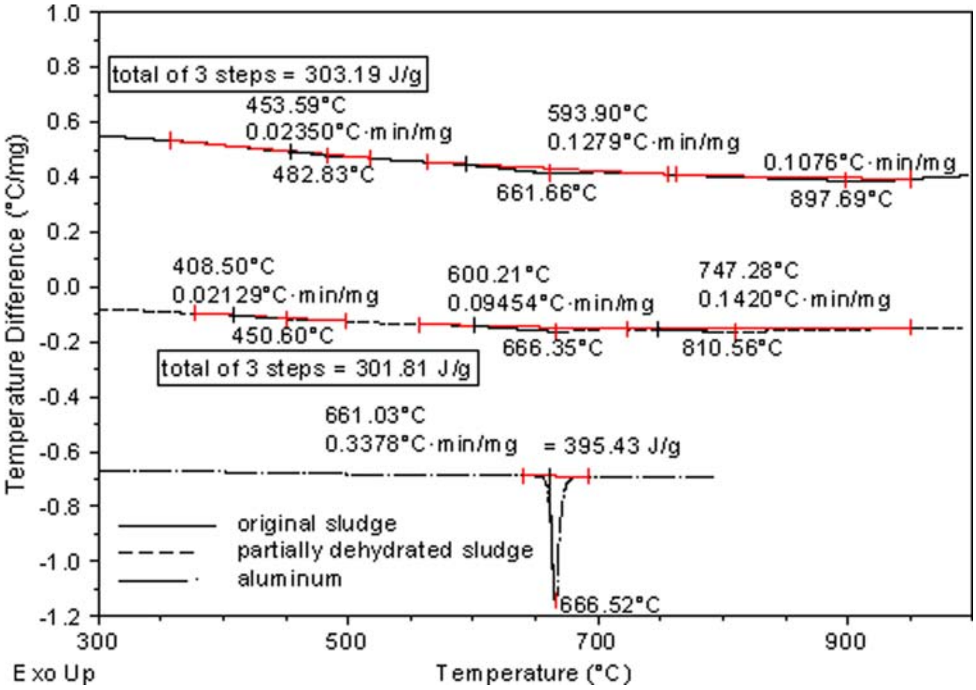


Fig. 5 DTA curves of standard aluminum sample and of OS and PDS samples at the temperature range where the pyrolysis of the heavier organic components occurs (original curves were shifted and sludge curves are on OS initial mass basis)



As shown in Fig. 5, the total estimated enthalpies for these steps, calculated on initial OS mass basis, are very similar in both cases (303.19 and 301.81 kJ/kg). The estimated enthalpies of each of the three main pyrolysis steps of the OS sample are 27.51, 149.7 and 125.96 kJ/kg due to the organic components pyrolysis, decomposition and transformation steps. For the PDS sample the estimated energy consumption of these steps are 24.92, 110.67 and 166.2 kJ/kg.

This confirms that during the long term storage natural dehydration process, practically all the organic components of the original sludge remain in the oil phase and shows that, the estimated energy needed to pyrolize the organic components is much lower than the energy needed to release the water present in the sludges as shown in Fig. 4.

Figures 6 and 7 show the equivalent DSC heat flow curves obtained from respective DTA curves of Figs. 4 and

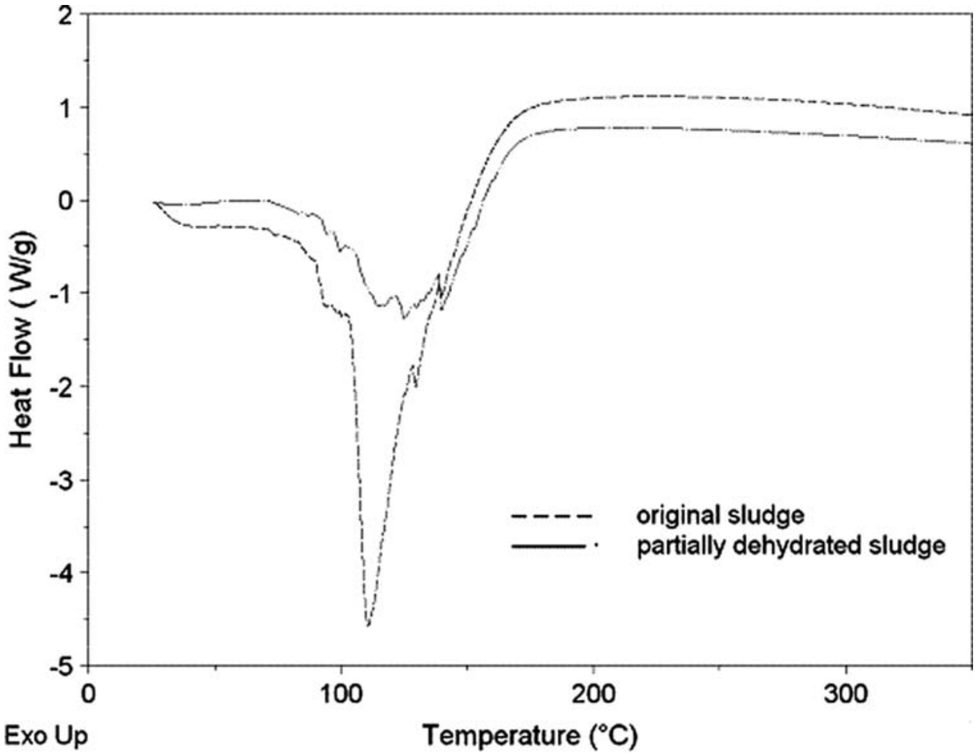


Fig. 6 DSC curves of OS and PDS samples on OS initial mass basis, for the initial water and low temperature organic volatilization steps

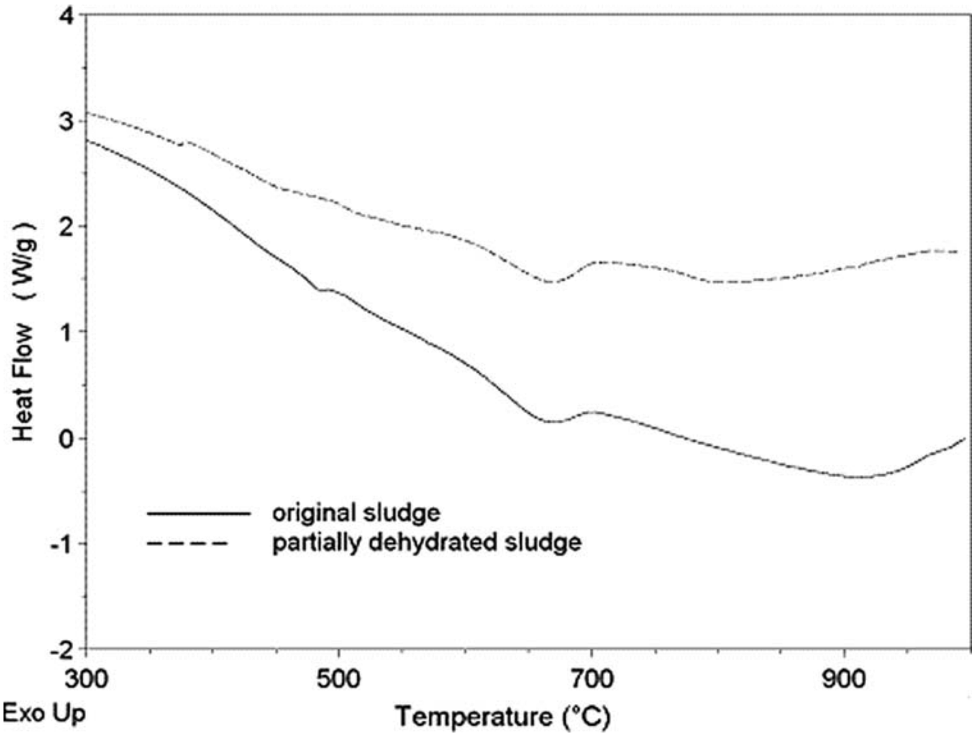


Fig. 7 DSC curves OS and PDS samples on OS initial mass basis, for the high temperature pyrolysis steps

5, by multiplying their differential temperature values by the respective transformation factors f_{In} and f_{Al}.

Conclusions

- The water content of oil sludges may be estimated from the TG curves of their original and lyophilized samples on calcined mass basis.
- This procedure can be useful to control the water content in industrial sludge processing.
- Higher water content increases significantly the energy consumption needed for the first thermal processing step of the sludge.
- The water content of oil sludges may significantly affect the thermal balance of their industrial pyrolysis processes.
- The partial natural dehydration process of the oil sludge, which may occur during long-term storage, can contribute to energy saving during pyrolysis.

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