

Thermogravimetric Investigation of the Influence of Colloidal Phase on the Processing Properties of Crude Oil Residues

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Résumé — Analyse thermogravimétrique de l'influence de la phase colloïdale sur les propriétés de traitement des résidus pétroliers — Un résidu pétrolier atmosphérique, un résidu de distillation sous vide, un résidu de viscoréduction, les fractions maltènes qui en sont séparées, des mélanges du résidu atmosphérique avec le résidu sous vide et un résidu de l'extraction surcritique du résidu sous vide, ainsi que des résidus mélangés avec des agents dispersants d'asphaltes ont été soumis à la thermogravimétrie, à trois vitesses de chauffage différentes. On en a déterminé les énergies d'activation pour la réaction de décomposition. L'énergie d'activation correspond à l'enthalpie de vaporisation, pour des températures inférieures ou égales à 400 °C, et à l'enthalpie de séparation, pour des températures supérieures à 400 °C. L'intensité des forces d'interaction, agissant entre la phase colloïdale dispersée et les composants du milieu de dispersion, en est déduite. On constate l'influence de la concentration de la phase dispersée ainsi que l'influence significative de la stabilité de celle-ci sur les résidus, et particulièrement sur l'enthalpie de vaporisation. Afin d'apprécier la stabilité des résidus, le point de floculation a été déterminé. Les dépendances de l'enthalpie de vaporisation obtenues se reflètent dans les produits de distillation, surtout pour une température de 300 à 400 °C. Elles s'expriment toutefois aussi dans le résidu ATG (analyse gravimétrique) à 500 °C. Ainsi la thermogravimétrie s'avère-t-elle être une méthode efficace de détermination d'importants paramètres du traitement des résidus pétroliers, prenant en compte l'influence de la phase colloïdale dispersée de ces mélanges complexes.
Mots-clés : résidus pétroliers, asphaltènes, stabilité colloïdale, thermogravimétrie, points de floculation, enthalpie de vaporisation.

Abstract — Thermogravimetric Investigation of the Influence of Colloidal Phase on the Processing Properties of Crude Oil Residues — An atmospheric residue, a vacuum residue, a visbreaking residue, the maltene fractions of the residues, mixtures of the atmospheric residue with the vacuum residue and the residue from the supercritical extraction of the vacuum residue as well as residues mixed with dispersing agents were investigated by thermogravimetry at three different heating rates. From that, the activation energies of the weight loss were estimated. At temperatures up to about 400 °C the activation energy corresponds to the evaporation enthalpy, above 400 °C to the cracking energy. Comparing the results the strength of the interactions between colloid disperse phase and the components of dispersion medium was evaluated. It was found that besides the content of colloid disperse phase its stability has a significant influence on the properties of the residues, especially on the evaporation enthalpy. The stability of residues was investigated by the flocculation point determination. The obtained dependencies of evaporation enthalpies are also reflected in the yields of distillates and in the thermogravimetric residues at 500 °C. Thermogravimetry proves to be an effective method for the determination of important parameters of processing of crude oil residues considering the influence of the colloidal character of these complex mixtures.

Keywords: crude oil residues, asphaltenes, colloidal stability, thermogravimetry, flocculation points, evaporation enthalpy.

INTRODUCTION

Crude oil residues are complex mixtures of different organic compounds characterised by the existence of a colloidal disperse phase. The formation of the colloidal disperse phase is based on the low solubility of the asphaltenes compounds which are insoluble in *n*-alkanes as *n*-pentane and *n*-heptane but soluble in toluene. The asphaltenes associate to crystallites as nucleus of colloid particles. The solvation of these nuclei by resins and other compounds determines the stability of the colloid particles and hinders the further aggregation.

The processing characteristics of crude oils are adversely influenced by the colloidal asphaltene phase. Depending on colloidal stability the colloidal phase is among other things the reason of fouling, coke formation and deactivation of catalysts, especially at the conversion of residues (Zou and Lin, 1994). Mixing of different products and the addition of dispersing agents are possibilities to stabilise the colloidal disperse phase and by that to improve the processing conditions.

But the effectiveness of such measures is difficult to assess, because the colloidal stability depends on different factors as the solubility parameters of asphaltenes and of dispersion medium (Laux *et al.*, 1997a).

Kopsch (1995) has shown that information on the processing behaviour of crude oils and crude oil residues at higher temperatures can be obtained by thermogravimetry analysis (TGA). Among other things it is possible to calculate the activation energy of evaporation and cracking examining both processes as first order reactions:



In this case the conversion is a function as described by Equation (2):

$$q \left(\frac{dx}{dT} \right) = A \left[\exp \left(- \frac{E}{RT} \right) \right] (1 - x) \quad (2)$$

where:

q rate of heating

x weight loss

A frequency factor

E activation energy

R universal gas constant

T temperature

Using the thermogravimetric curves from at least three test runs at different heating rates, *A* and *E* can be calculated on the basis of the method according to Flynn and Wall (1966). In the temperature region below 400°C the activation energy corresponds to the evaporation enthalpy at the thermogravimetric conditions; above 400°C activation energy is determined by the cracking enthalpy.

It was found that the activation energies depend on the interaction forces between the colloidal disperse phase and components of the dispersion medium, too (Laux and Kopsch, 1996; Laux *et al.*, 1998). In this way the influence of colloidal disperse phase on the processing behaviour of residues can be evaluated.

In this article the results of thermogravimetric investigations of different residues in dependence on the composition and the colloidal stability are presented and discussed.

1 EXPERIMENTAL

Three residues were chosen to investigate the influence of colloidal disperse phase on the thermogravimetric behaviour: an atmospheric residue, a vacuum residue and the atmospheric residue of the visbreaking product of the vacuum residue.

These residues were fractionated into asphaltenes, resins and dispersion medium according to Neumann and Wilkens (1974) by precipitation of the complete colloids with ethyl acetate. Afterwards, the resins were extracted by *n*-pentane and the asphaltenes by toluene. The asphaltenes were characterised by fractionation in three solubility classes according to Zenke (1989): asphaltenes were dissolved in boiling cyclohexane and subfractions were precipitated by stepwise addition of isooctane. At the cyclohexane/isooctane ratio 1:1 the low soluble fraction precipitated and at 1:2 the middle soluble fraction. The easily soluble fraction remains dissolved at this ratio.

Supercritical fluid extraction (SFE) was applied to prepare another subfraction of vacuum residue using CO₂ at 40°C and 14 MPa in the first step and CO₂ + isooctane as entrainer at 100°C and 30 MPa in the second step. The resulting extraction residue was enriched with aromatic and polar compounds in comparison to the vacuum residue.

The colloidal composition of the residues are given in Table 1.

TABLE 1
Colloidal composition of residues (wt%)

Residue	Atmospheric	Vacuum	Visbreaking
Dispersion medium	96.1	91.5	91.1
Resins	traces	traces	traces
Asphaltenes	3.2	8.2	8.9
Asphaltene subfractions			
Easily soluble	21.8	27.6	1.3
Middle soluble	22.0	15.5	0.4
Low soluble	56.1	56.4	97.0
Loss	0.7	0.3	0

Further information about the composition can be taken from Laux *et al.*, 1999.

Besides the original residues the following fractions and mixtures were subjected to thermogravimetry:

- the maltene fractions of residues;
- mixtures of the atmospheric and vacuum residues;
- mixtures of the atmospheric residue with supercritical extraction residue from the vacuum residue;
- mixtures of the atmospheric resp. the visbreaking residues with different amounts of two dispersing agents (one of phenolic basis, one of amine amide basis).

Thermogravimetry was carried out using the *TA Instruments* thermal analyzer 951. The sample size for the analysis was 8 to 10 mg. The heating rates were 5, 10 and 20 K/min at a stream of argon of 50 cm³/min. The kinetic parameters of evaporation and cracking were calculated by the *TA Instruments* software according to Flynn and Wall (1996).

The results of the thermogravimetric analysis of the *n*-alkanes with carbon numbers 18, 32, 44 and 54 were used to ascertain the correlation between TGA-temperature and normal boiling point and for the calculation of enthalpy of evaporation in dependence on the carbon number (Laux *et al.*, 1998). It was found that the correlation coefficients are analogous to those of Kopsch (1995).

The flocculation points of the products as the measure of colloidal stability were determined by a titration method as described in Laux *et al.* (1997a). A precipitant is added at constant rate to the solution of the petroleum product under intensive stirring. The titration is monitored by a light intensity meter. After flocculation onset the light intensity decreases and the maximum of the curve is defined as the flocculation point. In this case chlorobenzene was used as the solvent and isooctane as the precipitant. The concentration of the solution was 5 wt%.

On the basis of the flocculation point determination it was found that the Flory Huggins interaction parameter χ can be used as a criterion of stability (Laux *et al.*, 1997a, 1997b):

$$\chi = \frac{v_{dm}}{RT} (\delta_{as} - \Delta\delta - \delta_{dm})^2 \leq \chi_{crit} \quad (3)$$

where:

- χ Flory Huggins interaction parameter
- v_{dm} molar volume of the dispersion medium
- R universal gas constant
- T temperature
- δ_{as} solubility parameter of asphaltenes
- δ_{dm} solubility parameter of the dispersion medium
- $\Delta\delta$ correction term considering the influence of asphaltene solvation
- χ_{crit} critical Flory Huggins interaction parameter

The solubility parameters of asphaltenes δ_{as} were calculated by Equation (4) (Laux, 1992):

$$\delta = 16.55 + \left(0.00464 + \frac{3.2285}{n_c} \right) (z_{Ra} - 2) + \Delta\delta_{He} \quad (4)$$

According to Equation (4) the solubility parameter is a function of the hydrogen deficit z_{Ra} in relation to alkanes and of the carbon number n_c . z_{Ra} is calculated by Equation (5):

$$z_{Ra} = 0.5 (2n_c + 2 - n_H) \quad (5)$$

The value $\Delta\delta_{He}$ considering the influence of the heteroatom influence is obtained from Equation (6):

$$\Delta\delta_{He} = \rho \sum F_i \frac{y_i}{A_i} \quad (6)$$

where ρ is the density of the sample, F_i is the increment value, y_i is the content of heteroatom i and A_i is the atomic weight.

At the flocculation point can be accepted:

$$\delta_{fp} = \delta_{dm} \quad (7)$$

The average solubility parameters of the solvent-precipitant mixture at the flocculation point δ_{fp} was determined by Equation (8):

$$\Delta_{fp} = \Phi_s \delta_s + \Phi_p \delta_p \quad (8)$$

ϕ_s and ϕ_p are volume fractions, δ_s and δ_p the solubility parameters of solvent and precipitant.

The differences between the solubility parameter of low soluble asphaltenes and of solvent-precipitant mixture at the flocculation points are given in Table 2.

The small difference of solubility parameters of the visbreaking residue indicates the low colloidal stability of this product. The colloidal stability of the atmospheric and vacuum residues are nearly identical.

TABLE 2

Solubility parameters of the low soluble asphaltenes δ_{lsas} and of the solvent-precipitant mixtures at the flocculation point δ_{fp} and their differences in (MJm⁻³)^{0.5}

Residue	Atmospheric	Vacuum	Visbreaking
Δ_{lsas}	19.98	19.92	20.45
Δ_{fp}	15.21	15.23	16.16
Difference	4.77	4.69	4.29

2 RESULTS AND DISCUSSION

The comparison of the activation energies of the original products and maltenes (*Figs. 1 to 3*) shows that:

- at temperatures up to 375°C the original products have higher evaporation enthalpies than their maltenes. The difference increases with the asphaltene content;

– the influence of asphaltenes on the cracking energy is not significant.

The influence of colloidal stability is represented by the mixtures of the atmospheric and vacuum residues. In Figure 4 the activation energies (evaporation enthalpies) at different temperatures in the region from 300 to 375°C are displayed as a function of vacuum residue percentage. It is evident that the evaporation enthalpies show extreme dependencies. A similar behaviour was found for the mixtures of atmospheric residue and the residue of supercritical extraction (Fig. 5).

The flocculation points show a minimum only in dependence on the vacuum residue percentage (Fig. 6).

The thermogravimetric residues at 500°C as measure of the coke formation are shown in Figure 7.

The influence on the weight loss by evaporation at different temperatures is demonstrated by Figure 8. One can

conclude that the addition of the components of vacuum residue to the atmospheric residue may lead altogether to increasing distillate yield.

The addition of dispersing agents to the atmospheric and visbreaking residues produces the following results:

- the effects of the dispersing agents are more pronounced in the relatively unstable visbreaking residue than in the atmospheric residue;
- in the case of the visbreaking residue an extreme dependence of activation energies on the concentration of dispersing agent is found (Fig. 9). The corresponding flocculation points are shown in Figure 10;
- the TGA residues at 500°C are decreased by addition of dispersing agents (Table 3), but at higher concentrations the residue begins to increase again;
- the distillation yield was not significantly influenced by the dispersing agents.

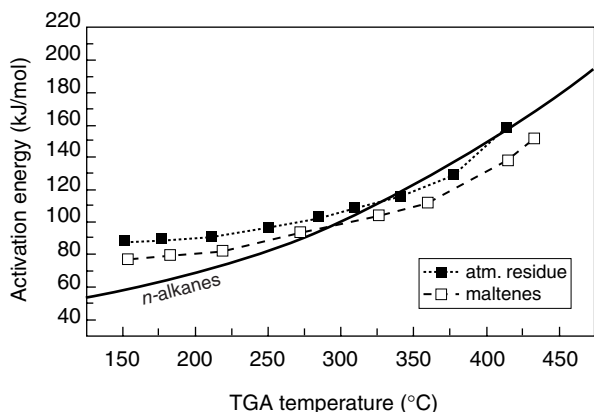


Figure 1
Activation energies of the components of the atmospheric residue.

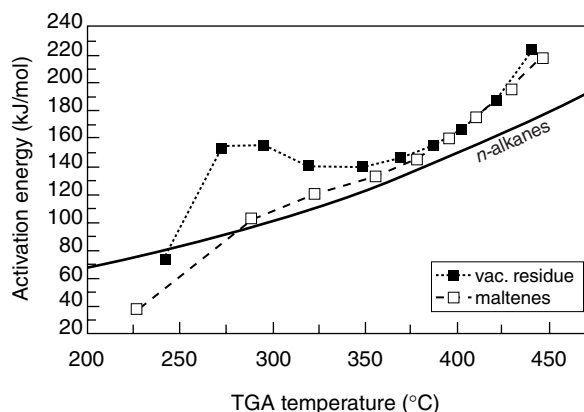


Figure 2
Activation energies of the components of the vacuum residue.

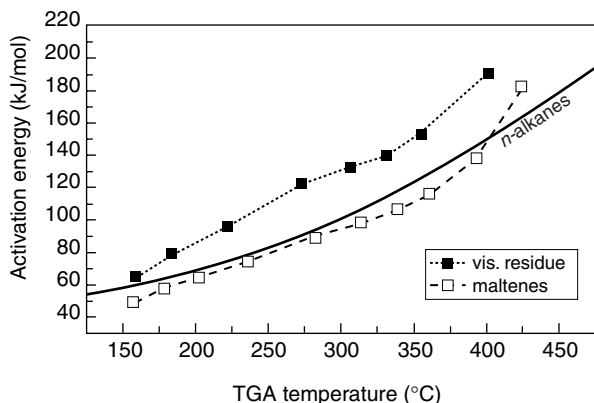


Figure 3
Activation energies of the components of the visbreaking residue.

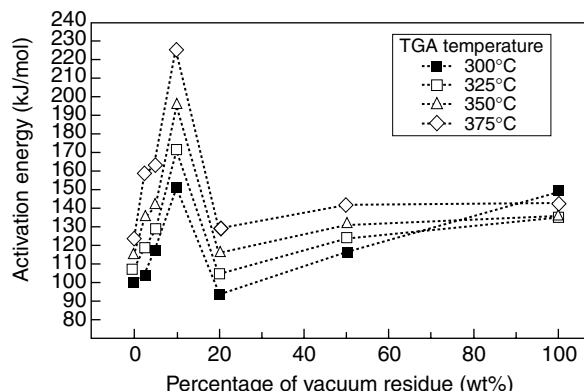


Figure 4
Activation energies of the mixtures of atmospheric and vacuum residues in dependence on the percentage of the vacuum residue.

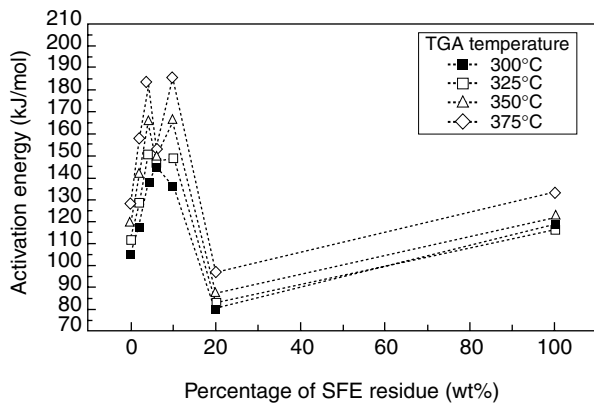


Figure 5
Activation energies of the mixtures of atmospheric and SFE residues in dependence on the percentage of the SFE residue.

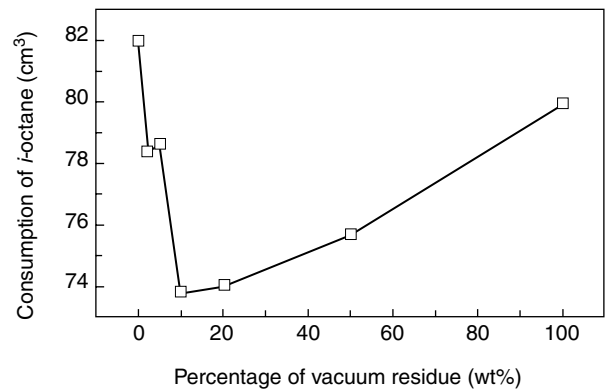


Figure 6
Flocculation points of the mixtures of atmospheric and vacuum residues.

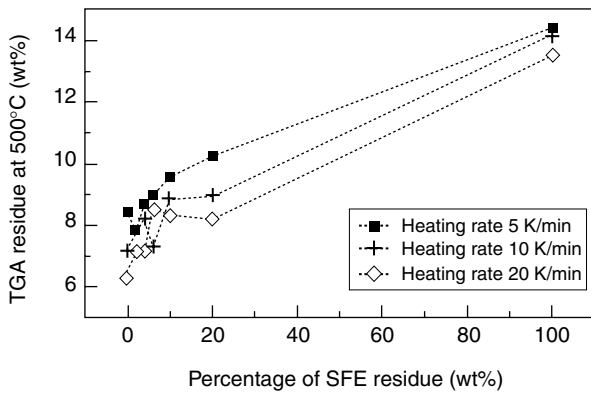


Figure 7
Dependence of the TGA residue at 500°C on the percentage of SFE residue in the mixture with the atmospheric residue.

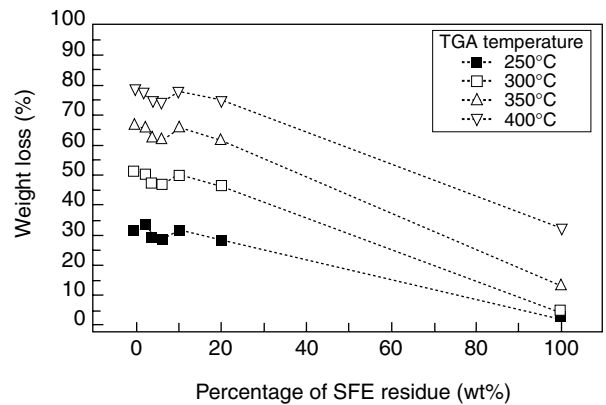


Figure 8
Yields of distillates in dependence on the part of SFE residues in the mixtures with the atmospheric residue.

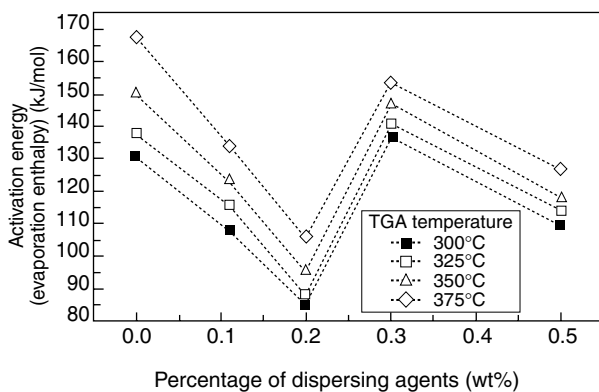


Figure 9
Activation energies of the components of the visbreaking residue in dependence on the dispersing agent concentration.

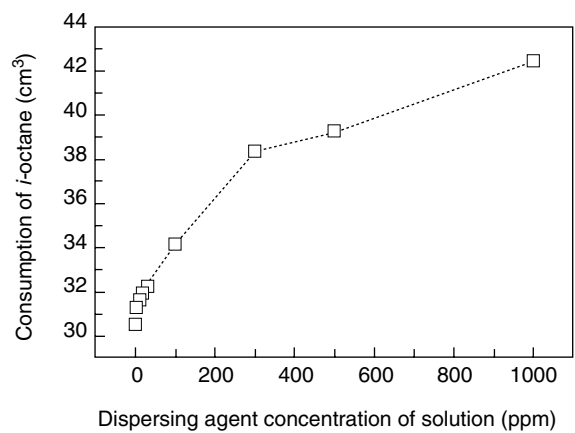


Figure 10
Flocculation points of the visbreaking residue in dependence on the dispersing agent concentration.

TABLE 3

Influence of the dispersing agents on the TGA residues at 500°C (wt%)

Dispersing agent	Concentration of dispersing agent (wt%)	Residue at 500°C of the	
		atmospheric residue	visbreaking residue
A	0	8.4	21.5
	0.1	6.9	16.0
	0.2		17.9
	0.3	7.0	16.8
	0.5	6.9	16.0
B	0.5	6.5	16.4
	1.0	6.8	17.5
	2.0	9.5	18.3

Since the difference of the activation energies of the crude oil residues and their dispersion media (maltenes) is a measure of interaction forces between the disperse phase and the components of the dispersion medium we may conclude.

The influences on these interactions are not additive when different crude oil residue products are mixed. Obviously the simultaneous variation of degree of aggregation and degree of solvation of asphaltenes leads to extreme changes. Hereby, a maximum of interaction is found if the flocculation point is minimal. This condition causes also decreased distillate yields and increased coke residues. Such behaviour was also found by Syunyaev *et al.* (1990, 1997) while investigating disperse crude oil systems.

The stabilisation by dispersing agents displays other results. In spite of continuously increasing stability the activation energy develops extreme. This behaviour indicates that the mechanisms of stabilisation by dispersing agents on the one hand and by solvation by petroleum components on the other hand have to be distinguished.

CONCLUSION

It has been shown that the thermogravimetry can be used to investigate the influence of the colloidal phase on the distillation and cracking behaviour of crude oil residues. This influence is exhibited for the activation energies, for the distillation yield and for the cracking residue at 500°C. The complexity of interactions is illustrated especially by the extreme dependence of evaporation enthalpies on the mixing of residues and on the additivation. Therefore, calculation methods for evaporation enthalpies as have been developed for hydrocarbon mixtures cannot be used in the case of crude oil residues (Laux *et al.*, 1998). The mixing of different crude oil residues and the addition of dispersing

agents need an experimental verification, which can be realised by thermogravimetry.

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