CRITICAL DESCRIPTORS FOR HYDRATE PROPERTIES OF OILS: COMPOSITIONAL FEATURES

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ABSTRACT

In petroleum production systems, hydrate morphology is observed to be influenced by the crude oil composition. This work is aimed at identifying which crude oil compositional parameters that need to be determined in order to evaluate natural anti-agglomerating properties of crude oils, i.e. the critical compositional descriptors. The compositional features of 22 crude oils have been studied, and multivariate data analysis has been used to investigate the possibility for correlations between several crude oil properties. The results show that biodegradation together with a relatively large amount of acids are characteristic for non-plugging crude oils, while excess of basic compounds is characteristic for plugging crude oils. The multivariate data analysis shows a division of the non-biodegraded oils, which are all plugging, and the biodegraded oils. In addition, the biodegraded oils seem to be divided into two groups, one with plugging oils and one with mostly non-plugging oils. The results show that the wettability can be predicted from the variables biodegradation level, density, asphaltene content and TAN.

Keywords: crude oil compositional features, multivariate data analysis, hydrate plugging tendency

NOMENCLATURE

GPC Gel permeation chromatography
PCA Principal component analysis
PLS Partial least square
TAN Total acid number
TBN Total base number

INTRODUCTION

Hydrates can cause problems in petroleum production lines, e.g. plugging of pipelines. Reliable physical models for prediction of hydrate formation are available [1]. However, these models do not describe the morphology of the hydrate particles, i.e. whether the particles agglomerate and grow into a plug or remain as a dispersion of small hydrate particles in oils. Some crude oils have been observed to have lower tendencies to form hydrate plugs in petroleum production lines than others when operated within the thermodynamic conditions for hydrate formation. Hence, the morphology of the hydrates is influenced by crude oil composition. The oils with low tendencies to form hydrate plugs probably contain natural inhibiting components that prevent hydrate plugging [2–6]. A possible mechanism for formation of a dispersion is adsorption of special compound types onto the hydrate surface, preventing the small hydrate particles from agglomerating into large plugs.

In a previous work [5], standard compositional parameters alone, like asphaltene content, and total acid- and base numbers, were found insufficient in describing the black oil hydrate behavior. Although
some properties are found to be more important than others, e.g. the acid profile, the complex chemical interplay between interfacial active components and bulk oil most likely excludes the possibility of identifying one single compositional parameter that explains the hydrate behavior for all crude oil systems. Acid fractions extracted from certain non-plugging crude oils were previously found to be able to alter hydrate behavior from plugging to non-plugging at operationally relevant PT conditions [7]. Other acid fractions, however, fail to do so, even though they too have been extracted from non-plugging oils. In order to develop a fundamental understanding of natural anti-agglomerating behavior of crude oils in terms of inhibiting mechanisms and critical compositional features, more knowledge of the interaction between the acid fraction and the bulk oil is crucial. Understanding these aspects is important for assessment of hydrate plug risk as well as for searching for ways to obtain non-plugging hydrate behavior through modification of the chemical composition of the system.

In this work, the wettability of freon hydrates in crude oil/brine emulsions is used to evaluate the plugging tendencies of crude oils [5]. Chemical characterization with special focus on the petroleum acids is performed. Multivariate techniques are utilized to find interaction effects among the parameters. The evaluation procedure for limiting the number of compositional parameters necessary for predicting the black oil hydrate behavior is described, and the critical descriptors are presented.

**MATERIALS AND METHODS**

**Materials**

The data set consists of 22 crude oils, spanning from heavy biodegraded oils enriched in asphaltenes to light non-biodegraded oils and condensates. Two of the oils were supplied by Chevron ETC and the rest by StatoilHydro ASA. The oils supplied by StatoilHydro have been investigated for several years, and published data have been assembled [5–11]. In this data set, the crude oils are marked with a letter, B - biodegraded oils and S - sweet, non-biodegraded oils, followed by a number indicating production field and a letter denoting different wells or different batches within one field.

**Experimental methods**

The crude oils are characterized with respect to the following properties and compositional features:

**Plugging tendencies in crude oil/water/gas systems**

In order to characterize whether a crude oil will have a tendency to form hydrate plugs or not, both field experience and laboratory tests performed at field conditions in a stirred, high pressure sapphire cell are considered [2, 5, 6]. In this paper, oils that form dispersed hydrates are termed non-plugging crude oils, and oils with high tendencies to form hydrate plugs are termed plugging oils.

**Wettability**

The wettability of freon hydrates in crude oil/brine emulsions is directly correlated to the plugging tendency of the crude oil, see Høiland et al. [5] for details of the emulsion method. In the emulsion method, phase inversion in oil/brine/hydrate emulsion systems is used for evaluating the wetting state of the system [12]. The wetting state, termed as "wettability" in this paper, is a direct measure of the expected morphology in terms of whether the hydrates generated in the system tend to agglomerate or not. The wettability is thus related to the anti-agglomerating behavior. The wettability parameter ($\Delta \phi^*$) is given as a number between -1 and 1, where large positive values are correlated to non-agglomerating systems, and non-plugging crude oils. Negative values and values close to zero are correlated to agglomerating systems, and plugging crude oils.

**Biodegradation level, density and asphaltene content**

The biodegradation level of the crude oils are determined using the Peters and Moldowan scale [13]. The densities of the crude oils are determined at 20 °C using an Anton Paar DMS60 densitometer connected to an Anton Paar DMA602HT measuring cell.

The amount of asphaltenes is found from refluxing a portion of the oil with 40 times excess of hexane for 6 hours, filtering through a Whatman
GF/F glass fibre filter, and solving the residue in dichloromethane:methanol 93:7.

**Titration: TAN and TBN**

A Metrohm autotitrator (model 798 MPT Titriino) connected to a Metohm Solvotrode combined LL PH glass electrode (model 6.0229.100) is used for the titrations.

The amount of titratable acids (TAN, total acid number) is determined by the standard method ASTM664-89 [14], and is defined as the amount (mg) of potassium hydroxide (KOH) necessary to titrate 1 g of sample to a well-defined inflection point.

The amount of titratable bases (TBN, total base number) is determined by the standard method ASTM2896-88 [15], with modifications according to Dubey and Doe [16], and is defined as the amount (mg) KOH necessary to titrate 1 g sample to a well-defined inflection point.

**Extraction of acids and analysis by GPC**

The acids have been extracted by the use of ion exchange material, as described by Mediaas et al. [17]. The molecular weights of the acid fractions have been determined by gel permeation chromatography (GPC). In this technique molecules are separated according to their size and shape, and standards with known molecular weights are used to make a calibration curve for determination of the molecular weight of the samples. More information can be found in Borgund et al. [9].

**Multivariate data analysis**

Characterization of crude oil is performed by many different analytical procedures, and correlations are sometimes found between two compositional parameters. In some cases a combination of several variables can correlate to other variables, and multivariate data analysis can be used to investigate how several variables affect each other at the same time. A systematization of a large data set in terms of internal correlations can in some cases reveal that approximately the same information can be obtained from fewer analyses.

**Principal component analysis (PCA)**

Principal component analysis is used to extract systematic information from large data sets [18]. The systematic variation in the data set can be described by principal components that describe common information in several variables. The first principal component (PC1) is a linear combination of the original variables that explains as much as possible of the variance in the data set. PC2 is a vector that explains most of the variance that is not explained by PC1, and that is orthogonal to PC1. PC3 can be extracted in the same way, and explains the variance that is not described by PC1 and PC2. Principal components can be extracted until all the variance in the data set is explained. However, the purpose of PCA is a reduction of variables, and two or three principal components are the optimal to extract for a data set [19].

The samples and the variables in a data set are projected in a plane defined by the principal components [20], see Figure 1.

![Figure 1: The samples in a data set are projected in a plane defined by the principal components, adapted from Wold [20].](image-url)
**Partial least squares (PLS)**

In the PLS technique one set of variables (X) is used to describe another set of variables (Y), e.g. only the information in X that is relevant for Y is used to explain Y [19]. From the calculations, a model that predicts results can be obtained.

Details of the statistical techniques can be found in the cited literature [18–21].

**RESULTS AND DISCUSSION**

**Review of previously reported data**

As mentioned above, acids extracted from crude oils have previously shown to hold inhibiting properties [5–7]. From the collected data set, a moderately high TAN value seems to be characteristic for non-plugging crude oils. However, not all the oils with high TAN values are non-plugging. In addition to the TAN value, the amount of extractable acids is important.

The biodegradation level has previously been shown to be important, in the sense that all the non-biodegraded oils are plugging and all the non-plugging oils are biodegraded. However, not all the biodegraded oils are non-plugging, so other factors must be considered (biodegradation seems to be a necessary, but not sufficient criterion for non-plugging crude oils) [5, 6].

Multivariate data analysis was also previously used on these oils, and the TBN value and the amount of asphaltene were shown to be characteristic parameters for the biodegraded, plugging crude oils [22]. Most of the biodegraded, plugging oils in this data set contain significantly more asphaltenes compared to the non-plugging oils.

The amount of bases relative to the acids was previously indicated as important [8]. From inspecting the collected data we find that most of the plugging oils have excess base (TBN is higher than TAN), and for the plugging, biodegraded oils the TBN number is significantly higher than the TAN value. In fact, for most of the non-plugging oils, the TAN value is higher than the TBN value (excess acid), see Figure 2.

**Evaluation of the plugging tendency of new oils**

In this present work, two new oils, B5a and B6a, have been characterized in the same way as the other oils. Both oils are found to be biodegraded, and thus from the current know-how, they might be non-plugging. Quite large amount of titratable acids are found in the oils, i.e. more than 2 mg KOH/g oil for both oils.

Both oils also contain a significant amount of extractable acids, but B5a contains considerable more extractable acids compared to B6a. From combining GPC analysis of the acids with TAN results, B5a is found to mostly contain compounds with one acid group, while B6a contains a high level of compounds with more than one acid group.

The TBN values of the oils are quite high, i.e. more than 2 mg KOH/g oil for both oils. A comparison with the TAN value shows that B5a has a small excess of acids, while B6a has an excess of bases. These results indicate that B5a is a non-plugging oil, and that B6a is a plugging oil, see Figure 2. However, it should be emphasized that the estimation of plugging tendency from this criteria alone is far from certain.

The amount of asphaltenes is clearly lower in B5a compared to B6a. This is another indication that B5a is a non-plugging oil and B6a is a plugging oil, see Figure 3.

**Results from multivariate data analysis**

The different crude oil properties are correlated with the plugging tendency by the use of multivariate data analysis in order to define critical descriptors for hydrate plugging.

A PCA (principal component analysis) plot of the data comprising both new and collected data from literature, is shown in Figure 4. A similar analysis was previously presented by Høiland et al. [22], although without the new oils. The different oil samples are shown in red (coded: B - biodegraded oils and S - sweet, non-biodegraded), and the variables in blue. The first principal component (x-axis) explains much of the variance in this data set (56.4 %). On this axis the biodegraded oils are separated from the non-biodegraded oils. All the biodegraded oils can be found to the right in the plot (inside dark-green square), and the non-biodegraded oils are found to
Figure 2: TBN subtracted from TAN for the crude oils. The black bars represent non-plugging crude oils and the grey bars represent plugging crude oils. The new oils, B5a and B6a, are marked with white bars.

the left in the plot (inside green square). The second principal component (y-axis) explains 26.4% of the variance in the data set. The biodegraded oils are separated into two groups on this axis. In the lower right corner of the plot plugging oils are found, and higher in the plot a group of B2 and B4 oils are found in addition to the B5a oil. Most of these oils are non-plugging. However the B4b oil have tendencies to form hydrate plugs. The wettability seems to be an important parameter for the non-plugging crude oils, while the amount of asphaltene (Asph.cont) and the base number (TBN) seem to be important for the plugging, biodegraded crude oils, corresponding to results previously presented by Høiland et al. [22]. The oil B5a is situated amongst the non-plugging crude oils, and the B6a oil is situated with the plugging, biodegraded crude oils. The variable TAN-TBN (the TBN value is subtracted from the TAN value) is found in the same direction as the wettability variable, but does not seem to have a direct correlation with any of the other variables.

The results from the multivariate analysis show that a high total base number and large amount of asphaltenes are indicative of plugging systems. However, low amount of bases and asphaltenes do not directly correspond to non-plugging systems. In order to separate the non-plugging oils from plugging biodegraded oils with low amounts of asphaltenes (B2 and B4 oils, in top circle) more information is needed.

Figure 3: The amount of asphaltenes in the biodegraded crude oils. The black bars are non-plugging oils and the grey bars are plugging oils. The new oils, B5a and B6a, are marked with white bars.

Selected variables are used to make a regression model (PLS analysis), in which the wettability is predicted from other variables. The variables biodegradation level, density, asphaltene content and the TAN value, are used for predicting the wettability, see Figure 5. Only 13 samples are used for this regression model, because the other samples lack data for the wettability or a reliable value for biodegradation.

The R value for the regression equation (R = 0.808) is not very good, but a clear trend can be seen from the plot in Figure 5. The analysis indicates that biodegradation level, density, asphaltene content and the TAN value are important variables for the wettability of a system, and hence the plugging
tendency. It is unexpected that the density is important for the wettability of the system. The density values for the different oils alone do not reveal any correlation with plugging tendency. Thus, the variables must be combined in order to obtain a prediction of the plugging tendency of crude oils.

For a validity check, the oil B4a was removed from the data set, and a new model for prediction was made. The wettability of the oil was predicted from the new model, and a value of 0.32 was obtained compared to 0.35 which is the measured value. The same was performed with the oil Sb2, and the predicted value was -0.06 compared to the measured value at -0.12. The model did not give a good prediction for the B4b oil. Thus, the model might not be very adequate for biodegraded oils with relatively

Figure 4: A PCA plot of all the samples (red) and the variables (blue). The non-biodegraded oils (plugging) are found in the small green square to the left, and the biodegraded oils are found in the large dark green square to the right. The biodegraded oils are separated into two groups: circle in the lower right corner - plugging oils and higher circle - mostly non-plugging oils.

Figure 5: Predicted versus measured for the wettability, based on 13 samples (PLS analysis). The wettability is predicted from using biodegradation level, density, asphaltene content and the TAN value. The regression model equation is omitted due to restriction from industry partners.
low amounts of asphaltenes. By using the model for prediction of the wettability, the B5a oil is predicted to 0.30, which indicate an oil-wet system and non-plugging tendencies. B6a is predicted to -0.19, which indicate a water-wet system and plugging tendencies. The accuracy of the prediction is yet to be verified.

To summarize, the results from the multivariate analysis give a group with plugging, biodegraded oils. The oil B6a can be found in this group. This oil also obtain a negative value of wettability from the prediction model. Thus, this oil is most likely a plugging oil. The B5a oil is situated in a group in the PCA-plot that mostly contain non-plugging, biodegraded oils. The prediction model also gives a positive value, indicating a non-plugging oil. However, this group in the PCA-plot also contains a plugging oil, which was predicted wrongly by the prediction model.

CONCLUSIONS
The plugging tendency of crude oils can be predicted from information of the composition of the oil. Biodegradation and moderately high amount of acids seem to be necessary for non-plugging crude oils. An excess of acids relative to the bases in the crude oil (TAN - TBN), as well as low amount of asphaltenes for biodegraded oils, also seem to be important for having non-plugging systems. The PCA analysis confirmed that large amounts of basic compounds and asphaltenes are connected with plugging, biodegraded oils, and that the non-plugging oils are connected with the wettability parameter.

From regression analysis it is shown that in most cases it is possible to predict the wettability of crude oils, based on the variables biodegradation level, density, asphaltene content and the TAN value.

ACKNOWLEDGMENTS
StatoilHydro and Chevron ETC are acknowledged for funding and permission to publish data. The Norwegian Research Council, the Petromaks program, is thanked for funding. The HYADES project group consists of experienced research personnel from both university, research institution and industry, that actively participates in planning of activities and discussion of results. The in-kind contributions from both university and industry partners are of essential value for the quality of the project, and are thus highly appreciated. The project group consists of the following persons:

- SINTEF Petroleum Research: Roar Larsen, David Arla, Sylvi Høiland, and Jon Harald Kaspersen.
- University of Bergen: Tanja Barth, Alex Hoffmann, Pawel Kosinski, Anna E. Borgund, Guro Aspenes (PhD student), Boris Balakin (PhD student), Ziya Kilinc (MSc student), and Håkon Pedersen (MSc student).
- Chevron ETC (Houston): Ramesh Kini, Lee Rhyne, and Hari Subramani.
- StatoilHydro: Per Fotland and Kjell M. Askvik.

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