WAX PRECIPITATION IN CRUDE OIL BY COUTINHO MODEL BASED ON CONVENTIONAL GAS CHROMATOGRAPHY DATA

PRESIPITASI WAX DALAM MINYAK BUMI DENGAN MODEL COUTINHO BERDASARKAN DATA KROMATOGRAFI GAS KONVENSIONAL

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ABSTRAK

Presipitasi wax dalam minyak bumi dapat menyebabkan berbagai masalah dalam operasional produksi dan transportasi. Kunci dalam menghindari dan mengatasi masalah flow assurance terkait wax adalah kemampuan untuk memprediksi presipitasi wax. Di antara model termodinamika yang lazim digunakan untuk memprediksi wax, model Coutinho dapat diterapkan dengan menggunakan data laboratorium yang terbatas, tetapi hasilnya cukup akurat. Sebagai input, model tersebut membutuhkan data distribusi n-parafin, yang umumnya ditentukan melalui analisis kromatografi gas temperatur tinggi (HTGC). Lemigas memiliki database lengkap minyak bumi Indonesia, termasuk data kromatografi gas konvensional (bukan HTGC). Dalam makalah ini, distribusi n-parafin diperluas dengan melakukan ekstrapolasi dan normalisasi terhadap data kandungan wax total. Distribusi prafin tersebut kemudian diaplikasikan ke dalam model Coutinho untuk memprediksi presipitasi wax pada sebuah sampel minyak bumi. Hasilnya, WAT yang dihasilkan dari model berselisih hanya 2C dari data DSC. Hasil prediksi jumlah wax yang terpresipitasi sepanjang temperatur juga dinyatakan valid terhadap data DSC.

Kata kunci: kromatogrfi gas, model Coutinho, presipitasi wax

ABSTRACT

Wax precipitation in crude oils can produce problems in oil production and transportation operations. Prediction is the key of avoidance or remediation of the wax problem of flow assurance. Among the wax prediction thermodynamic model, Coutinho model can be run using limited laboratory data, but the result is comparably accurate. The model requires n-paraffin distribution, which commonly determined by high-temperature gas chromatography (HTGC) analysis. However, only few laboratories could perform the HTGC. Lemigas has abundant database of crude oil with conventional gas chromatography data. An extended n-paraffin distribution was calculated based on the conventional GC data by performing extrapolation and normalization to total wax content. The n-paraffin distribution was applied in Coutinho model to predict wax precipitation of a crude oil sample. The WAT obtained from the model deviated only 2°C from DSC data. The result was also valid to DSC data in term of precipitated wax amount along temperature range.

Keywords: *Coutinho model, gas chromatography, wax precipitation*

I. INTRODUCTION

With the on-going trend to heavy oil and deep water developments, flow assurance has become a major technical and economic issue. The avoidance or remediation of wax problem is one key aspect of flow assurance. Wax precipitation in crude oils can produce problems in production and transportation operations.

Due to the high melting point and low solubility of these compounds, they precipitate from the crudes as they cool down to ambient temperature. The temperature where wax crystals start to appear is called wax appearance temperature (WAT). When temperature goes down below the WAT, the flow behavior of crude oil changes to non-Newtonian, therefore increase the pumping energy. Wax crystals can also precipitate on pipeline wall creating solid deposit that then narrowing the inner diameter. Wax crystals grow as the temperature decreases further, creating crystalline net, which begins to trap the crude until it cannot flow (called as pour point). All above wax behavior can occurs at tropical ambient temperature such as in Indonesia.

Pipe blockage due to wax has enormous technical and economic implications. When this happens, it takes technical effort is not easy and very expensive, while production should stop. Anticipation of wax deposition prevention is more advanced than remediation. The key to preventing the occurrence of precipitation is the ability to predict the condition of the formation of wax.

The wax prediction can be taken by using a thermodynamic approach. Modeling of wax precipitation is quite complicated because it involves solid-liquid phase equilibria in the multi-component system of petroleum. A number of engineering models have been proposed for calculating oil-wax equilibria, for example the work of Won[1], Hansen *et al.*[2], Erickson *et al.*[3], Pedersen [4], Rønningsen et al. [5], and Lira-Galeana *et al.*[6] and Coutinho[7].

Coutinho and co-workers have developed a wax model that is directly based on high-quality laboratory data for the properties of liquid and solid hydrocarbons and their mixtures. Coutinho went on to show that the model accurately predicts the waxing behaviour of diesel fuels, jet fuels[8] and crude oils[9]. Physical and thermodynamic properties are provided; therefore the Uniquac based model can be applied when laboratory data is limited.

At minimum condition, the model requires simply the n-paraffin distribution and a single bulk characteristic (i.e. molecular weight)

The n-paraffin distribution is commonly determined by high-temperature gas chromatography (HTGC) analysis. HTGC operates at severe temperature up to 425°C, requires special column and conditions. Only few laboratories could perform the HTGC analysis.

In other hand, Lemigas has abundant database of Indonesian crude oils with conventional GC data. A conventional GC operates at up to 325°C, thus has deficiencies compared with HTGC in term of analyzing wax that has high molecular weight.

This paper will propose a utilization of conventional GC data into Coutinho model to predict wax precipitation in crude oil. The result will be validated with wax precipitation data obtained from differential scanning calorimetry (DSC).

II. EXPERIMENTAL

A. Crude oil physical properties

The sample that was used in this work came from Java Island, and named as Crude A. Crude A is selected because of its characteristic as light-paraffinic crude oil.

A series of laboratory test was performed to describe the physical properties of crude sample. The tests are density (ASTM D-4052), pour point (ASTM D-5853), kinematic viscosity (ASTM D-4052), average molecular weight (ASTM D-4052), wax content (IFP alkyl-ether) and Hempel distillation.

B. Gas Chromatography

The experiment was carried out in a Agilent 7890A chromatograph, equipped with a HP5 column 30 m long, 0.32 mm internal diameter, and 0.25 μm thick stationary phase. For detection, a flame ionization detector (FID) with a flame of air and hydrogen at a temperature of 350°C was used. The method is based on the ASTM D-2887 analysis. The samples were directly injected on column. The carrier gas used was helium, with a flow of 1 mL/min. The initial temperature of the column oven is 35°C, and it is heated to 300°C using a rate of 10°C/min. Then temperature remains constant for 78 min. For calibration of the retention times a standard n-paraffin mixtures were used: a mixture of C5 - C14 n-paraffins from Analytical Controls.

C. Differential Scanning Calorimetry

Oil sample to be analyzed were heated to 80^{o}C in closed containers and shaken thoroughly to ensure complete dissolution of precipitated solids. About 10 mg of sample was put into aluminum pan, covered, and then pressed to be a capsule. The closed sample capsules were heated to 80°C for 10 min to check for leakage by visual inspection before being placed in the sample holder for analysis.

The analysis was performed using a Shimadzu DSC 06A. Liquid N2 was used to cool the sample and reference temperature to -140°C, and left for 10 minute before heating. In heating scan the temperature program started at -140°C and proceeded with a +3°C/min gradient to +60°C. Calorimetric signal was recorded at interval of 5 seconds. A thermogram curve of heat flow vs temperature was obtained.

III. MODELING

Coutinho introduce a thermodynamic model concerning on the non-ideality of n-alkane solid solution and using correlations to simplify input data. The solid-liquid equilibrium is related to melting and crystal transition properties, expressed as Equation 1.

$$ln\frac{x^s\gamma^s}{x^l\gamma^l} = \frac{\Delta H_{fus}}{RT_{fus}}\left(\frac{T_{fus}}{T} - 1\right) + \frac{\Delta H_{tr}}{RT_{tr}}\left(\frac{T_{tr}}{T} - 1\right) \qquad (1)$$

Using the heats and temperature of phase transition available in the literature, the composition and the size of the phases in equilibrium can be calculated as a function of the temperature provided that models for the non-ideality of the solid and liquid phases are available.

Liquid phase was considered as ideal, meanwhile the solid phase non-ideality was described by modified Uniquac equation.

$$\frac{g^E}{RT} = \sum_{j=1}^{n} x_i ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2}\sum_{j=1}^{n} q_i x_i ln\left(\frac{\theta_i}{\phi_i}\right) - \sum_{j=1}^{n} q_i x_i ln\left[\sum_{j=i}^{n} \theta_j exp\left(\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT}\right)\right] \qquad (2)$$

with

$$\phi_i = \frac{x_i r_i}{\sum_{i=j}^{n} x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_{i=j}^{n} x_j j_j} \qquad (3)$$

Parameter r and q are respectively van Der Waals volume and area, which can be correlated to number of carbon atom in n-alkane:

$$r_i = 0.1C_{ni} + 0.0672 \qquad (4)$$

$$q_i = 0.1C_{ni} + 0.1141 \qquad (5)$$

The pair interaction energies between identical molecules are estimated by relating them to the heat of sublimation from the orthorhombic crystalline phase of the pure component

$$\boldsymbol{\lambda_{ii} = -\frac{2}{z}\left(\Delta H_{sblm_i}\right) - RT} \qquad (6)$$

where Z is the coordination number (6 for the n-alkanes orthorhombic crystal). The unlike pair interaction energy is given by

$$\lambda_{\boldsymbol{ij}} = \lambda_{\boldsymbol{jj}} \qquad (7)$$

where j is the n-alkane with the shorter chain of the pair ij.

Flash algorithm is required to solve such multi-component equilibrium equation. The calculation, which involves n x n matrix, was carried on using MS Excel. Macro Visual Basic script was compiled to solve the iteration of flash calculation.

IV. RESULT

A. Crude oil physical properties

The physical property of Crude A was described in Table 1. The crude is categorized as light-paraffinic oil due to its 41.4 °API Gravity and 12.2 K_{UOP} Factor. Although it is light oil, Crude A has quite high wax content, 14.08%w. Crude A is liquid at room temperature because the pour point is 24ºC.

B. Gas Chromatography

Chromatogram of Crude A (Figure 1) shows the n-paraffin distribution up to n-C38. To look closer at n-C20+, there is an ascending trend from C20 to C26. A descending trend is found at above C26. This is typical pattern for most of light to heavy crude oil in LEMIGAS' database. For condensate and very light crude, the trend is usually straightly descending without any ascending part.

For Crude A, reversal of the trend is occurred at n-C26. This reversal point varies in different crude, depend on its characteristic. Typically, the heavier is the crude, the higher is the reversal point.

As described previously, there is a limitation of conventional GC in detecting hydrocarbon greater than C40. Therefore,

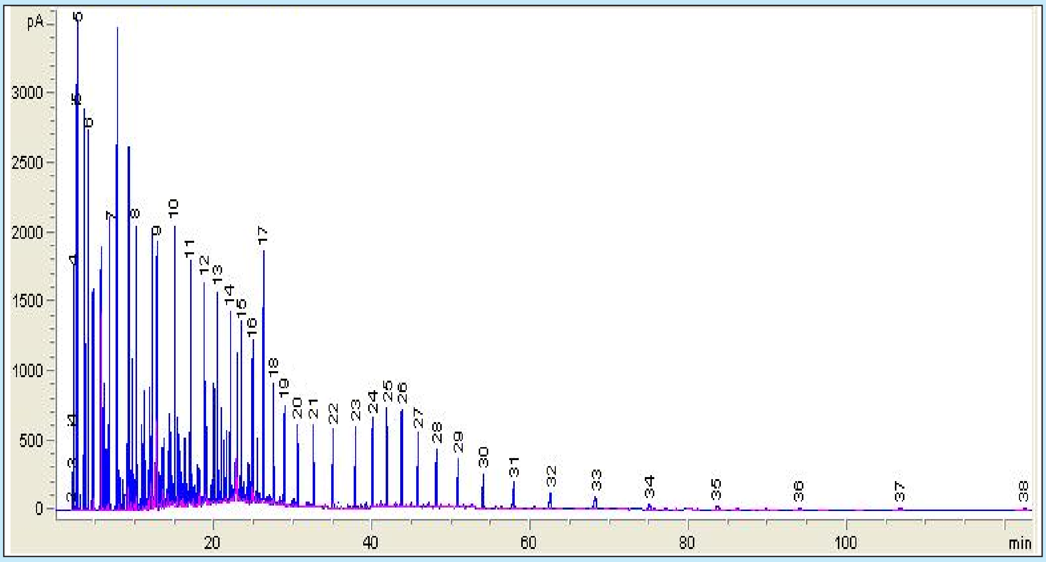

Figure 1
Chromatogram of Crude A

it is necessary to define the C40+ composition by extrapolation.

The decay of the n-alkanes in oils is an exponential decay[9,10]. Factor α will be defined here as the ratio between the mass fractions of two neighbor n-alkanes (eq. 8). The factor is used to determine the further composition of n-alkanes until a defined insignificant value.

$$\alpha = \frac{wC_n}{wC_{n-1}} \qquad (8)$$

The α values of Crude A is shown in Table 2 Column 4. At Column 5, the values are averaged to obtain two average α, i.e. α1=1.03 (ascending, C20~C26) and α2=0.80 (descending, C26+). Extrapolation of C38+ was done based on the α2, and it was stopped when the %w of Cn fall below 0.01, a concentration that can be neglected in common wax calculation.

Beside extrapolation, it is also necessary to normalize the GC's total nC20+ by referring to total wax content obtained from solvent extraction method (IFP alkyl-ether). The total nC20+ tend to be overvalued because GC is less sensitive to non n-alkanes. For Crude A, the total nC20+ of 15.60% w is normalized to total wax content of 14.08%w.

Extrapolation and normalization can be done simultaneously. The new n-paraffin distribution that obtained after extrapolation and normalization is shown in Table 2 Column 6. The highest significant carbon number for this crude is 48. Finally, the n-paraffin distribution was converted to %mole (Column 7) and ready to be input to the Coutinho Model.

Table 1
Physical Properties of Crude A

Parameter	Unit	Value
Specific Gravity		0.8185
°API Gravity		41.4
Kin. Viscosity 100 °F	[cSt]	3.080
Pour Point	[ºC]	18
Wax Content, %wt)	[%w]	14.08
K_{UOP} Factor		12.2
Average Molecular Weight	g/mol	162.9
Distillation Yield		
100 ºC	[%w]	15.1
150 ºC		31.1
250 ºC		54.2
307 ºC		64.7
419 ºC		82.7

C. Modeling

The main output of the model is a total wax formation curve (%w) as a function of temperature (Figure 2). The highest temperature that solid wax precipitated is defined as wax appearance temperature (WAT). WAT of Crude A is 40°C. As the temperature went down, amount of wax formed is increased. At -20°C, 13.86 %w solid wax was formed.

Table 2
n-paraffin Distribution Obtained from Normalization-Extrapolation of GC Data

Component	MW	%w, GC	α	average α	%w, normalized, extrapolated	% mole
1	2	3	4	5	6	7
n-C20	282	1.060		α_1=1.03	1.109	0.558
n-C21	296	1.098	1.04		1.146	0.549
n-C22	310	1.082	0.99		1.185	0.542
n-C23	324	1.163	1.08		1.225	0.536
n-C24	338	1.190	1.02		1.266	0.531
n-C25	352	1.242	1.04		1.308	0.527
n-C26	366	1.290	1.04		1.352	0.524
n-C27	380	1.272	0.99	α_2=0.80	1.087	0.406
n-C28	394	1.145	0.90		0.873	0.314
n-C29	408	1.130	0.99		0.702	0.244
n-C30	422	0.993	0.88		0.564	0.190
n-C31	436	0.907	0.91		0.453	0.147
n-C32	450	0.637	0.70		0.364	0.115
n-C33	464	0.543	0.85		0.293	0.089
n-C34	478	0.361	0.67		0.235	0.070
n-C35	492	0.206	0.57		0.189	0.054
n-C36	506	0.109	0.53		0.152	0.043
n-C37	520	0.094	0.86		0.122	0.033
n-C38	534	0.075	0.80		0.098	0.026
n-C39	548	NA			0.079	0.020
n-C40	562	NA			0.063	0.016
n-C41	576	NA			0.051	0.013
n-C42	590	NA			0.041	0.010
n-C43	604	NA			0.033	0.008
n-C44	618	NA			0.026	0.006
n-C45	632	NA			0.021	0.005
n-C46	646	NA			0.017	0.004
n-C47	660	NA			0.014	0.003
n-C48	674	NA			0.011	0.002
non-wax	129		84.40		14.08	5.586
Crude oil	163		100.00		100.00	100.00

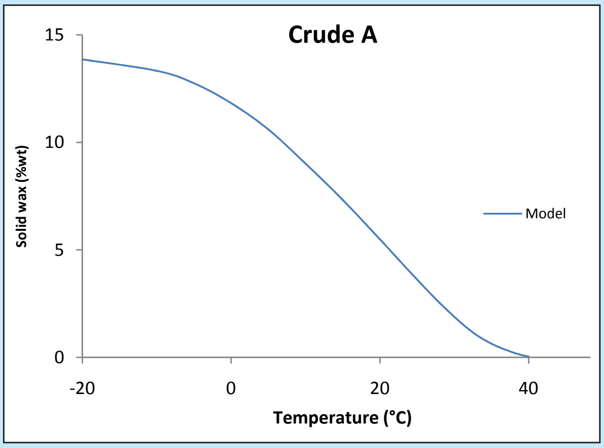

Figure 2
Total Solid Wax Precipitted
as Function of Temperature

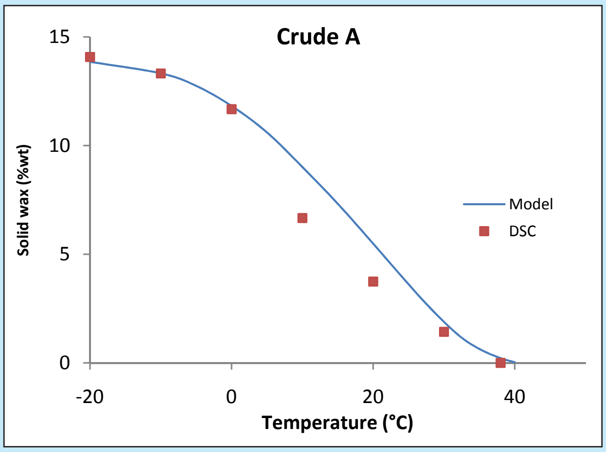

Figure 5
Overlay of Total Solid Wax Precipitated Obtained
from Model and DSC

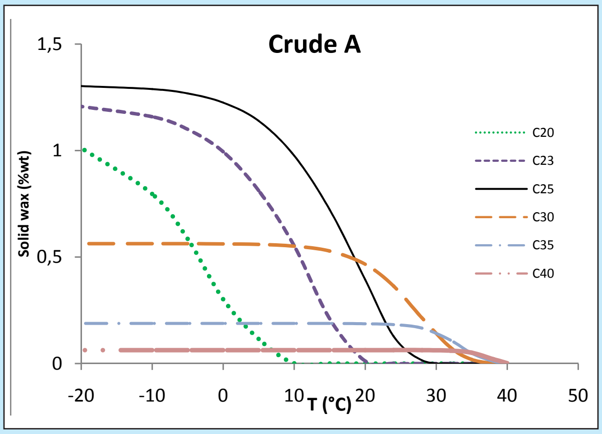

Figure 3
Components' Solid Precipitated
as Function of Temperature

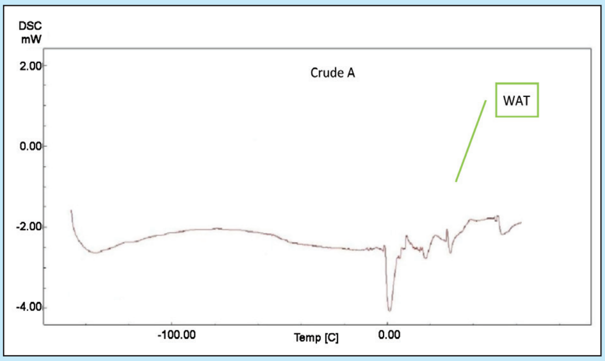

Figure 4
DSC Thermogram of Crude 4

The total wax formation curve is a summation of each n-alkane component. Figure 3 describe curves of several components' solid formation. It can be found that solid C40 was formed at 40°C, meanwhile the shorter n-alkanes started being formed at lower temperature. The shorter C chain, the lower is solid formation temperature.

We can also define composition of wax formed at a certain temperature. For example, at 30°C the solid wax would contain C26+, while C25 will be remained in liquid phase.

D. Validation using DSC data

DSC thermogram can be used to identify the phase change of a substance as a function of temperature. Wax precipitation in crude oil can be identified in the thermogram as an exothermic peak. The peak onset, the point where the signal leaving the baseline, is identified as wax appearance temperature (WAT). In the thermogram of Crude A (Figure 4), the WAT is observed at 38°C. WAT value obtained from the model is 40°C. There is 2°C WAT deviation between model and DSC, and it is considered as acceptable.

Beside determining WAT, DSC thermogram also can be used to determine amount of solid formed as a function of temperature. The determination utilizes a method proposed by Alcazar-Vara[11] and an assumption that entire wax compound had been solid at -20^{o}C proposed by Zhang[12]. The result is shown in Figure 5.

In Figure 5, total solid wax precipitated according to the model is overlaid with total solid obtained from

DSC. There are slight differences at several points, however both curves can be considered as close enough. It can be concluded that the model is valid to DSC data in term of WAT as well as amount of precipitated wax along temperature range.

In the future, this work would be extended to wide range characteristics of crude oil.

V. CONCLUSION

An extended n-paraffin distribution was calculated based on conventional gas chromatography data by performing extrapolation and normalization to total wax content. The n-paraffin distribution was applied in Coutinho model to predict wax precipitation of Crude A. The WAT obtained from the model deviated only 2°C from DSC data. The result was also valid to DSC data in term of precipitated wax amount along temperature range.

In the future, this work would be extended to wide range characteristics of crude oil.

NOMENCLATURE

C_n	n-alkane with n carbon atoms or number of carbon atoms of that n-alkane
g	Gibbs free energy
H	enthalpy
Mw	Molecular weight
q	UNIQUAC structural parameter
r	UNIQUAC structural parameter
R	universal gas constant
T	temperature
x	molar fraction
Z	coordination number

Greek letters

α	n-alkane decay defined by eq 8
γ	activity coefficient
λ	pair interaction energy

Subscripts

i	component i
j	component j
fus	fusion
sblm	sublimation
tr	solid-phase transition

Superscripts

E	excess property
l	liquid phase
s	solid phase

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