Prediction Model between Emulsified Water Fractions and Physicochemical Properties of Crude Oil Based on the Exergy Loss Rate

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ABSTRACT: The quantitative calculation of emulsified water fractions of crude oil—water systems is of great significance for the study of flow characteristics of multiphase flow pipelines. For a crude oil—water system with a high water fraction, the emulsified water fraction under different influencing factors was determined by emulsification experiments. It was found that the emulsified water fraction under different shearing conditions correlated well with the exergy loss rate and could be described by a power-law equation, in which two undetermined parameters relate to the crude oil physicochemical properties. Six representative parameters were selected to describe the crude oil physicochemical properties, i.e., the sum of asphaltene and resin contents, wax content, mechanical impurity content, crude oil acid number, crude oil average carbon number, and crude oil viscosity. Further, the correlations between the two undetermined parameters and the crude oil physicochemical properties were derived by regression analysis. Thus, the prediction model of emulsified water fraction was determined, which could be conveniently adopted to predict the emulsified water fraction with different crude oils and shearing conditions. The validation results showed that the mean relative deviation of the model prediction is 4.5%.

1. INTRODUCTION

Highly efficient utilization of energy is essential to industrial development, and there has been great progress in the use of renewable energy.1−4 At the same time, fossil fuels such as crude oil are still indispensable. During the process of crude oil exploitation, gathering, and transportation, the crude oil—water mixture is easy to form an emulsion. The formation of the emulsion has a significant influence on the flow pattern and pressure drop of pipelines.5,6 Crude oil contains various natural surfactants, including asphaltenes, resins, wax particles, etc. These natural surfactants can be aggregated and adsorbed at the oil−aqueous interface, decreasing the interfacial tension and forming a strong interfacial film, thus forming and stabilizing the emulsion. The emulsifying characteristics of the crude oil−water two-phase system are closely related to the crude oil physicochemical properties.7,8 Asphaltenes are mixtures containing macromolecular non-hydrocarbon compounds with many complex and changeable molecular structures.9,10 Being special in structure, asphaltenes have good interfacial activity; therefore, an interfacial film with specific structural strength would be formed by the adsorption of asphaltenes at the oil−aqueous interface, leading to a stable emulsion.11−13 Studies by Chang et al.14 pointed out that asphaltenes could be adsorbed at the oil−aqueous interface to form an interfacial film with viscoelasticity, thereby delaying or preventing the coalescence of emulsion droplets. According to Duan et al.,15 the rigid mechanical strength of the asphaltene interfacial membrane was derived from the polycyclic aromatic hydrocarbons (PAHs) with rigid structures in asphaltene and the π−π bond interaction among PAHs. Furthermore, when the asphaltene concentration was high, the nanoaggregates of asphaltenes acted as a spatial fortress at the W/O interface, making the coalescence of droplets difficult. Zhao et al.16 also suggested that the strength of the interfacial film was an important factor in the stability of emulsion and a higher asphaltene content in crude oil led to greater strength of the interfacial film and made the emulsion more stable. In addition, the research of Angle et al.17 revealed that the asphaltenes forming aggregates had stronger polarity and interfacial activity compared with the asphaltenes in the dissolved state, which made the formed emulsion more stable.

The stabilizing ability of resins to emulsion is weaker than that of asphaltenes.18,19 Al-Sahhaf et al.20 researched the impact of asphaltenes and resins on the stability of the emulsion using simulated oil and concluded that different...
resin/asphaltene ratios would lead to the formation of emulsions with different stabilities. Yang et al.\textsuperscript{23} pointed out that the emulsion stabilized by asphaltene alone could remain stable for a long time; however, the addition of resins could decrease the emulsion’s stability, and the stability of the experimental emulsion decreased dramatically when the resin/asphaltene ratio reached 0.5–1.0. Research by Álvarez et al.\textsuperscript{22} also revealed that resins could enhance the asphaltene solubility in the oil phase and reduce the interaction between asphaltene and liquid droplets; the formed emulsion was more stable with a decreasing ratio of resins/asphaltene.

Regarding crude oils from different oilfields, the composition of hydrocarbon and carbon number distribution of the oil phase are generally different, which makes differences in the solubility and aggregation morphology of asphaltene, thus affecting the emulsion stability.\textsuperscript{33,34} McLean and Kilpatrick\textsuperscript{25} carried out research on the emulsification characteristics of an asphaltene-containing simulated oil emulsion. It was found that the aromaticity of the simulated oil was closely related to the stability of the emulsion and increasing the aromaticity of the oil might cause the emulsion to become unstable.

Wax particles in crude oil are also important interface-active substances. During the formation of emulsion, wax particles will be adsorbed at the oil–aqueous interface, which may change the rheological properties of the interface film and increase the mechanical strength of the interface film, thus making the emulsion more stable.\textsuperscript{26} Binks and Rocher\textsuperscript{27} indicated that wax particles were hydrophobic and an effective emulsifier that can stabilize emulsions. Research by Hodge and Rousseau\textsuperscript{36} found that the ability of wax particles to stabilize the emulsion was closely related to their size. Small-sized wax particles were more likely to adsorb and arrange at the oil–aqueous interface, which was more conducive to the stability of the emulsion. Furthermore, mechanical impurities such as small solid particles can play a similar role to wax particles in promoting emulsification.\textsuperscript{29} Poindexter and Marsh\textsuperscript{30} indicated that the content of inorganic solid particles in crude oil was one of the most critical factors determining the stability of emulsions, i.e., a higher content of inorganic solids resulted in an emulsion with higher stability. Gavrielatos et al.\textsuperscript{31} researched the effect of solid nanoparticles on the stability of simulated oil. It was found that with increasing nanoparticle concentration, the separation rate of oil/water decreased gradually; moreover, large particles could not stabilize the emulsion as effectively as small particles.

The acid compound in crude oil is also a significant factor in promoting the forming of emulsion.\textsuperscript{32} The acids in crude oil could react with metal cations, and the resulting salts might enhance the strength of the interfacial film and stabilizing the emulsion. Poteau et al.\textsuperscript{38} believed that naphthenic acids in crude oil could interact with asphaltene to promote the arrangement of asphaltene molecules at the oil–aqueous interface.

Many investigations have qualitatively reported on the effect of physicochemical properties of crude oils on the emulsified characteristics of crude oil–water mixing systems. However, quantitative research studies on the relationship between physicochemical properties of crude oil and emulsification characteristics are quite lacking. In our published work,\textsuperscript{39} it was found that the emulsified water fraction under varying circumstances of shear rate, water fraction, and temperature could be quantitatively correlated with the exergy loss rate of shearing in a unitive way for incomplete emulsification; moreover, a power-law equation between the emulsified water fraction and the exergy loss rate of shearing was presented, with two undetermined parameters relating to physicochemical properties of crude oils. However, the unknown and unquantified undetermined parameters limited the application of the mentioned power-law equation in the calculation of multiphase flow. Therefore, the object of this further work is to study the quantitative relationship between the two undetermined parameters in the power-law equation and physicochemical properties of crude oils. The factors related to crude oil physicochemical properties that affect the emulsification characteristics were examined, and then, the representative parameters using to describe the physicochemical properties of crude oils were determined. Finally, the correlations between the two undetermined parameters in power-law equation and the representative parameters were developed.

2. RESULTS AND DISCUSSION

2.1. Relationship between the Emulsified Water Fraction and Exergy Loss Rate. As our published work,\textsuperscript{30} it was found that complete emulsification occurred within a certain shear rate range when the water fraction ($\phi_w$) decreased to lower than a certain threshold value, but only incomplete emulsification occurred when the water fraction was higher than the threshold value, as shown in Figure 1. However, the emulsified water fraction decreased with an increasing water fraction and temperature for incomplete emulsification, as shown in Figures 2 and 3.

The emulsification process of the crude oil–water mixture is an energy-consuming process. The amount of energy dissipation determines the emulsification degree of the crude oil–water mixture. The exergy loss rate of shearing can be used to characterize the energy dissipation in the emulsification.
where $N$ is the stirring speed, $r\cdot s^{-1}$, $M$ is the stirring torque, $N\cdot m$, and $\rho$ is the density of the crude oil–water mixture, $kg\cdot m^{-3}$.

In the case of incomplete emulsification with high water fraction, it was found that the emulsified water fraction under different shear rates, water fractions, and temperatures could be quantitatively correlated to the exergy loss rate of shearing in a unitive way, as shown in Figure 4.

Furthermore, a power-law equation was developed for describing the quantitative relation between the emulsified water fraction and exergy loss rate of shearing with two undetermined parameters relating to physicochemical properties of crude oils, as follows:

$$\phi_e = k_1 \hat{I}^{k_2};$$

where $\hat{I}$ is the exergy loss rate of shearing and $k_1$ and $k_2$ are the undetermined parameters closely relating to the crude oil physicochemical properties.

2.2. Additional Results of Current Research. To facilitate the application of eq 2 in the calculation of multiphase flow, parameters $k_1$ and $k_2$ must be quantified. For different crude oils, $k_1$ and $k_2$ can be acquired by regression analysis. Generally, the difference of temperatures may result in different emulsification characteristics. Taking this into account, two temperature conditions were specially set in the emulsification experiments, i.e., 40 and 50 °C. The experimental data under the two temperature conditions are fitted by eq 2, and the fitting results of $k_1$ and $k_2$ are given in Tables 1 and 2.

It can be seen from Tables 1 and 2 that $k_1$ and $k_2$ values are quite different for different crude oils, meaning that $k_1$ and $k_2$ values are closely related to the crude oil physicochemical properties.

2.3. Choice of Representative Physicochemical Property Parameters. On the basis of the analysis of various factors affecting the emulsification characteristics of oil–water
mixing systems in the Introduction section, six parameters were selected as representative parameters to characterize the crude oil physicochemical properties, i.e., the sum of asphaltene and resin contents \((c_{as+r})\), wax content \((c_w)\), mechanical impurity content \((c_m)\), crude oil acid number \((AN)\), crude oil average carbon number \((CN_{oil})\), and crude oil viscosity at the studied temperature \((\mu)\). The reasons for the choice of these six parameters are as follows.

The existence of asphaltenes and resins is the crucial factor affecting the stability of the emulsion. The physicochemical properties of asphaltenes and resins are almost similar, and there is no clear boundary between them. Therefore, the contents of both asphaltenes and resins were added together as the first parameter, i.e., the sum of asphaltene and resin contents \((c_{as+r})\). The wax in crude oil is also a crucial surfactant, and its adsorption at the oil–aqueous interface may change the rheology of the interfacial film and reinforce the strength of the interfacial film, making the emulsion more stable. Thus, the wax content \((c_w)\) was determined as the second parameter. The mechanical impurity content \((c_m)\) was determined as the third parameter because the mechanical impurities in crude oil can also be adsorbed at the oil–aqueous interface to reinforce the strength of the interfacial film, thus increasing the stability of the emulsion. There are many kinds of acidic components in crude oil, including carboxylic acids, naphthenic acids, etc. It is scarcely possible to quantify all of these acidic components because of their complex molecular structure and physicochemical properties. Therefore, the crude oil acid number \((AN)\) was selected as the fourth parameter to quantify the effect of these acidic components on emulsification characteristics. The aggregation and solubility of the asphaltenes and resins are affected by the hydrocarbon components of crude oil, thus affecting the formation and stability of the emulsion. Therefore, the crude oil average carbon number \((CN_{oil})\) was chosen as the fifth parameter. The viscosity of crude oil has a significant influence on the emulsification characteristics. The higher viscosity of the crude oil leads to a more stable emulsion. Therefore, the crude oil viscosity at the studied temperature \((\mu)\) was taken as the sixth parameter.

### 2.4. Establishment of Correlations between \(k_1\), \(k_2\), and Crude Oil Physicochemical Properties

After determining the representative physicochemical property parameters, the correlations between parameters \(k_1\) and \(k_2\) and the crude oil physicochemical properties were derived by regression analysis.

Taking \(k_1\) as an example, the correlation between \(k_1\) and the representative parameters is assumed as follows:

\[
k_1 = a_0 + a_1 c_{as+r} + a_2 c_w + a_3 c_m + a_4 AN + a_5 CN_{oil} + a_6 \mu
\]

where \(a_0, a_1, a_2, a_3, a_4, a_5, a_6\) are the fitting parameters. Taking the logarithm of eq 3 as follows:

\[
\ln k_1 = \ln a_0 + a_1 \ln c_{as+r} + a_2 \ln c_w + a_3 \ln c_m + a_4 \ln AN + a_5 \ln CN_{oil} + a_6 \ln \mu
\]

Letting \(X_1 = \ln c_{as+r}, X_2 = \ln c_w, X_3 = \ln c_m, X_4 = \ln AN, X_5 = \ln CN_{oil}, X_6 = \ln \mu,\) and \(Y = \ln k_1,\) eq 4 can be rewritten as follows:

\[
Y = \ln a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_4 + a_5 X_5 + a_6 X_6
\]

Based on the above emulsification experimental data, the multiple linear regression is performed on eq 5 to obtain

\[
Y = -0.727 + 0.051 X_1 + 0.053 X_2 + 0.010 X_3 - 0.015 X_4 - 0.323 X_5 + 0.107 X_6
\]

After obtaining the above hypothesis correlation, the null hypothesis test is conducted to verify whether there exists a significant linearity between \(Y\) and \(X_i (i = 1, 2, \ldots, 6)\). According to eq 5, if \(a_1 = a_2 = \ldots = a_6 = 0\), it can be considered that there is no linearity between \(Y\) and \(X_i (i = 1, 2, \ldots, 6)\). Therefore, to verify whether there is a linearity between \(Y\) and \(X_i (i = 1, 2, \ldots, 6)\), it corresponds to take the null hypothesis as follows:

\[
H_0: a_1 = a_2 = \ldots = a_6 = 0
\]

\[
H_1: \text{not all } a_i (i = 1, 2, \ldots, 6) \text{ equal zero}
\]

In mathematical statistics, the F test is employed to examine whether the null hypothesis is valid at a certain significance level \(\alpha\) (in general, taking \(\alpha = 0.05\)). The statistic expressions are

\[
F = \frac{\text{SSR}/p}{\text{SSE}/(n - p - 1)}
\]

where

\[
\text{SSR} = \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2
\]

\[
\text{SSE} = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2
\]

where SSR represents the sum of squared regression; SSE represents the sum of squared errors; \(n\) denotes the sample size; \(p\) denotes the independent variable number; and \(\hat{y}_i, y_i, \bar{y}\) are respectively the estimated, observed, and average values of the dependent variable.

If \(F > F_{1-p}(p, n - p - 1)\), reject \(H_0\) if not, accept \(H_0\). For eqs 7–9, in such case, \(p = 6\).

### Table 1. \(k_1\) and \(k_2\) Values in eq 2 (40 °C)

| oils | \(k_1\)     | \(k_2\)     | mean relative deviation (%) |
|------|-------------|-------------|-----------------------------|
| A    | 0.1265      | 0.4244      | 8.1                         |
| B    | 0.1333      | 0.3735      | 5.1                         |
| C    | 0.0940      | 0.3992      | 8.6                         |
| D    | 0.1179      | 0.3976      | 9.1                         |
| E    | 0.1434      | 0.4114      | 5.2                         |
| F    | 0.1204      | 0.3332      | 5.8                         |
| G    | 0.1096      | 0.3559      | 7.3                         |
| H    | 0.1079      | 0.3709      | 8.3                         |

### Table 2. \(k_1\) and \(k_2\) Values in eq 2 (50 °C)

| oils | \(k_1\)     | \(k_2\)     | mean relative deviation (%) |
|------|-------------|-------------|-----------------------------|
| A    | 0.1304      | 0.3882      | 6.2                         |
| B    | 0.1278      | 0.4084      | 6.4                         |
| C    | 0.0952      | 0.3499      | 6.2                         |
| D    | 0.1163      | 0.4204      | 6.6                         |
| E    | 0.1364      | 0.4360      | 5.9                         |
| F    | 0.1202      | 0.3234      | 3.6                         |
| G    | 0.1053      | 0.3626      | 5.5                         |
| H    | 0.1070      | 0.3530      | 6.8                         |
n = 16

\[ SSR = \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2 = 0.03512 \]

\[ SSE = \sum_{i=1}^{n} (y_i - \hat{y})^2 = 0.00841 \]

\[ F = \frac{SSR/p}{SSE/(n - p - 1)} = \frac{0.03512/6}{0.00841/(16 - 6 - 1)} = 6.26 \]

The critical point for significance level \( \alpha = 0.05 \) is \( F_{0.05}(6, 9) = 3.37 \). Because \( F > F_{0.05}(6, 9) \), \( H_0 \) should be rejected, i.e., there is a significant linearity between \( y \) and \( x_i \) (\( i = 1, 2, ..., 6 \)). Therefore, eq 5 is highly significant to describe the quantitative relation between independent variables and dependent variables. Further, it indicates that eq 3 is reasonable to show the quantitative relation between \( k_1 \) and the representative parameters.

By regression analysis, the following correlation between \( k_1 \) and the representative parameters was obtained:

\[ k_1 = 0.187 \epsilon_{r+1}^{0.0512} \epsilon_{w}^{0.053} \epsilon_{m}^{0.010} AN^{-0.015} CN_{oil}^{-0.323} \mu^{0.107} \quad (10) \]

Similarly, the correlation between \( k_2 \) and the representative parameters was obtained as follows:

\[ k_2 = 0.069 \epsilon_{r+1}^{0.104} \epsilon_{w}^{-0.124} \epsilon_{m}^{0.085} AN^{-0.015} CN_{oil}^{0.720} \mu^{-0.075} \quad (11) \]

The mean relative deviations of eqs 10 and 11 are 4.2% and 5.1%, respectively, as shown in Figures 5 and 6.

2.5. Prediction Model Validation. For crude oils I and J, the proposed prediction model of emulsified water fraction was used to calculate the emulsified water fraction of the crude oil—water system under different shearing conditions and compared with the measured emulsified water fraction. The comparison results are shown in Figure 7. According to the statistics of 88 groups of experimental data of crude oils I and J, the mean relative deviation between the emulsified water fraction calculated by the proposed prediction model and the measured value of emulsified water fraction is 4.5%, as shown in Figure 8.

As can be seen from Figures 7 and 8, the calculated values of the emulsified water fraction of different crude oil—water systems under different shearing conditions are in good agreement with the measured values of emulsified water fraction. The predicted deviation is low, showing a good prediction effect.

3. CONCLUSIONS
The main conclusions are shown as follows:

1. The emulsified water fraction under varying circumstances of shear rate, water fraction, and temperature can be quantitatively correlated to the exergy loss rate of shearing in a unitive way for incomplete emulsification, and the power-law equation, i.e., \( \phi_E = k_1 \phi^2 \), well describes the quantitative relationship.

2. Parameters \( k_1 \) and \( k_2 \) in equation \( \phi_E = k_1 \phi^2 \) relate to the crude oil physicochemical properties. Six parameters were selected as representative parameters to characterize the crude oil physicochemical properties, i.e., the sum of asphaltene and resin contents \( (\epsilon_{r+1}) \), wax content \( (\epsilon_{w}) \), mechanical impurity content \( (\epsilon_{m}) \), crude oil acid number \( (AN) \), crude oil average carbon number \( (CN_{oil}) \), and crude oil viscosity at the studied temperature \( (\mu) \).

3. The correlations between parameters \( k_1 \) and \( k_2 \) and the crude oil physicochemical properties were derived by regression analysis. Thus, the complete expressions of the prediction model of emulsified water fraction based on the exergy loss rate of shearing are drawn as follows:

\[
\begin{align*}
\phi_E &= k_1 \phi^2; \\
k_1 &= 0.187 \epsilon_{r+1}^{0.0512} \epsilon_{w}^{0.053} \epsilon_{m}^{0.010} AN^{-0.015} CN_{oil}^{-0.323} \mu^{0.107} \\
k_2 &= 0.069 \epsilon_{r+1}^{0.104} \epsilon_{w}^{-0.124} \epsilon_{m}^{0.085} AN^{-0.015} CN_{oil}^{0.720} \mu^{-0.075}
\end{align*}
\]

The model is quantitatively correlated to the crude oil physicochemical properties and can be applied to different crude oil—water systems.

4. According to the statistics of 88 groups of experimental data from crude oils I and J, the mean relative deviation between the calculated emulsified water fraction and the measured emulsified water fraction is 4.5%, which indicates that the prediction model has a good prediction effect on the emulsified water fraction of crude oil—water systems.
the crude oil–water system under different shearing conditions.

4. EXPERIMENTAL SECTION

4.1. Materials. The physicochemical properties of crude oil specimens are shown in Table 3. Oils A−H are the same as the oils used in our previous works.39,40 Two new crude oils, named oils I and J, are used to validate the prediction model of the emulsified water fraction.

4.2. Experimental Device and Method. The emulsification experiments were carried out in a stirring vessel, as shown in Figure 9. The details of the experimental device, experimental procedures, and the method for measuring the emulsified water fraction under flowing conditions are presented in previous works.39,40 Some brief and necessary information is provided here.

The accumulated free water separation volume change with time after stirring was stopping was measured by sampling. The emulsified water fraction under flowing conditions was determined by a time extended method. The crude oil and water were added to the stirring vessel according to a certain mass ratio, the mixture was kept at the experimental...
temperature for 10 min to achieve a stable temperature, and then the stirring was started. After reaching the predetermined time, stirring was stopped and the crude oil–water mixture was transferred to the water separation metering device through the valve at the bottom of the stirring vessel to measure the accumulated free water separation volume change with time. Then, the correlation between the accumulated free water separation volume \( (V_f) \) and time \( (t) \) was obtained by fitting.

The volume of free water at \( t = 0 \) min, i.e., the moment the stirring had just stopped, was calculated by the time extended method, which can be taken as the volume of free water under flowing conditions. Combined with the total volume of water phase in the crude oil–water mixture, the emulsified water fraction under flowing conditions can be calculated by the following equation:

\[
\phi_E = \frac{V_w - V_f}{V_m}
\]  

where \( \phi_E \) is the emulsified water fraction under flowing conditions, \( V_m \) is the total volume of mixture, mL, \( V_w \) is the volume of the water phase, mL, and \( V_f \) is the volume of free water at \( t = 0 \) min, mL.

Herein, \( V_f \) is calculated by the following equation:

\[
V_f = a \ln(t + b) + c
\]  

where \( V_f \) is the volume of free water after the stirring was stopped, mL; \( t \) is the time, min; and \( a, b \) and \( c \) are the fitting parameters.

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