# Pyrolysis of Heavy Oil in the Presence of Supercritical Water: The Reaction Kinetics in Different Phases

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*In the presence of supercritical water (SCW) and $N_2$, the pyrolysis of heavy oil was investigated to distinguish the difference in the reaction kinetics between the upgrading in the SCW and oil phases. The pyrolysis in the SCW phase is faster than that in the oil phase, but the reaction in whichever phase is retarded by vigorous stirring. The pyrolysis can be preferably described by a four-lump kinetic model consisting of the condensation of maltenes and asphaltenes in series. In the SCW phase, highly dispersed asphaltenes are isolated by water clusters from maltenes dissolved in SCW surroundings, by which the condensation of asphaltenes is drastically accelerated. Benefited from excellent mass transfer environments in SCW, the condensation of maltenes is promoted simultaneously. The introduction of SCW into the pyrolysis of heavy oil results in an effectively increased upgrading efficiency, but its influence on the properties of equilibrium liquid products is minor.* © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 857–866, 2015
*Keywords: pyrolysis, heavy oil, supercritical water, reaction kinetics, stirring intensity*

## Introduction

Suffered from the deteriorating quality of feedstock, refineries worldwide now are facing great challenges in the processing of heavy oil with traditional hydrogenation and decarbonization technologies. Since the 1990s, the pyrolysis and the hydrocracking of heavy oil in the presence of supercritical water (SCW, $T_c = 647$ K, $P_c = 22.1$ MPa), an environmentally benign solvent for organic reactions, have been attracting increasing attention in academia.[1–8] It was believed that the unique solubility and diffusivity of organics in SCW might have a positive influence on the upgrading of heavy oil in the SCW medium.

A close analysis of the literature available however shows that there exists a dispute on the essential issue, that is, whether the product distribution of the pyrolysis of heavy oil can be improved by the introduction of SCW. At the temperature of 723 K and water densities between 0.10 and 0.20 g/cm$^3$, Watanabe et al. ran the upgrading of oil sand bitumen in a bomb reactor without stirring.[9] The formation of coke was found to be significantly promoted at increasing water densities. In a similar bomb reactor, Morimoto et al. performed the upgrading of oil sand bitumen at the temperatures between 693 and 723 K and the water density of 0.16 g/cm$^3$.[10] Compared with the product obtained under $N_2$ environments, the improvement to the quality of liquid products obtained in SCW was just marginal. Different results were reported by Cheng et al. and Han et al. who performed the upgrading of vacuum residue and coal tar in SCW in the autoclave with vigorous stirring. Cheng found that a simultaneous increase in the water density and $H_2O$/oil ratio would increase the yield of light oil fractions and depress the formation of coke.[11] Han observed that the pyrolysis at the water densities between 0.29 and 0.47 g/cm$^3$ and temperatures between 673 and 753 K has a much higher yield of maltenes than the reaction in the presence of $N_2$ does.[12]

Despite of the conflicting opinions mentioned above, it is commonly acknowledged that the nonpolar fraction of maltenes in heavy oil can be dissolved into SCW especially at high water densities. Watanabe et al. suggested a partially miscible water/oil two-phase structure for the mixture of heavy oil and SCW. The existence of two-phase structure was confirmed by Sato et al. who applied a visual observation of the oxidation of heavy oil in SCW in an optical cell.[13] Cheng et al. proposed that the mixture of heavy oil and SCW could maintain an oil-in-water emulsion structure as the result of the dissolution of maltenes into the continuous SCW phase. By theoretical calculation, Bai and Liu considered that in the near or supercritical region of water the heavy oil/water system might evolve between the partially miscible two-phase structure and the pseudo-single phase structure.[14,15]

The presence of SCW makes it possible for the pyrolysis of heavy oil to be run in various phase structures. As a result, the reaction in the oil phase or in the SCW phase could occur simultaneously or separately. In light of the huge differences in mass transfer environments and solvent surroundings, the pyrolysis in the oil and SCW phases may vary greatly in reaction kinetics. Many factors, such as the thermodynamic state of water, the ratio of water to oil, and the mixing intensity all present a delicate influence on the phase structure of the heavy oil/SCW system. Unfortunately,

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**Table 1. Basic Properties of the Raw Heavy Oil**

| Molecular Weight (kg/kmol) | API Gravity (°) | Dynamic Viscosity (353 K, Pa·s × $10^3$) | H/C ratio | Maltenes (wt %) | Asphaltenes (wt %) |
|---|---|---|---|---|---|
| 811 | 14 | 2931.58 | 1.41 | 95.0 | 5.0 |

no clear definition of the phase structure was provided in most related studies. Also, the difference in the reaction kinetics between the pyrolysis occurring in the oil and SCW phases, which is essential to the understanding of the upgrading of heavy oil in the presence of SCW, was seldom touched in the literature.

Hereby, the reaction kinetics of the pyrolysis of heavy oil in the presence of dense SCW and high pressure $N_2$ was measured in an autoclave. By adjusting the stirring rate, the effect of mixing intensity on the pyrolysis was also examined. With a four-lump kinetic model, the kinetic parameters of the pyrolysis of heavy oil occurring in the oil phase and in the SCW phase were estimated. The characteristics of the pyrolysis in different phases then were discussed. Based on the characterization on the boiling point distribution of liquid products, the upgrading efficiency of the pyrolysis in SCW was further evaluated.

## Experimental

### *Apparatus and reaction runs*

A Parr 4598-HPHT autoclave made of SS316L steel with a capacity of 0.1 L was applied in the pyrolysis of heavy oil. The reactor is equipped with flat paddles. A vacuum residuum sample obtained from Sinopec Shanghai Petrochemical Company, whose basic properties are listed in Table 1, was used as the raw heavy oil. According to the preliminary thermogravimetric analysis, the heavy oil starts cracking at temperatures around 623 K.

For the pyrolysis in the presence of SCW, heavy oil of 10 g and water of 25 g were loaded into the autoclave, followed by purging with $N_2$ of high purity. For the pyrolysis in the presence of $N_2$, heavy oil of 20 g was loaded into the autoclave. Purged with $N_2$ of high purity, the autoclave was charged with high pressure $N_2$ of 8.0–9.0 MPa. After that, the sealed autoclave was heated from the ambient temperature to reaction temperatures ranging from 663 to 703 K at a slope of 15 K/min, during which the stirring rate was kept at 200 rpm to reduce the temperature difference within the autoclave. Once the reaction temperature reached a preset value, the stirring rate might be kept at 200 rpm or be increased immediately to 800 rpm. Finally, the pyrolysis was terminated by subjecting the autoclave in forced air cooling.

Although a heat insulation jacket was installed outside, still there existed an axial temperature distribution within the autoclave. The measured reaction pressures, 23 to 31 MPa in the presence of SCW and 19 to 20 MPa in the presence of $N_2$, were slightly lower than theoretical values.

Each experimental run was repeated three times, while the maximum errors of the product distribution fell within a reasonable range of ±5%. Only the average values were reported and were adopted in the calculation on reaction kinetics. To facilitate differentiating the difference in pyrolysis behavior in the SCW and oil phases, "Oil phase" and "SCW phase" were labelled in figures and tables hereinafter when necessary. In which phase the pyrolysis occurred was determined by the fraction of maltenes transferred from the oil phase into the SCW phase in the kinetic model suggested afterwards.

### *Product separation and analytical procedures*

After pyrolysis, the gas product was collected over water first. Then the autoclave was washed with toluene to collect liquid and solid products. Following the Industrial Standard of Chinese Petrochemical NB/SH/T 0509-2010 shown in Figure 1, the obtained collection was separated sequentially into coke, asphaltenes, and maltenes.

The mass balance in each experimental run was evaluated by

$$\mathrm{MB}=\sum m_i/m_{\mathrm{raw}}\times 100\% \quad (1)$$

where $m_i$ denotes the weight of any collected component in the product. $m_{\mathrm{raw}}$ is the weight of the loaded raw heavy oil. Usually, the value of MB varied between 92 and 96%.

The weight fractions of each collected component in the product were evaluated by

$$Y_i=m_i/\sum m_i\times 100\% \quad (2)$$

The dynamic viscosity and the H/C ratio of oil samples were measured on an ARES high-temperature rheometer and a vario EL III element analyzer, respectively. The density of oil samples was determined on an Anton Paar DMA 5000 density meter. The distribution of boiling points of oil samples was analyzed on an Agilent 7890 simulated distillation gas chromatography (GC) with the ASTM method of D2887. Based on the Industrial Standard of Chinese Petrochemical SH/T 0583-94, the number average molecular weight of oil samples was measured on a KNAUER K7000 vapor pressure osmometer. Calibration curves were prepared by measuring the osmolality of toluene solutions dissolved with benzyl.

## Results and Discussion

### *Reaction behavior of pyrolysis of heavy oil*

The kinetic data of the pyrolysis of heavy oil in the presence of SCW and $N_2$ were measured at three temperatures, that is, 663, 683, and 703 K. During the reaction, the stirring

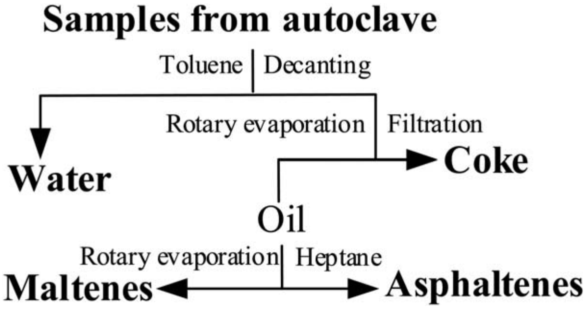

**Figure 1. Standard procedure for the separation of pyrolysis products and raw heavy oil.**

Table 2. Equilibrium Product Distribution of Pyrolysis of Heavy Oil in the Presence of SCW and $N_2$

| Reaction Media | Temperature (K) | Asphaltenes (wt %) | Maltenes (wt %) | Coke (wt %) | Gas (wt %) |
|---|---|---|---|---|---|
| $N_2$ | 663 | 2.7 | 30.6 | 30.9 | 35.8 |
| | 683 | 0.5 | 23.7 | 35.6 | 40.3 |
| | 703 | 0.1 | 15.6 | 38.8 | 45.5 |
| SCW | 663 | 0.0 | 34.9 | 31.8 | 33.3 |
| | 683 | 0.0 | 27.8 | 31.5 | 40.7 |
| | 703 | 0.0 | 22.7 | 32.7 | 44.7 |

rate was maintained at 200 or 800 rpm. Within the limited reaction time ranging from 15 to 120 min, the product distribution of the pyrolysis was found to be determined simultaneously by the reaction temperature, the stirring rate, and the reaction medium. When the reaction time was extended long enough, the equilibrium product distribution of the pyrolysis listed in Table 2 depended only on the reaction temperature and the reaction medium.

*Effect of Reaction Temperature on Pyrolysis.* For the pyrolysis of heavy oil in both reaction media, the reaction temperature plays a dominant role not only on reaction kinetics but also on equilibrium product distribution. Typical results of the temperature dependence of the reaction kinetics of the pyrolysis in the presence of SCW and $N_2$ are illustrated in Figures 2 and 3. The experimental data included were measured at the fixed stirring rate of 800 rpm.

Take the pyrolysis in the presence of SCW, for example. At the temperature of 663 K, the fraction of maltenes in the product decreases gradually from 95.0 to 70.7 wt % with the extension of reaction time. Meanwhile, the fraction of asphaltenes maintains at values between 5.0 and 6.0 wt %. The formation of coke can be observed at the reaction time of 60 min, and the fraction of coke in the product at the reaction time of 120 min is only 11.2 wt %. With the increase in the reaction temperature to 703 K, only after 15 min's reaction the fraction of maltenes in the product decreases drastically to 47.0 wt %. At the reaction time of 30 min, asphaltenes can hardly be detected in the product. A rapid decrease in the fraction of asphaltenes suggests that the quality of the liquid product is significantly improved. However, it is at the cost of the undesired high yields of coke and gas. At the reaction time of 90 min, the fractions of coke and gas in the product may reach 30.0 and 38.7 wt %, respectively. At increasing temperatures, the product distribution of the pyrolysis in the presence of $N_2$ varies similarly with that of the pyrolysis in the presence of SCW. The only difference is that at the temperature of 703 K a maximum fraction of asphaltenes of 16.7 wt % appears at the reaction time of 15 min.

When the pyrolysis is at equilibrium, the fractions of coke and gas in the product obtained in the presence of $N_2$ increase monotonically along with the increase in the temperature from 663 to 703 K. On the contrary, the fraction of maltenes decreases continuously by 15.0 wt %. Only at high enough temperatures, such as 703 K, can the content of asphaltenes in the liquid oil product be negligible. In the presence of SCW, the equilibrium fraction of coke in the product varies around 32.0 wt % at any reaction temperature. Meanwhile, no asphaltenes could be detected any more. At increased temperatures, a decreasing equilibrium fraction of maltenes in the product from 34.9 to 22.7 wt % is balanced by the increasing fraction of gas.

*Effect of Stirring Rate on Pyrolysis.* The stirring rate also has an important influence on the reaction kinetics of the pyrolysis of heavy oil in both reaction media, but its influence on the equilibrium product distribution is just marginal. In the presence of SCW or $N_2$, typical results of the dependence of the reaction kinetics of the pyrolysis on the stirring rate are illustrated in Figures 4 and 5. The experimental data included were measured at the fixed reaction temperature of 683 K.

Consider first the pyrolysis in the presence of SCW. With the increase in the stirring rate, the fraction of maltenes in the product increases monotonically but the fractions of coke

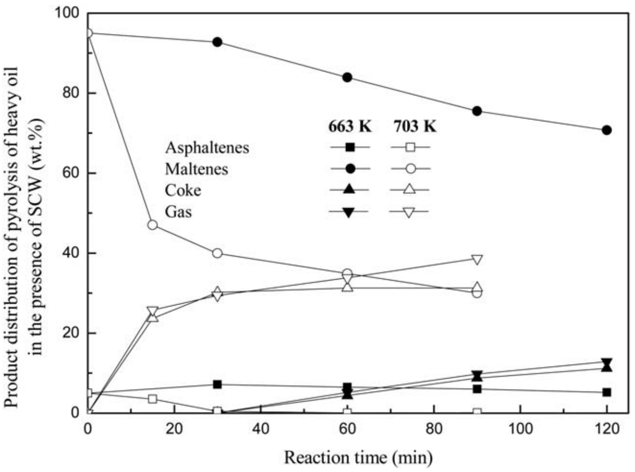

**Figure 2. Effect of reaction temperature on the product distribution of the pyrolysis in the presence of SCW; stirring rate of 800 rpm.**

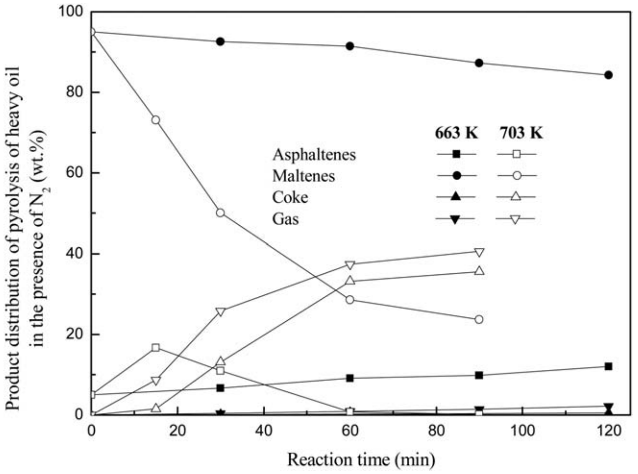

**Figure 3. Effect of reaction temperature on the product distribution of the pyrolysis in the presence of $N_2$; stirring rate of 800 rpm.**

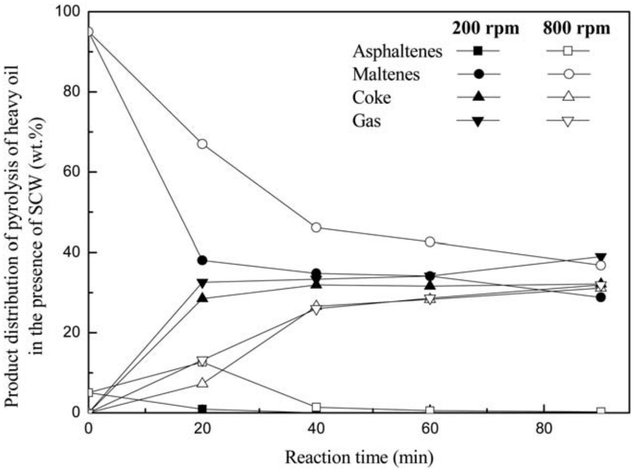

**Figure 4. Effect of stirring rate on the product distribution of the pyrolysis in the presence of SCW; reaction temperature of 683 K.**

and gas vary oppositely. In the meantime, the fraction of asphaltenes in the product shows a complicated variation tendency. At the stirring rate of 200 rpm, the fraction of asphaltenes decreases consistently with the extension of reaction time, approaching zero at the reaction time of 40 min. At the stirring rate of 800 rpm, the fraction of asphaltenes presents a maximum value of 12.6 wt % at the reaction time of 20 min, falling nearly to zero in the following reaction time. Eventually, the product distributions at different stirring rates come closer to each other.

For the pyrolysis in the presence of $N_2$, the fraction of asphaltenes in the product varies little with respect to the increase in the stirring rate. As for the fractions of maltenes, coke and gas, they all change in the same way as the pyrolysis in the presence of SCW. Nevertheless, there are evident differences in the fractions of these components at two stirring rates when the reaction is terminated at the reaction time of 120 min.

*Effect of Reaction Media on Pyrolysis.* Comparing the data presented in Figures 2–5, one may notice that the pyrolysis of heavy oil in the presence of SCW is much faster than that in the presence of $N_2$. Take the reaction at the temperature of 683 K and the stirring rate of 200 rpm for example. Merely after 20 min's pyrolysis in SCW, the fraction of maltenes in the product has already decreased from 95.0 to 38.0 wt %. Also, the fraction of asphaltenes decreases from 5.0 to 0.9 wt %. What is more, the total fraction of coke and gas increases drastically to 61.1 wt %. By contrast, the pyrolysis in the presence of $N_2$ seems to be retarded. At the reaction time of 30 min, the fraction of maltenes in the product remains at a relatively high value of 79.6 wt % and the formation of coke can nearly be neglected. Only the fraction of asphaltenes increases significantly to 14.9 wt %. For the rest of the reaction time, the product distribution varies slightly in the presence of SCW but keeps changing considerably in the presence $N_2$.

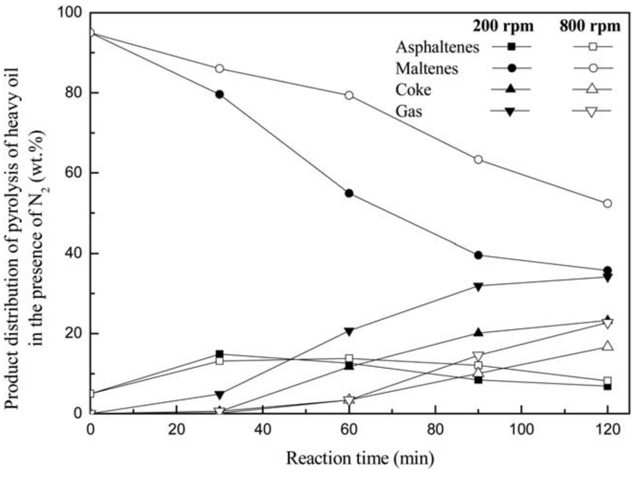

**Figure 5. Effect of stirring rate on the product distribution of the pyrolysis in the presence of $N_2$; reaction temperature of 683 K.**

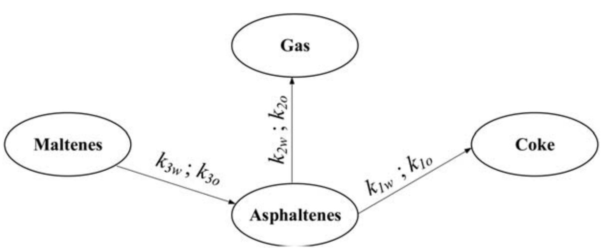

**Figure 6. Four-Lump kinetic model for the pyrolysis of heavy oil.**

The equilibrium data listed in Table 2 clearly show that the presence of SCW suppresses the formation of coke in the pyrolysis of heavy oil. At any temperature, the equilibrium fraction of maltenes in the product obtained in the presence of SCW is consistently higher than that obtained in the presence of $N_2$. The suppression of coke formation and the improvement of the yield of maltenes become more obvious at higher temperatures.

### *Development of kinetic model for pyrolysis*

The pyrolysis of heavy oil in SCW is still determined by the free radical mechanism; In addition, SCW is virtually an inert medium for the reactions involving hydrocarbon radicals.[10,16] It can be reasonably proposed that the reaction mechanism and the reaction network developed under conventional environments can be applied to the reaction under SCW environments. A four-lump kinetic model was adopted in this work to describe the pyrolysis of heavy oil in the presence of SCW and $N_2$.[17] Asphaltenes, maltenes, coke, and gas are treated as lump components, transforming into each other through the network as shown in Figure 6.

As the pyrolysis of heavy oil in the presence of SCW could occur in the oil and SCW phases simultaneously or separately, rate constant vectors $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ and $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}}$ are used to distinguish the reaction kinetics of the pyrolysis occurring in different phases. The elements of these vectors, corresponding to their respective lump reaction, are labeled in Figure 6.

For the pyrolysis of heavy oil, the transformation between lump components usually was treated as first-order reactions.[18,19] Based on the understanding of the pyrolysis in the presence of SCW, several additional hypotheses were introduced.

1. When the pyrolysis of heavy oil in the presence of SCW is run in the water/oil two-phase structure, the phase equilibrium can be rapidly achieved. The proportion of maltenes transferred from the oil phase into the SCW phase ($\alpha$)

depends only on the thermodynamic state of water and on the ratio of water to oil.

2. Asphaltenes resulted from the condensation of maltenes in the SCW phase are still retained in the original phase, following the reaction kinetics in the SCW phase.

3. The condensation of maltenes is driven by the difference with respect to its equilibrium concentration in the oil or SCW phase.

The kinetic equations for the pyrolysis of heavy oil in the presence of SCW, therefore, can be established as follows.

$$-\frac{\mathrm{d}C_{\mathrm{As}}}{dt}=\left\{(k_{1o}+k_{2o})(C_{\mathrm{As}}-C_{\mathrm{As.SCW}})-k_{3o}(1-\alpha)(C_{\mathrm{M}}-C^{\mathrm{eq}}_{\mathrm{M.oil}})\right\}+\left\{(k_{1w}+k_{2w})C_{\mathrm{As.SCW}}-k_{3w}\alpha(C_{\mathrm{M}}-C^{\mathrm{eq}}_{\mathrm{M.SCW}})\right\} \tag{3}$$

$$-\frac{\mathrm{d}C_{\mathrm{M}}}{dt}=k_{3o}(1-\alpha)(C_{\mathrm{M}}\text{-}C^{\mathrm{eq}}_{\mathrm{M.oil}})+k_{3w}\alpha(C_{\mathrm{M}}-C^{\mathrm{eq}}_{\mathrm{M.SCW}}) \tag{4}$$

$$-\frac{\mathrm{d}C_{\mathrm{C}}}{dt}=-k_{1o}(C_{\mathrm{As}}-C_{\mathrm{As.SCW}})-k_{1w}C_{\mathrm{As.SCW}} \tag{5}$$

$$-\frac{\mathrm{d}C_{\mathrm{G}}}{dt}=-k_{2o}(C_{\mathrm{As}}-C_{\mathrm{As.SCW}})-k_{2w}C_{\mathrm{As.SCW}} \tag{6}$$

$$-\frac{\mathrm{d}C_{\mathrm{As.SCW}}}{dt}=(k_{1w}+k_{2w})C_{\mathrm{As.SCW}}-k_{3w}\alpha(C_{\mathrm{M}}-C^{\mathrm{eq}}_{\mathrm{M.SCW}}) \tag{7}$$

where $C_i$ in the unit of kg·m$^{-3}$ denotes the weight concentration of lump components in the reaction system. The subscript $i=$ M, As, C and G represents maltenes, asphaltenes, coke and gas, respectively. The weight concentration of the asphaltenes formed in the SCW phase is denoted as $C_{\mathrm{As.SCW}}$. $C^{\mathrm{eq}}_{\mathrm{M.SCW}}$ and $C^{\mathrm{eq}}_{\mathrm{M.oil}}$ are the equilibrium concentrations of maltenes in the SCW and oil phases, calculated by the data listed in Table 2.

There are two special cases for Eqs. 3–7. In the case of $\alpha=0$, the pyrolysis of heavy oil is run in a completely immiscible two-phase structure, with the reaction occurring exclusively in the oil phase. In the case of $\alpha=1$, the interface between the oil and SCW phases no longer exists. The mixture of heavy oil and SCW is in the pseudo-single phase structure, and the reaction occurs in the continuous SCW phase.

The parameters to be determined in Eqs. 3–7 are $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}}$ and $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ as well as $\alpha$. Parameter identification relies on solving the nonlinear least-squares problem $U$ by minimizing the residual sum of squares (RSS) criterion.

$$\begin{cases}\mathrm{RSS}\left(\overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}},\ \overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}},\ \alpha\right)=\sum_{i=1}^{n}\sum_{j=1}^{m}(\overline{y_{ij}}-y_{ij})^2\\ \overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}},\ \overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}\geq 0;\ 0\leq a\leq 1\end{cases} \tag{8}$$

where $Y_{ij}$ is the $j$th state variable from the $i$th experimental run in the kinetic dataset $P=\{P_i,\ i=1,\ n;\ P_i\in\Re_n\}$, and the bar stands for the model predicted values.

The regression of kinetic parameters was applied with the software package of Matlab R2012. The values of $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}}$ and $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ as well as $\alpha$ were first estimated by a multivariable nonlinear minimization (fmincon function) combined with a Runge–Kutta integration algorithm (ode45 function). Then, an $F$-test at the 5% significance level was applied to verify the kinetic model. Arrhenius parameters, apparent activation energy $Ea$ and pre-exponential factor ln *(A)*, were subsequently estimated by the linear regression of $\ln(k_{i)}$ vs. $1/T$ from the slopes and intercept of Arrhenius plots.

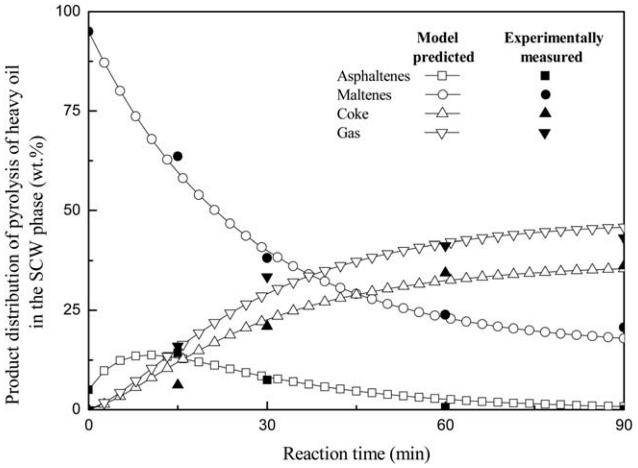

**Figure 7. Model predicted vs. experimentally measured product distributions of pyrolysis in the oil phase; reaction temperature of 703 K and stirring rate of 200 rpm.**

### *Kinetic parameters of pyrolysis of heavy oil*

*Pyrolysis in the Oil Phase.* When a hydrocarbons/SCW system maintains the partially miscible two-phase structure, hydrocarbons are transferred substantially from the oil phase into the SCW phase. On the contrary, the fraction of water solubilized into the oil phase usually keeps at a negligible level till to the supercritical state of the mixture.[20,21] The solubilization of a small quantity of water into the oil phase should have no essential effect on the original mass transfer environments and solvent surroundings in the oil phase. For the pyrolysis in the presence of SCW, the kinetic parameters of the reaction occurring in the possible oil phase thus can be estimated approximately from the pyrolysis in the presence of $N_2$. For Eqs. 3–7, the pyrolysis in the presence of $N_2$, occurring primarily in the liquid oil phase, corresponds to the special case of $\alpha=0$.

The pyrolysis of heavy oil occurring in the oil phase was found to be preferably described by the kinetic model suggested. Typical results of the model predicted vs. experimentally measured product distribution are illustrated in Figure 7. The values of RSS under different operating conditions are always limited within a reasonable range. According to the following $F$-test, the model predicted and experimentally measured product distributions come from normal distributions with the same variance.

The estimated values of $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ are listed in Table 3, with the corresponding results of the RSS analysis and $F$-test attached. Basically, the values of $k_{1o}$, $k_{2o}$, and $k_{3o}$ are of the same order of magnitude. At any stirring rate, the rate constants of three lump reactions all increase to varying degrees with the increase in the reaction temperature. At any reaction temperature, they however show a monotonically decreasing tendency with the increase in the stirring rate.

*Pyrolysis in the SCW Phase.* The pyrolysis of heavy oil in the presence of SCW might be run in the water/oil two-phase structure or in the pseudo-single phase structure. Provided that the pyrolysis in the possible oil phase could be characterized by $\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ determined from the pyrolysis in the presence of $N_2$, the kinetic parameters of the pyrolysis in the SCW phase were estimated subsequently. After an exhaustive calculation, the transferred proportion $\alpha$ during the

Table 3. Rate Constant Vectors $\overrightarrow{k}_o$ of the Pyrolysis of Heavy Oil in the Oil Phase

| Temperature (K) | Stirring Rate (rpm) | $k_{1o}$ ($s^{-1}$) | $k_{2o}$ ($s^{-1}$) | $k_{3o}$ ($s^{-1}$) | RSS | $F$-test (5%) |
|---|---|---|---|---|---|---|
| 663 | 200 | 2.50 E − 05 | 1.30 E − 04 | 7.00 E − 05 | 2.36 E + 01 | pass |
| | 800 | 9.05 E − 06 | 3.50 E − 05 | 2.03 E − 05 | 1.44 E + 01 | pass |
| 683 | 200 | 2.75 E − 04 | 4.38 E − 04 | 2.33 E − 04 | 4.46 E + 01 | pass |
| | 800 | 1.77 E − 04 | 2.42 E − 04 | 1.12 E − 04 | 4.98 E + 01 | pass |
| 703 | 200 | 1.12 E − 03 | 1.44 E − 03 | 6.72 E − 04 | 3.92 E + 01 | pass |
| | 800 | 8.20 E − 04 | 1.02 E − 03 | 4.93 E − 04 | 5.30 E + 01 | pass |

Table 4. Rate Constant Vectors $\overrightarrow{k}_w$ of the Pyrolysis of Heavy Oil in the SCW Phase

| Temperature (K) | Stirring Rate (rpm) | $k_{1w}$ ($s^{-1}$) | $k_{2w}$ ($s^{-1}$) | $k_{3w}$ ($s^{-1}$) | RSS | $F$-test (5%) |
|---|---|---|---|---|---|---|
| 663 | 200 | 2.23 E − 03 | 2.48 E − 03 | 4.35 E − 04 | 1.52 E + 01 | Pass |
| | 800 | 2.67 E − 04 | 2.85 E − 04 | 7.17 E − 05 | 2.62 E + 01 | Pass |
| 683 | 200 | 1.03 E − 02 | 1.18 E − 02 | 1.42 E − 03 | 1.66 E + 01 | Pass |
| | 800 | 1.20 E − 03 | 1.23 E − 03 | 4.90 E − 04 | 2.21 E + 01 | Pass |
| 703 | 200 | 3.15 E − 02 | 3.78 E − 02 | 2.67 E − 03 | 1.64 E + 01 | Pass |
| | 800 | 5.00 E − 03 | 5.47 E − 03 | 1.00 E − 03 | 2.71 E + 01 | Pass |

pyrolysis of heavy oil in the presence of SCW was confirmed to be 1 despite of the change of operating conditions. In other words, at the temperatures ranging from 663 to 703 K, the water density of 0.25 g/cm$^3$, and the water to oil ratio of 2.5:1 (wt), the pyrolysis of heavy oil in the presence of SCW actually is run in the pseudo-single phase structure.

At the thermodynamic states applied, SCW has a low dielectric constant $\varepsilon$ around 3.7. At that time, the solubility of heavy oil in SCW is equivalent to that in toluene ($\varepsilon = 2.4$) or carbon disulfide ($\varepsilon = 2.6$). Also, a high water to oil ratio was adopted in this work. Accordingly, maltenes in the heavy oil are dissolved completely into dense SCW, leaving asphaltenes highly dispersed in the continuous SCW phase. The following discussion, thus, corresponds to the pyrolysis of heavy oil occurring exclusively in the SCW phase, a special case of $\alpha = 1$ for Eqs. 3–7.

Based on the kinetic model developed, the estimated values of $\overrightarrow{k}_w$ are listed in Table 4, with the corresponding results of the RSS analysis and $F$-test attached. Typical results of the model predicted vs. experimentally measured product distribution are illustrated in Figure 8.

Similar to the pyrolysis in the oil phase, the rate constants of lump reactions $k_{1w}$, $k_{2w}$, and $k_{3w}$ increase consistently with the increase in the reaction temperature but decease monotonically with the increase in the stirring rate. A comparison of the data listed in Tables 3 and 4 indicates that the elements of $\overrightarrow{k}_w$ are significantly higher than the corresponding values of $\overrightarrow{k}_o$ by one or two orders of magnitude. One may deduce that the pyrolysis of heavy oil occurring in the SCW phase is greatly accelerated on the whole.

## *Characteristics of pyrolysis of heavy oil in different phases*

The pyrolysis of heavy oil is significantly promoted in the SCW phase but seriously retarded at increasing stirring rates in both phases. To characterize the pyrolysis in the presence of SCW, the Arrhenius parameters of the lump reactions occurring in the oil and SCW phases were evaluated. The calculated values of $Ea$ and ln$(A)$ at different stirring rates, together with their errors, are listed in Table 5.

*Pyrolysis in the Oil Phase.* In the oil phase, the apparent activation energy of the condensation of maltenes to asphaltenes is roughly at the same level with that of the condensation of asphaltenes to gas. In the meantime, the apparent activation energy of the condensation of asphaltenes to coke is much higher than that of other two lump reactions, increasing drastically from 370 to 438 kJ/mol along with the increase in the stirring rate from 200 to 800 rpm.

The condensation of asphaltenes is accomplished by the deep dehydrogenation of polyaromatic heterocycles. There is possibility that the radicals located on polyaromatic heterocycles are capped through the H-abstraction from any H-donor nearby with an intrinsic activation energy lower to 40 kJ/mol.[22] The potential H-donors, mainly hydrogen atoms of the $H_\beta$ type, come from the aliphatic chains or cycloparaffins in the fraction of maltenes. In the oil phase, an increase in the stirring rate improves the contact between asphaltenes and hydrocarbon surroundings, by which the saturation of the radicals in asphaltenes is promoted. Once capped, the

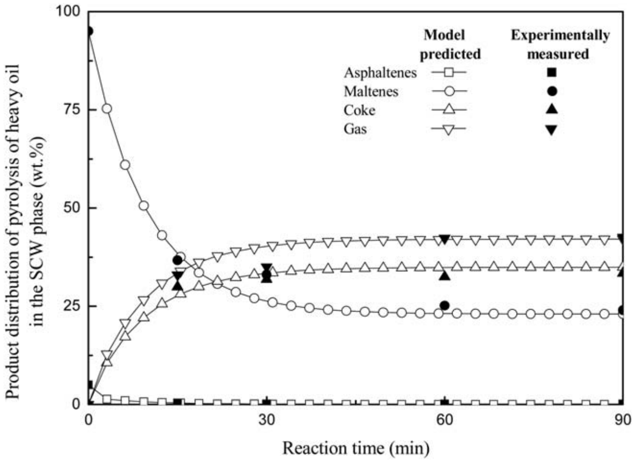

**Figure 8. Model predicted vs. experimentally measured product distributions of pyrolysis in the SCW phase; reaction temperature of 703 K and stirring rate of 200 rpm.**

**Table 5. Arrhenius Parameters of Lump Reactions in the Oil and SCW Phases at Varied Stirring Rates**

| Reaction Phase | Stirring Rate(rpm) | Asphaltenes → Coke *Ea*(kJ/mol) | Asphaltenes → Coke ln(A) | Asphaltenes → Gas *Ea*(kJ/mol) | Asphaltenes → Gas ln(A) | Maltenes → Asphaltenes *Ea*(kJ/mol) | Maltenes → Asphaltenes ln(A) |
|---|---|---|---|---|---|---|---|
| Oil phase | 200 | 3.70 E + 02 ± 4.95 E + 01 | 6.06 E + 01 ± 8.72 E + 00 | 2.33 E + 02 ± 2.34 E + 00 | 3.74 E + 01 ± 4.10 E − 01 | 2.19 E + 02 ± 4.50 E + 00 | 3.43 E + 01 ± 7.90 E − 01 |
|  | 800 | 4.38 E + 02 ± 7.29 E + 01 | 7.21 E + 01 ± 1.28 E + 01 | 3.27 E + 02 ± 2.22 E + 01 | 5.32 E + 01 ± 3.90 E + 00 | 3.10 E + 02 ± 7.20 E + 00 | 4.95 E + 01 ± 1.27 E + 00 |
| SCW phase | 200 | 2.57 E + 02 ± 1.86 E + 01 | 4.46 E + 01 ± 3.27 E + 00 | 2.64 E + 02 ± 1.79 E + 01 | 4.61 E + 01 ± 3.16 E + 00 | 1.76 E + 02 ± 2.76 E + 01 | 2.84 E + 01 ± 4.86 E + 00 |
|  | 800 | 2.84 E + 02 ± 1.02 E + 00 | 4.73 E + 01 ± 1.80 E − 01 | 2.86 E + 02 ± 6.62 E + 00 | 4.78 E + 01 ± 1.17 E + 00 | 2.57 E + 02 ± 6.31 E + 01 | 4.13 E + 01 ± 1.11 E + 01 |

formation of the radicals again on polyaromatic heterocycles will rely more on the direct dehydrogenation from aromatic rings with an intrinsic activation energy as high as 480 kJ/mol. As a result, an increasing apparent activation energy of the condensation of asphaltenes to coke occurs with the increase in the stirring rate.

Maltenes are always the primary component in both raw heavy oil and liquid oil products, so the radical reactions occurring throughout the pyrolysis serve mainly for the condensation of maltenes. The condensation of maltenes, participated by a number of molecules, can proceed through the radical reactions with relatively lower activation energies, such as addition of olefins to radicals and cyclization.[23,24] These radical reactions, especially bimolecular ones, can surely be promoted by improved mass transfer. However, the simultaneous termination of radicals through coupling will also be facilitated. An increase in the apparent activation energy of the condensation of maltenes by nearly 100 kJ/mol at increasing stirring rates suggests that the promotion resulted from the improved mass transfer is offset by the concurrent coupling of radicals. At that time, the condensation of maltenes has to follow the dehydrogenation among condensed aromatic rings with higher activation energies, a mechanism similar to the condensation of asphaltenes.

*Pyrolysis in the SCW Phase.* In the SCW phase, the apparent activation energy of the condensation of asphaltenes to coke is nearly the same with that of the condensation of asphaltenes to gas, increasing slightly by about 20 kJ/mol along with the increase in the stirring rate. Meanwhile, the apparent activation energy of the condensation of maltenes at the stirring rate of 200 rpm is only 2/3 that of other two lump reactions, but increases significantly to 257 kJ/mol at the stirring rate of 800 rpm. A detailed analysis of the data listed in Table 5 indicates that the condensation of asphaltenes in the SCW phase has a much lower activation energy than that in the oil phase does. The difference at the stirring rate of 800 rpm can even be as high as 154 kJ/mol.

Water clusters around solutes, whose scale and structure are sensitive to the thermodynamic state of water and the property of solutes, appear in a SCW solution.[25–27] Many a research has confirmed that the reaction behavior of the organic reactions occurring in SCW might be influenced by solvent clusters.[28,29] Once heavy oil is dissolved into SCW, water molecules prefer to form solvent clusters around polar asphaltenes rather than around nonpolar maltenes. Consequently, the original immediate contact between maltenes and asphaltenes in the oil phase is avoided. Without efficient H-donors, the asphaltenes trapped in water clusters can be readily transformed to coke through the deep dehydrogenation of condensed segments. By the fact that the apparent activation energy of the condensation of asphaltenes to coke in the SCW phase is always lower than that in the oil phase, asphaltenes should be isolated more efficiently by the water clusters in SCW surroundings than by the high viscosity in oil surroundings. The dynamic viscosity of SCW, normally between 10 and $10^2$ $\mu$Pa·s, is much lower than that of heavy oil by several orders of magnitude. Benefited from the excellent mass transfer environments in the SCW phase, the condensation of maltenes can be accomplished through the radical reactions mentioned before with lower activation energies. Accordingly, a low apparent activation energy of 176 kJ/mol is observed at the stirring rate of 200 rpm.

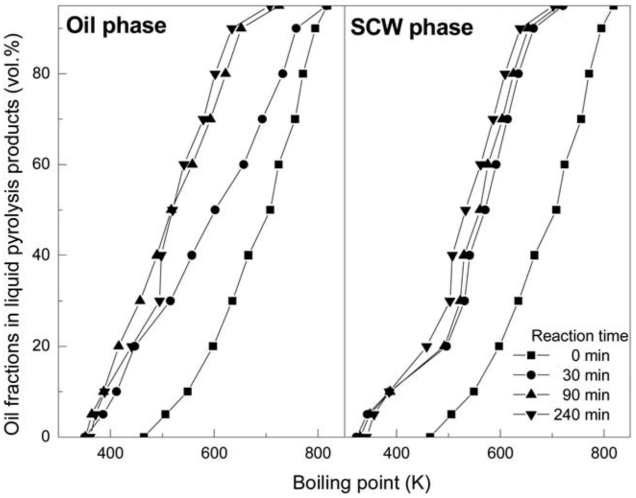

**Figure 9. Boiling point distribution of liquid products obtained at extended reaction times; reaction temperature of 683 K and stirring rate of 200 rpm; left: reaction in the oil phase, right: reaction in the SCW phase.**

After the introduction of vigorous stirring, the micromixing of the heavy oil/SCW system in the pseudo-single phase structure is intensified. On the one hand, the cluster structure around asphaltenes could be partially destroyed, by which the asphaltenes trapped in water clusters are likely to have effective contact with maltenes dissolved in SCW surroundings. On the other hand, the termination of radicals through coupling in the reaction system might be promoted. Apparently, the destruction of solvent clusters at high stirring rates can nearly be neglected since the activation energy of the condensation of asphaltenes to coke only increases slightly. However, a significant increase in the activation energy of the condensation of maltenes occurs at the increasing stirring rate. That is to say, the promoted coupling of radicals has a vital negative influence on the condensation of maltenes in the SCW phase.

### *Upgrading efficiency of pyrolysis of heavy oil in SCW*

The above discussion based on lumping approach suggests a positive influence of SCW environments on the reaction kinetics of the pyrolysis of heavy oil. However, a division of liquid products to maltenes and asphaltenes is far from sufficient to assess the upgrading efficiency of pyrolysis. By this consideration, the liquid products collected at extended reaction times were further characterized by simulated distillation GC to determine the distribution of boiling points. Typical results of the pyrolysis in the oil and SCW phases at the temperature of 683 K and stirring rate of 200 rpm are illustrated in Figure 9. By convention, the liquid products were divided into gasoline, diesel, vacuum gas oil (VGO), and residua with the boiling point ranges as follows: initial boiling point (IBP) to 477 K, 477 to 638 K, 638 to 773 K, and 773 K to final boiling point (FBP).

For the liquid products collected in the pyrolysis in the oil phase, the pattern of the boiling point distribution varies substantially with reaction progress. At the reaction time of 30 min, the upgrading is reflected chiefly by the increase in the oil fractions of lower boiling points. The fraction of gasoline in the liquid product increases from the initial value of 2 to 25 vol %, by which the value of IBP decreases from 465 to 351 K. Although the fraction of VGO decreases from 50 to 35 vol %, still there exist about 8 vol % of residua in the liquid product. Consequently, the value of FBP keeps at a high level of 816 K. With the extension of reaction time to 90 min, a decrease in the fractions of higher boiling points occurs and residua can no longer be found in the product. On the contrary, the fractions of gasoline and diesel increase to 36 and 49 vol %, respectively. When approaching equilibrium, the fraction of diesel in the liquid product increases continuously to 64 vol % but that of gasoline decreases to 27 vol %.

For the pyrolysis in the SCW phase, the rate approaching the equilibrium distribution of boiling points is greatly accelerated. After 30 min's reaction, the pattern of the boiling point distribution of the liquid product is already similar to that of the liquid product at equilibrium. On the one hand, the fractions of gasoline and diesel in the liquid product reach 18 and 63 vol %. On the other hand, the fraction of VGO decreases to 19 vol %. Furthermore, no residua exist in the product. In the following reaction, the fractions of gasoline and diesel increase slightly to the equilibrium values of 24 and 66 vol %. Meanwhile, the fraction of VGO decreases monotonically to 10 vol %. Comparing with the reaction in the oil phase, one may propose that the upgrading efficiency of the pyrolysis of heavy oil can be effectively increased by running reactions in the SCW phase.

Through pyrolysis, the raw heavy oil containing mainly VGO and residua is upgraded to lighter oil products, mostly in the boiling point ranges of gasoline and diesel. In whichever reaction medium, at the same temperature the liquid products collected at equilibrium, however, have a similar distribution of oil fractions. It is deduced that the presence of SCW in pyrolysis might have a minor influence on the properties of pyrolysis products. Such a deduction is confirmed by the subsequent characterizations on the liquid products collected at equilibrium. Detailed results are listed in Table 6.

No matter the pyrolysis is applied in the oil or SCW phase, the molecular weights of the equilibrium liquid products are all 1/3 to 1/4 that of the raw heavy oil. The dynamic viscosities of the liquid products are 2 to 4 times that of

**Table 6. Properties of Equilibrium Liquid Product of Pyrolysis of Heavy Oil in the Oil and SCW Phases**

| Reaction Phase | Temperature (K) | Molecular Weight (kg/kmol) | API Gravity (°) | Dynamic Viscosity (298 K, Pa·s × 10$^3$) | H/C Ratio |
|---|---|---|---|---|---|
| Oil phase | 663 | 250.4 | 33 | 3.98 | 1.54 |
| | 683 | 249.1 | 33 | 3.60 | 1.57 |
| | 703 | 225.3 | 35 | 2.41 | 1.61 |
| SCW phase | 663 | 250.1 | 33 | 2.21 | 1.53 |
| | 683 | 261.1 | 32 | 2.20 | 1.50 |
| | 703 | 258.0 | 34 | 1.89 | 1.52 |

ambient water. The API gravities vary between 32° and 35°, indicating the improved quality of liquid products. Due to the formation of coke during pyrolysis, the H/C ratios of the liquid product can be as high as 1.61.

## Conclusions

The pyrolysis of heavy oil accompanied by high pressure $N_2$ and dense SCW was described by a four-lump kinetic model. The condensation of maltenes and the condensation of asphaltenes occur in series, during which the former reaction is driven by the difference with respect to the equilibrium concentration of maltenes. The pyrolysis in the presence of $N_2$ and SCW was confirmed to be run in the oil and SCW phases, respectively. Due to the saturation of radicals on polyaromatic heterocycles and the termination of radicals through coupling, in whichever phase the lump reactions involved in the pyrolysis are suppressed at increasing stirring rates. In the SCW phase, the superior mass transfer environment facilitates the condensation of maltenes. Also, the condensation of asphaltenes isolated by solvent clusters is significantly promoted. Further characterization based on simulated distillation suggests that the pyrolysis in the SCW phase might reach its equilibrium distribution with accelerated reaction rate. Accordingly, the upgrading efficiency of pyrolysis is increased. Relatively speaking, the introduction of SCW into the pyrolysis of heavy oil exerts influence mainly on reaction kinetics rather than on the properties of equilibrium products.

## Acknowledgments

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## Notation

$C_i$ = eight concentration of lump components in the reaction system, kg.m$^{-3}$

$C_{\mathrm{As.SCW}}$ = weight concentration of the asphaltenes formed in the SCW phase, kg.m$^{-3}$

$C^{\mathrm{eq}}_{\mathrm{M.SCW}}$ = equilibrium weight concentration of maltenes in the SCW phase, kg.m$^{-3}$

$C^{\mathrm{eq}}_{\mathrm{M.oil}}$ = equilibrium weight concentration of maltenes in the oil phase, kg.m$^{-3}$

$Ea$ = apparent activation energy, kJ/mol

$k_{io}$ = rate constant of transformation between lump components in the oil phase, s$^{-1}$

$k_{iw}$ = rate constant of transformation between lump components in the SCW phase, s$^{-1}$

$\overrightarrow{\boldsymbol{k}}_{\boldsymbol{o}}$ = rate constant vector of transformation between lump components in the oil phase, s$^{-1}$

$\overrightarrow{\boldsymbol{k}}_{\boldsymbol{w}}$ = rate constant vector of transformation between lump components in the SCW phase, s$^{-1}$

ln(A) = natural logarithm of pre-exponential factor

$m_i$ = weight of the collect lump component, Kg

$t$ = reaction time, s

$Y_i$ = weight fraction of lump components in the product, wt %

### *Greek letters*

$\alpha$ = transferred proportion of maltenes from the oil phase into the SCW phase

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