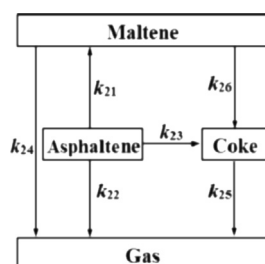# Kinetic and reaction pathway of upgrading asphaltene in supercritical water

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HIGHLIGHTS

- Asphaltene was converted to gas, maltene and coke in SCW (supercritical water).
- Asphaltene transformation in SCW obeyed the first-order kinetic.
- A new reaction pathway model was proposed for upgrading asphaltene in SCW.
- The possibility of secondary reaction of coke to gas was illustrated.

GRAPHICAL ABSTRACT

ABSTRACT

Experiments of upgrading asphaltene in Supercritical Water (SCW) were conducted in autoclaves with sealed gold tube reactors to elucidate the reaction pathway and reaction kinetics. The experiments were performed at temperature of 400–450 °C, pressure of 30 MPa and residence time ranging from 0 to 120 min. The products obtained from the upgrading asphaltene in SCW included gas, maltene and coke. Kinetic analysis showed that upgrading asphaltene in SCW obeyed a first-order kinetic with apparent activation energy of 51.11 kJ/mol. Three possible 4-lump kinetic models were proposed to discuss the detailed reaction pathway of upgrading asphaltene in SCW. The first-order kinetic equations were used to evaluate the reliability of each model from the aspect of correlation coefficient (R^2). The results showed that Model 2, considering the parallel reaction of asphaltenes transformation to gas, maltene and coke, the consecutive reaction from maltene to gas and coke, the secondary reaction of coke to gas, was illustrated as the optimal reaction pathway model for upgrading asphaltene in SCW.

1. Introduction

Asphaltene, insoluble in light *n*-alkanes and soluble in aromatic solvents, is known as the most complex and heaviest fractions of crude oil, bitumen, heavy oil, or vacuum residue (Savage and Klein, 1988; Sun et al., 2010; Yasar et al., 2001). It usually consists of highly condensed polyaromatic macromolecules bearing long aliphatic chains and alicyclic substituents (Mandal et al., 2012a, b). In the refining processes, asphaltene is prone to form coke and deactivate catalyst (Akmaz et al., 2012; Ayala et al., 2012; Zhao and Yu, 2011). Moreover, high concentrations of heteroatoms (N, S) and metal elements (Ni, V) in asphaltene will seriously interfere with the refining processes (Zhang et al., 2011; Zhao et al., 2011). These situations will become worse with the depletion of the conventional light crude oil reserve and the use of more heavy oils with significant portion of asphaltene as substitute (AlHumaidan et al., 2013). To

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maximize the useful value of heavy oil, it is necessary to optimize the utilization of asphaltene.

Nowadays, numerous technologies based on carbon rejection and hydrogen addition rout have been applied to address the problematic asphaltene. Among the technologies of carbon rejection, the technique of deasphalting is often used because of its effective removal of heteroatoms in the extraction processes (Ali and Abbas, 2006). However, the extraction processes usually need to consume large amounts of organic solvent and the mass loss of heavy oil after the asphaltene precipitation reaches highly 30% (Brons and Yu, 1995). The other techniques of carbon rejection, especially delayed coking, are also preferred by the refineries due to their lower investment (Rana et al., 2007). But with the decreasing demand for fuel oil, these processes will fall into dilemma as little liquid products but much coke were formed from these thermal processes (Siskin et al., 2006; Xu et al., 2007). Although the hydrogen addition processes can retard the formation of coke and convert heavy components into valuable light fraction, the cost of hydrogen is considerable (Furimsky, 2013; Zhao and Wei, 2008). Additionally, the deposition of coke and metals can easily deactivate the expensive catalysts for upgrading heavy oil (Xu et al., 2009). Therefore, novel processes, using alternative hydrogen sources to replace expensive molecular hydrogen and retard the coke formation, need to be developed.

SCW is defined as the thermodynamic state above the critical temperature and pressure (374.3 °C and 22.1 MPa). In recent years, the ubiquitous solvent properties and potential abilities to donate hydrogen of SCW have aroused great interest in the scientific community (Yan et al., 2009). Some researchers believe that SCW could not only serve as the solvent but also provide the active-hydrogen for capping of reactive fragments to form more light components and less coke in upgrading heavy oil (Cheng et al., 2009; Kozhevnikov et al., 2010; Morimoto et al., 2010; Sato et al., 2003; Watanabe et al., 2010; Zhao et al., 2006). It is also reported that C–O bonds in ethers and esters, C–S bonds in aliphatic chain and metal elements incorporated in asphaltene are easily broken in SCW (Mandal et al., 2011, 2012b; Savage, 1999). Unfortunately, upgrading asphaltene in SCW has not garnered attention until recently. Kozhevnikov et al. (2010) reported that the formation of gas and maltene was mainly through the dealkylation of aromatic substituents and aromatization for the cracking of asphaltene in SCW. Morimoto et al. (2012) discussed the influence of temperature and pressure on the extraction of asphaltene with SCW.

For upgrading asphaltene in SCW, kinetic study is an effective way to predict the product distribution and to optimize the reaction conditions (AlHumaidan et al., 2013; Galarraga et al., 2012). However, most of the kinetic studies were focused on asphaltene pyrolysis system while kinetic of upgrading asphaltene in SCW system was seldom investigated. Although temperature has a decisive effect on kinetic for upgrading asphaltene in both systems, effect of reaction environment on kinetic cannot be neglected. It is reported that the miscibility of SCW with most organic compounds and gases may provide a mass transfer environment that is completely different from the pyrolysis system. Considering the huge differences in mass transfer environments and the solvent effect of SCW, kinetic study of upgrading asphaltene in SCW is essential. The transformation of asphaltene, involving polymerization, condensation, carbonization and lots of intrinsic reactions among the products, is a complicated process (Zhao et al., 2011). Therefore, a simplified modeling approach, namely the discrete lumping, is adopted to study the kinetic of upgrading asphaltene in SCW. In this modeling approach, the products for upgrading asphaltene in SCW are lumped into gas, maltene and coke.

To avoid the catalytic effect of the reactor walls, experiments of upgrading asphaltene in SCW were conducted in an autoclave with gold tubes. In this study, effects of temperature and reaction time on upgrading asphaltene in SCW were studied. Meanwhile, the reaction pathway and kinetics for upgrading asphaltene in SCW were analyzed in detail based on experimental data.

2. Experimental section

2.1. Chemicals and materials

Asphaltene was separated from Tahe heavy crude oil following a method similar to the ASTMD 6560. The asphaltene samples were precipitated from crude oil by ultrasonic dispersion in 40:1 (v/v) excess of *n*-hexane overnight. The precipitate separated by centrifugation at 6000 r/min for 10 min was dissolved in toluene with a ratio of 20:1. Subsequently, after separation by centrifugation and concentration, the asphaltene was subjected to Soxhlet extraction with *n*-hexane until the reflux remained colorless. Finally, the extracted asphaltene was dried at 150 °C in the nitrogen gas atmosphere and was finely pulverized. The asphaltene elemental compositions and metal contents determined by a Vario EL-III Elemental analyzer and an inductively coupled plasma mass spectrometer (ICP–MS, Agilent 7700X, USA), respectively, are shown in

Table 1
Properties of the asphaltene.

Properties	Units	Values
Carbon	wt%	84.63
Hydrogen	wt%	6.97
Oxygen	wt%	2.75
Nitrogen	wt%	1.07
Sulfur	wt%	4.29
Nickel	mg/kg	90.4
Vanadium	mg/kg	720.1
Atomic ratio of H/C	–	0.98
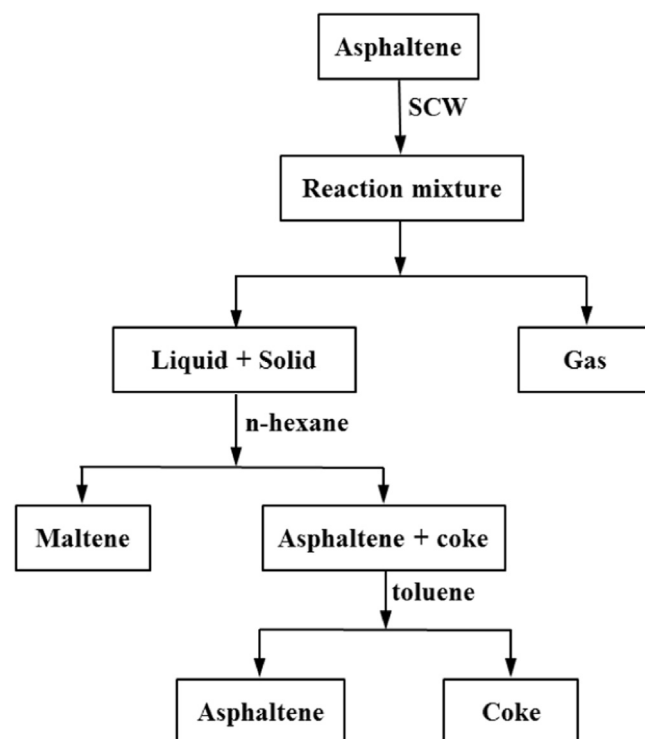
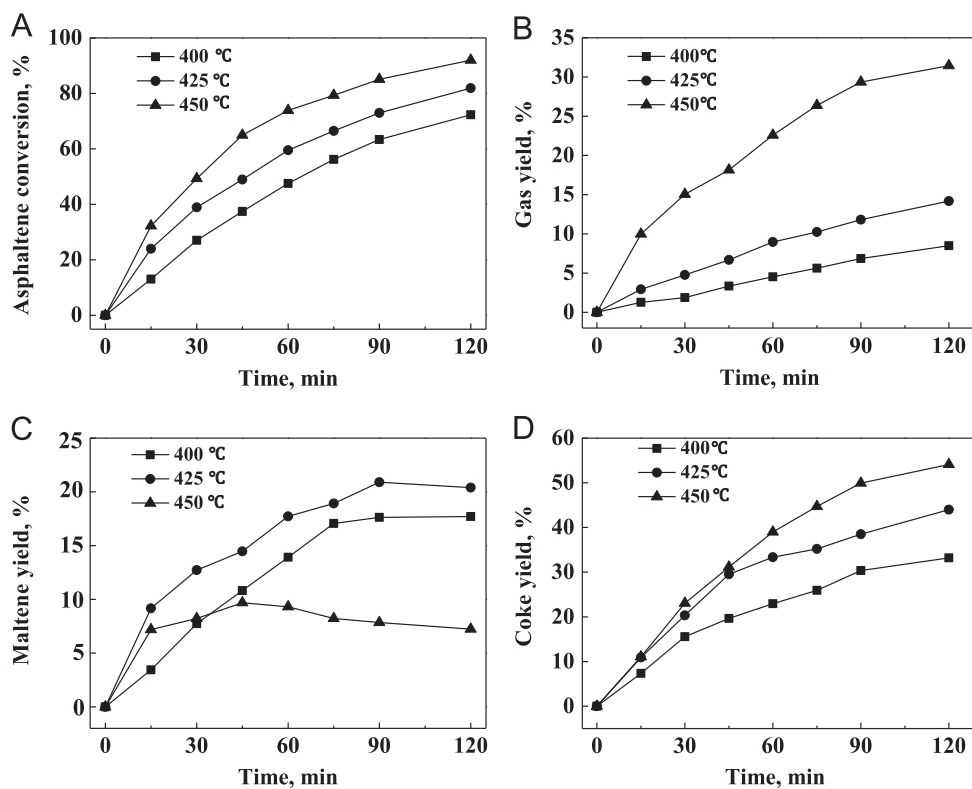**Fig. 1.** Product separation flowchart.

Fig. 2. Asphaltene conversion and product yield for asphaltene transformation in SCW (supercritical water) at 400, 425 and 450 °C: (A) asphaltene conversion, (B) gas yield, (C) maltene yield and (D) coke yield.
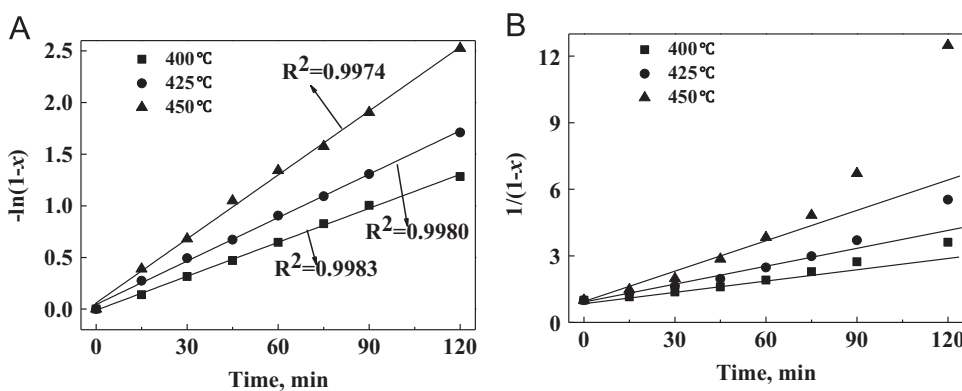

Fig. 3. First-order (A) and second-order (B) kinetic plot for upgrading asphaltene in SCW (supercritical water) at 400, 425 and 450 °C.

Table 1. In this experiment, *n*-hexane and toluene (with 99.99% purity) were purchased from J.T. Baker and were used as received.

2.2. SCW experiments

Experiments of upgrading asphaltene in SCW were performed in an autoclave with gold tube similar to the method described in literature (Hill et al., 2003). The length, inner diameter and wall thickness of gold tubes were 80 mm, 6 mm and 0.28 mm, respectively. The gold tubes were welded at one end and were incandesced in a muffle furnace at 800 °C for 6 h to remove any residual organic material. A 100 mg asphaltene sample and 200 μL water were carefully placed in the gold tubes using a glass funnel and a glass syringe, respectively. When loaded, the open end of each gold tube was flushed with argon gas to replace the air in the tube completely and then was welded in the argon gas atmosphere. Weight of the gold tube and sample was recorded before and after welding to ensure the accuracy of each

Table 2
First-order kinetic constants for upgrading asphaltene in SCW.

Temperature (°C)	Kinetic constant ($\times 10^2$ min^{-1})	Correlation coefficient (R^2)	Standard error ($\times 10^4$ min^{-1})	Activation energy E_a (kJ/mol)
400	1.096	0.9974	1.7	51.11
425	1.402	0.9980	2.4	
450	2.066	0.9983	4.0	

experiment. The sealed gold tubes were then loaded into stainless steel autoclaves, which was controlled by an automatic air-driven water pump/valve system to maintain pressure at (30 ± 1) MPa for all the experiments in this study. Two k-type thermocouple probes were used to monitor the inside and wall temperature of autoclave, respectively. The sealed autoclaves, pre-pressurized to 30 MPa with water, were quickly placed in a pre-heated, isothermal electrical furnace. The

reaction time varied from 0 to 120 min. Once the reaction time elapsed, the autoclave was removed from the electrical furnace and was quickly quenched to room temperature with a mixture of ice and water. The gold tubes were weighed before and after each reaction to determine whether they had leaked. If the mass of a gold tube decreased by 2 mg during the course of the reaction, the data from it was discarded.

2.3. Product analysis

After the reaction, the gold tube, cleaned with dichloromethane solvent, was placed into a vacuum collector, which was connected to a vacuum pump and an Agilent 7890 A gas chromatograph (GC). The gold tube was pierced by a steel needle attached to the vacuum collector into which the gas was released. After 30 s equilibration, the valve of the vacuum collector was switched to the channel connected to the GC. The gaseous hydrocarbons (C_{1-5}), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and hydrogen (H_2) were analyzed with a GC equipped with a flame ionization detector and two thermal conductivity detectors. High-purity nitrogen and hydrogen (99.999%)
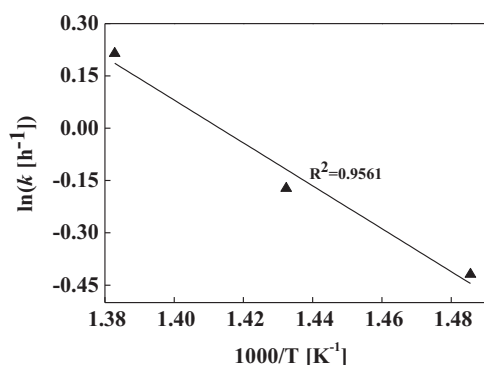
Fig. 4. Arrhenius plots for first-order kinetic model at 400–450 °C.

were employed as a carrier gas. A HP-AL/S capillary column (25 m × 0.32 mm × 8 μm) was operated at 60 °C for 3 min, sequentially programmed to step from 60 to 190 °C at 25 °C/min, and then held isothermally at 190 °C for 3 min. All the gases were quantified with external standard method.

Following gas analysis, the separation procedure of the gold tube residual was shown in Fig. 1. The pierced gold tube was cut open with a clipper and placed into a glass bottle filled with *n*-hexane. The maltene dissolved in *n*-hexane was extracted by ultrasound until the *n*-hexane solvent became colorless. Then, the maltene was dried with anhydrous sodium sulfate and weighed by evaporating the *n*-hexane. Subsequently, asphaltene was extracted with toluene and weighed after the removal of toluene. Finally, the mass of coke was determined by weighing the remainder. All the results were the average of two experiments. The following definitions (Eqs. (1)–(3)) were used to evaluate the asphaltene conversion, product yield and product selectivity:

$$\text{Asphaltene conversion } x(\text{wt}\%) = \left(1 - \frac{m_{t,\text{ asphaltene}}}{m_{0,\text{ asphaltene}}}\right) \times 100 \qquad (1)$$

$$\text{Product yield } y_i(\text{wt}\%) = \frac{m_i}{m_{0,\text{ asphaltene}}} \times 100 \qquad (2)$$

$$\text{Production selectivity}(\%) = \frac{y_i}{x} \qquad (3)$$

where $m_{0,\text{ asphaltene}}$ is the initial mass of asphaltene, $m_{t,\text{ asphaltene}}$ is the mass of remaining asphaltene at the reaction time of t, m_i is the mass of product i at the reaction time of t.

3. Results and discussion

3.1. Product composition of upgrading asphaltene in SCW

Upgrading asphaltene in SCW is a complex process involving side-chain cleavage, reorganization, condensation and polymerization
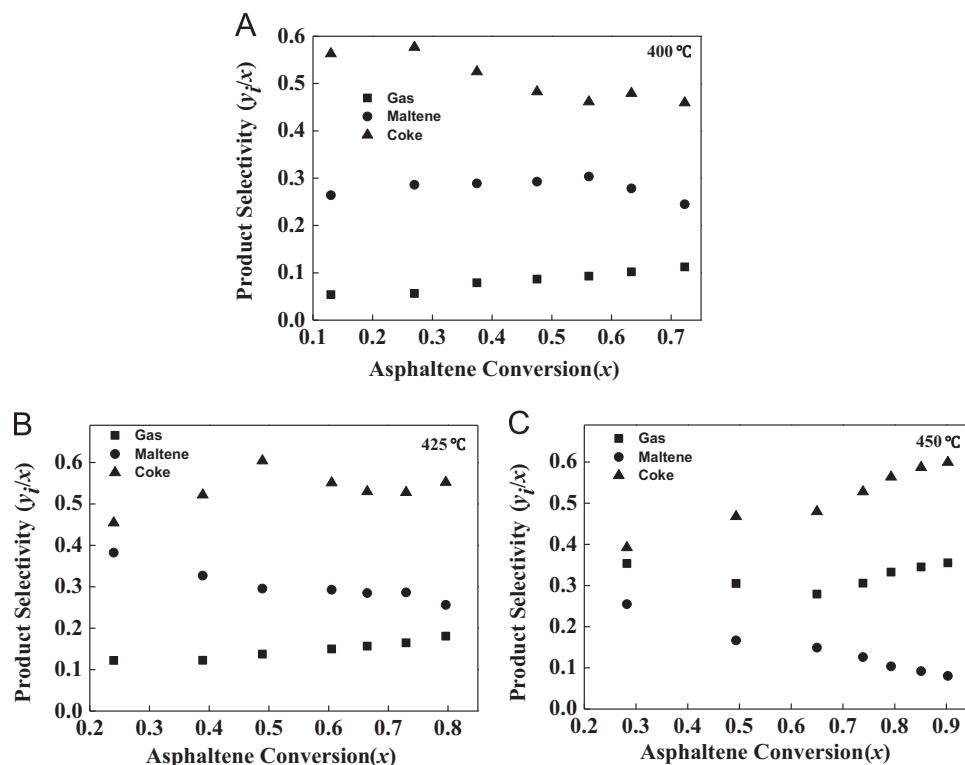
Fig. 5. The first rank delplot: product selectivity for upgrading asphaltene in SCW (supercritical water) at (A) 400 °C, (B) 425 °C and (C) 450 °C.
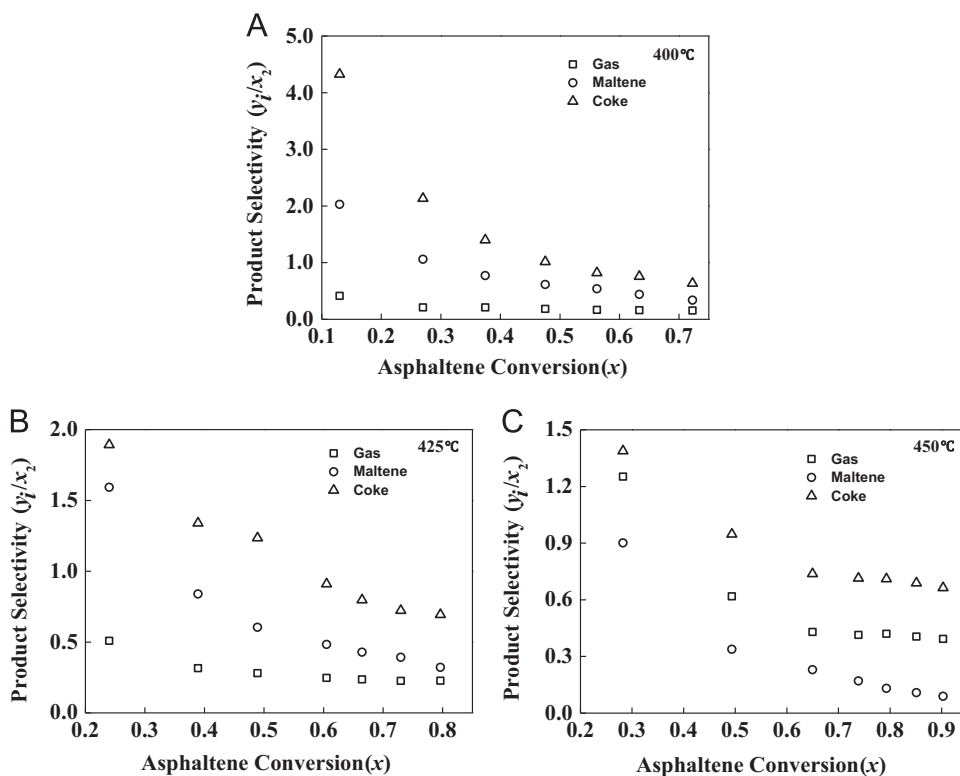
Fig. 6. The secondary rank delplot: product selectivity for upgrading asphaltene in SCW (supercritical water) at (A) 400 °C, (B) 425 °C and (C) 450 °C.
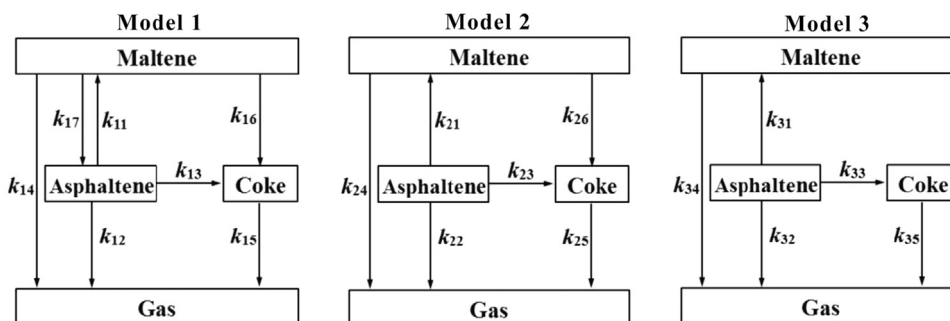

Fig. 7. Four-lump reaction pathway models for upgrading asphaltene in SCW (supercritical water).

reaction among intermoleculars. The main products of upgrading asphaltene in SCW can be classified into gas, maltene and undesirable coke based on the phase state. Effects of reaction time (0–120 min) and temperature (400–450 °C) on asphaltene conversion, yields of gas, maltene and coke were shown in Fig. 2(A)–(D), respectively.

As expected, longer reaction time and higher temperature favored the transformation of asphaltene, and the formation of more gas and coke. With the reaction temperature increasing from 400 to 450 °C, the asphaltene conversion, gas yield and coke yield increased from 72.27%, 8.50%, 33.19% to 91.99%, 32.05%, 54.11% respectively for upgrading asphaltene in SCW at 120 min. As for the maltene, the yield had a maximal value for each temperature. When the temperature was 400 °C, the maltene yield increased with the reaction time; while at 425 °C, the maltene yield reached the maximum of 20.89% at 90 min and then decreased with reaction time; as temperature increased to 450 °C, the maximal yield of maltene was achieved at 45 min and subsequently decreased with reaction time. This phenomenon was indicative of polymerization or condensation reactions of maltene (Yasar et al., 2001).

3.2. Kinetics of upgrading asphaltene in SCW

As most of the previous researches suggested, the asphaltene decomposition obeyed first-order (Trauth et al., 1992; Wiehe, 1993; Yasar et al., 2001; Zhao et al., 2001) or second-order kinetic (Martinez et al., 1997; Wang and Anthony, 2003; Zhao et al., 2011). Considering the complexity of upgrading asphaltene in SCW, a mathematical model with a power law was expressed in the following form:

$$-\frac{dy_1}{dt} = ky_1^n \tag{4}$$

where y_1 is the weight fraction of asphaltene, k is the apparent rate constant and n is the apparent reaction order.

Fig. 3(A) and (B) shows the fitting lines of first-order ($n=1$) and second-order ($n=2$) kinetic equation, respectively. It can be seen that all the data showed superior linear relation matching with the first-order kinetics model, but the data deviated the second-order kinetics model during 60–120 min. The linearity of these plots

Table 3
Rate constants of the 4-lump kinetic models.

Model	Rate constants	Temperatures (°C)		
		400	425	450
1	k_{11}	2.767E+07	6.072E−03	2.691E−02
	k_{12}	1.510E+01	1.790E−03	1.484E−25
	k_{13}	9.502E+03	8.869E−03	9.769E−20
	k_{14}	6.565E+03	1.123E−14	7.610E−01
	k_{15}	3.919E+03	1.504E−03	1.174E−17
	k_{16}	4.396E+01	2.542E−08	1.221E+00
	k_{17}	1.357E+08	7.231E−03	7.134E−01
	R^2	0.2534	0.9825	0.5442
2	k_{21}	3.565E−03	5.043E−03	5.894E−03
	k_{22}	7.495E−04	1.496E−03	6.761E−03
	k_{23}	5.859E−03	8.348E−03	9.099E−03
	k_{24}	1.577E−03	3.241E−03	2.613E−17
	k_{25}	1.474E−03	7.372E−04	4.725E−04
	k_{26}	7.539E−14	6.289E−13	2.007E−02
	R^2	0.9849	0.9888	0.9527
3	k_{31}	3.565E−03	5.043E−03	3.945E−03
	k_{32}	7.495E−04	1.496E−03	5.670E−03
	k_{33}	5.859E−03	8.348E−03	1.198E−02
	k_{34}	1.577E−03	3.241E−03	9.851E−03
	k_{35}	1.474E−03	4.725E−04	3.528E−17
	R^2	0.9849	0.9888	0.8147

Note: units of k_{ij} values, for 1st order case min^{-1}.
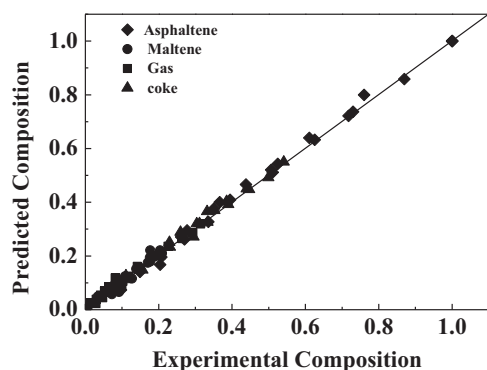
Fig. 8. Parity plots for upgrading asphaltene in SCW (supercritical water).

allowed one to conclude that upgrading asphaltene in SCW obeyed first-order kinetic rather than second-order kinetic.

The apparent rate constants determined from the slopes of first-order kinetics model were presented in Table 2 along with the correlation coefficient, R^2, and the standard error (SE). As expected, the kinetic parameter, k, increased with temperature. Additionally, it was worth noting that the values of SE increased with temperature but always within the normal error range.

The Arrhenius plot (ln k vs $1/T$) used to determine the activation energy (E_a) is displayed in Fig. 4. As a general result, the activation energy for this range of temperatures was 51.11 kJ/mol with a correlation coefficient, $R^2 = 0.9561$.

3.3. Reaction pathway model of asphaltene upgrading in SCW

For upgrading asphaltene in SCW, the goal is to optimize the utilization of asphaltene and enhance the quality of products. But just analyzing the asphaltene conversion kinetic was not sufficient to further predict the composition and quality of the obtained products. Therefore, a more detailed reaction pathway model is required.

3.3.1. Formulation of reaction pathway model

Upgrading asphaltene in SCW is a complex process accompanying with numerous secondary reactions of the products. Discriminating the rank of the products is helpful to optimize the reaction pathway (Martinez et al., 1997). This goal can be achieved with the help of the delplot technique (Bhore et al., 1990; Klein et al., 2012).

For the first delplot analysis, the rank of the product is determined by the intercept of the delplot model constructed by plotting product selectivity against the corresponding asphaltene conversion. Usually, primary products possess positive finite intercepts on a first-rank delplot, whereas species with zero intercept are secondary or higher rank products. Fig. 5(A)–(C) provides the first rank delplot for products (gas, maltene and coke) of upgrading asphaltene in SCW at 400, 425 and 450 °C. It can be seen that the extrapolated lines of maltene gave positive intercept but the extrapolated lines for gas and coke might give zero intercepts for all the cases. These results indicated that the products except maltene were secondary or higher rank products for asphaltene upgrading in SCW. According to the second delplot model theory proposed by Klein et al. (2012), parts of the gas and coke might be the secondary products, which could be demonstrated by the secondary rank delplot shown in Fig. 6(A)–(C). Furthermore, similar conclusions has been reported by previous researches. In the work of Trauth et al. (1992), gas formed from the secondary reaction of maltene was confirmed in the investigation of asphaltene pyrolysis kinetic. Martinez et al. (1997) reported the formation pathway of coke from maltene for asphaltene pyrolysis at 475 °C. Similar results were also found by Zhao et al. (2011) in the study of hydrocracking asphaltene.

Although the reaction pathways of asphaltene have been extensively reported, the secondary reactions of coke were always neglected. Among the previous reaction pathway of asphaltene, coke was always treated as an inert substance, which ignored the transformation of coke gas.

Based on the above analysis and conjecture, three possible reaction pathway models were proposed for upgrading asphaltene in SCW. These models, not only including the parallel reaction of asphaltene transformation to gas, maltene and coke but also considering the secondary reactions of maltene and coke, were shown in Fig. 7.

3.3.2. Optimization of reaction pathway model

For upgrading asphaltene in SCW, kinetic investigation may be a useful method to validate the reliability of the proposed reaction pathway model. In this paper, the product yield data was used to fit the first-order kinetic equations in order to determine the possible reaction pathway of asphaltene. And the kinetic rate constants k_{ij} ($i=1$–3; $j=1$–7) for each corresponding model were calculated with 1stOpt statistical analysis software (version 5.0), according to the Runge–Kutta–Fehlberg (RKF) method and Universal Global Optimization (UGO) algorithms. The suitability of each model was evaluated by R^2, which is defined as:

$$R^2 = \frac{SST - SSE}{SST} \tag{5}$$

where

$$SSE = \sum_{i=1}^{N} (y_i^{exp.} - y_i^{pred.})^2 \quad \text{and} \quad SST = \sum_{i=1}^{N} (y_i^{exp.} - \bar{y})^2 \tag{6}$$

N is the number of lumps, $y_i^{exp.}$ and $y_i^{pred.}$ are the experimental and predicted weight fraction of product i, respectively, while $\bar{y}$ is the average of the experimental weight fraction.

The rate constants for the first-order kinetic were summarized and listed in Table 3, together with R^2. It can be seen that the first-order kinetic fit the Model 2 best from the evaluation aspect of R^2, which might indicate that Model 2 was the optimal reaction pathway model for upgrading asphaltene in SCW. As observed
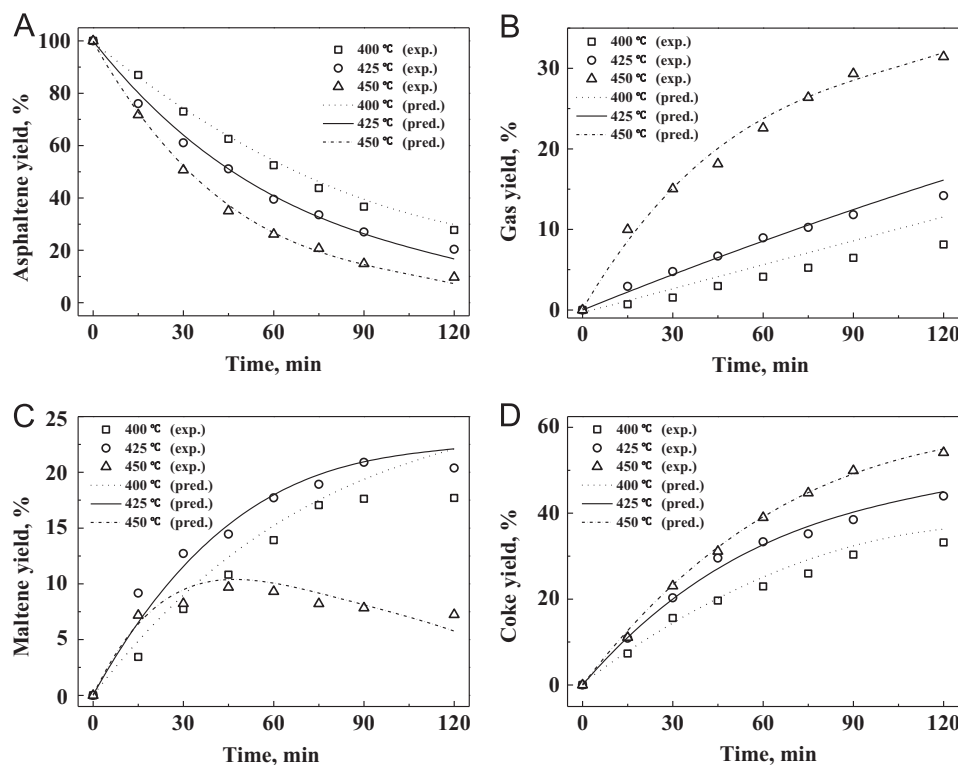
Fig. 9. Comparison between experimental and predicted values of various components for upgrading asphaltene in SCW (supercritical water) at 400, 425 and 450 °C, (A) asphaltene yield; (B) maltene yield; (C) gas yield; (D) coke yield.

from Model 2, the secondary reaction of coke to gas was possible. Additionally, the comparison between Model 1 and Model 2 showed that the secondary reaction of maltene to asphaltene was suppressed by SCW.

As observed from Table 3, the first-order rate constant for coke (k_{13}) was highest among the parallel reactions of asphaltene transformation to gas, maltene and coke, indicating that the transformation of asphaltene to coke was main reaction of upgrading asphaltene in SCW. Table 3 also showed the effect of temperature on first-order rate constants of Model 2. As expected, all the rate constants except k_{24} and k_{25} for Model 2 increased with temperature increasing. For the rate constants of k_{24}, it achieved the maximum value of at 425 °C and then decreased with temperature. The abnormities of k_{24} at 450 °C might be related to the temperature increasing. For asphaltene upgrading in SCW, maltene was mainly formed from the cracking of asphaltene. However, these intermediates formed from the cracking of asphaltene would directly decompose to form gas without through transformation to maltene at severity condition. Additionally, the increasing of temperature would decrease the SCW solubility to maltene (Meng et al., 2006), which subsequently lead the formation of coke due to the condensation and polymerization of maltene. These reasons above might explain the sudden decrease of k_{24} at 450 °C. As for k_{25}, its decease with reaction time might be related to some entrapped alkyl groups, whose crack might happened before the formation of coke at the severity condition.

3.3.3. Evaluation of reaction pathway model

In the kinetic study, parity plot, providing the predicted value on the *y*-axis and the experimental value on the *x*-axis, is a useful tool to evaluate the quality of the kinetic model. Fig. 8 is a parity plot for the yields of asphaltene, maltene, coke and gas. The diagonal line indicated the location of perfect agreement between the predicted

and experimental values. In addition, the comparison between experimental and predicted values of remaining asphaltene, gas, maltene and coke for upgrading asphaltene in SCW at 400, 425 and 450 °C are shown in Fig. 9(A)–(D), respectively. Generally, the experimental data for upgrading asphaltene in SCW at 400, 425 and 450 °C fit the proposed model very well. But there were some deviations between experimental and predicted data for the gas yield at 400 °C despite their trends increasing with temperature were consistent. As shown in Fig. 9(B), the experimental data at 400 °C was lower than the predicted data might be due to some undetected gases.

4. Conclusions

Reaction pathway and kinetic of upgrading asphaltene in SCW was studied at temperature of 400, 425 and 450 °C, pressure of 30 MPa and residence time ranging from 0 to 120 min. Kinetic analysis showed that upgrading asphaltene in SCW obeyed a first-order kinetic. Among the three 4-lump kinetic model, Model 2, considering the parallel reaction of asphaltenes transformation to gas, maltene and coke, the consecutive reaction from maltene to gas and the secondary reaction of coke to gas, was illustrated to predict the product data very well.

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