



Article A Study on the Hydro-Liquefaction Kinetics of Shengli Lignite during the Heating-Up and Isothermal Stages under Mild Conditions

Liang Li ¹, Quan Zhang ¹, Shunjin Huang ², Yanyan Yan ², Yingyue Qin ¹, Xiaochen Huang ¹, Muxin Liu ^{1,*}, Shiyong Wu ³ and Jinsheng Gao ³

- ¹ School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, China; liliang8008@bbc.edu.cn (L.L.); zhangquan0419@yeah.net (Q.Z.); qyy@bbc.edu.cn (Y.Q.); xiaochenhuang@yeah.net (X.H.)
- ² School of Chemistry & Chemical Engineering, Anhui University of Technology, Ma'anshan 243002, China; Huangshunjin@yeah.net (S.H.); Yanyyah@yeah.net (Y.Y.)
- ³ College of Resource & Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China; wsy@ecust.edu.cn (S.W.); gjs@ecust.edu.cn (J.G.)
- * Correspondence: liumuxin@bbc.edu.cn

Abstract: Studying the hydro-liquefaction kinetics of lignite contributes to optimizing the mild liquefaction process for lignite. In this paper, the direct liquefaction performance of Shengli lignite (SL) was investigated using a H_2 /THN system with 4 MPa of initial pressure, and reaction kinetic models were established for the heating-up stage and the isothermal stage. The result showed that the liquefaction performance of the SL was excellent, with a conversion of 62.18% and an oil and gas (O + G) yield of 29.88% at 698.15 K. After one hour of reaction, the conversion and O + G yield were 94.61% and 76.78%, respectively. During the heating-up stage, the easily reactive part of the SL was 50.07%, and it was converted directly into oil, gas, asphaltene (AS), and preasphaltene (PA) simultaneously. There was no significant secondary hydrogenation conversion of the AS and PA products. During the isothermal stage, the hard-to-react part was predominantly converted into AS and PA, while the remaining easily reactive part continue to react completely. The conversion of AS and PA into oil and gas was a rate-controlling step during this stage. The amount of unreacted coal estimated using the model calculated in the isothermal stage was 2.98%, which was significantly consistent with the experimental value of 2.81%.

Keywords: lignite; hydro-liquefaction; kinetic; heating up; isothermal

1. Introduction

Coal is the most abundant fossil fuel in China, with reserves of lignite accounting for approximately 13% of its total coal reserves. Direct coal liquefaction (DCL) is an advantageous technique for the clean and effective utilization of lignite, despite its high moisture content and low heating value [1,2]. Additionally, due to its high H/C ratio, lignite is particularly suitable for liquefaction to obtain fuel. In the industrial application of coal liquefaction technology, the coal hydrogenation reactor is a significant unit, which can be optimized by studying the kinetics of coal liquefaction [3–5].

The process of DCL is complex, involving a reaction network formed by multiple reactions, such as the pyrolysis of coal's macromolecular structure and the formation and interactions of free radicals. Simultaneously, due to the wide molecular weight distribution and complex structure of coal's liquefaction products, it is difficult to describe the reaction process of DCL [6,7]. Currently, the most reliable method for dividing coal liquefaction products into distinct components with similar properties is based on their molecular weights. The reactions between different components are treated as the fundamental



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elementary reactions, allowing for a simplified coal liquefaction reaction network to approximate the real reaction mechanism. During the development of DCL kinetics, various mechanisms have been proposed, with a transition from single-stage and single-component models to multi-stage and multi-component models. These mechanisms differ based on the solvent, coal, and reaction conditions. As the dynamic model of DCL becomes increasingly complex, it aligns more closely with the practical applications of industrial systems [8–10].

In the earlier proposed kinetic models, researchers treated coal as a single component and did not differentiate between its various reactive components. This approach simplified the study of the kinetic process. Several investigators proposed that coal should be considered a single component in their kinetic analyses of sub-bituminous coal liquefaction [8,10]. They argued that coal directly produces gas, oil, asphaltene, and preasphaltene, which should be classified as its liquefaction products. Preasphaltene was converted into asphaltene, which was then converted into oil. This process ignored the differences in the reactivity of the different components of the coal, as well as the reverse reactions caused by an insufficient hydrogen supply. As the research progressed, researchers noticed that there were components of coal with different reactivities, with one component reacting quickly and the other reacting slowly. Brunson et al. [9] proposed classifying coals into three fractions according to their reactivity: an instantaneously converted fraction γ , a volatile-free fraction α , and an inactive fraction ω . Direct coal liquefaction involves the rapid conversion of component γ into a product, while a portion of the volatile-free component α is converted into another product. Another portion of α is converted into component β , which is then converted into another product. The inactive component ω does not undergo conversion. However, the reaction behaviors of the different reactive components in coal are not similar during each stage of liquefaction. At the beginning of the liquefaction reaction, the easily reactive part of coal is rapidly transformed, while the other parts remain unreactive. As the reaction progresses, the hard-to-react part only reacts once the easily reactive part has been completely transformed, while the generated asphaltene and preasphaltene undergo hydrogenation [11]. Therefore, when considering the existence of differences in the reactivity of different components of coal, it is important to discuss the kinetics of the coal liquefaction reactions at different reaction stages separately. Li et al. [6] concluded that significant chemical reactions occurred in coal liquefaction during the heating-up stage. The rate-dominant process of coal liquefaction was the reaction of oil and gas generation from PAA, with oil coming mainly from the coal in the heating phase and from the PAA in the isothermal phase, respectively. The direct coal liquefaction process was divided into temperature rise stages and constant temperature stages. The predicted results were in excellent agreement with the experimental data, which were consistent with the actual liquefaction process. Onozaki et al.'s kinetic models were highly representative of the NEDOL coal liquefaction process [12]. They demonstrated that during the early stage of liquefaction (preheater), the fast-reacting components were rapidly converted into gas, oil, asphaltene, and preasphaltene; in the middle stage of the reaction, the slow-reacting components were converted into asphaltene and preasphaltene and then into oil and gas.

It Is widely acknowledged that oil can be formed directly from coal without intermediate stages. For low-rank coals such as lignite, the conversion relationship between the intermediate products from coal pyrolysis and the liquefaction products during the heating-up and isothermal stages is still poorly understood. Under mild conditions (e.g., 350–400 °C), lignite demonstrated a high liquefaction conversion rate, indicating its significant liquefaction activity at a mild temperature, in our previous work [13]. However, in coal liquefaction plants, the reactor temperatures usually exceed 400 °C [14]. This means that by the time the temperature of the coal slurry reaches the desired liquefaction temperature, a partial liquefaction reaction has already occurred.

The maceral and rank determine the differences in the kinetic models and the reaction mechanisms during coal liquefaction under the same conditions [15,16]. It is evident that the coal begins to lose weight during heating up, and its rate varies continuously with temperature. It is not reasonable to exclude this when calculating the kinetic constants

of the coal liquefaction process, regardless of the duration of the heating stage. When discussing a kinetic model of coal liquefaction, it is important to consider that the coal is divided into components with different reactivities and that the liquefaction process is divided into a heating-up stage and an isothermal stage.

Therefore, the kinetic study of lignite liquefaction can be clarified by using a multicomponent and multi-stage liquefaction model due to its low rank of coalification, high content of reactive components, and significant conversion during the heating-up phase in industrial plants. In this study, the liquefaction of Shengli lignite using a Fe-based catalyst was investigated. Two kinetic models of the heating-up stage and the isothermal stage were estimated, and their kinetic parameters were obtained, respectively. The predicted values agreed perfectly with the experimental data. Furthermore, the long-term upper limit of coal liquefaction conversion agreed with the predicted value from the kinetic model.

2. Materials and Methods

2.1. Materials

The lignite feedstock originated from the Shengli Coal mine in the Inner Mongolia Autonomous Region of China. Prior to its use, the Shengli lignite (SL) was ground to a particle size below 0.2 mm and then dried in a vacuum at 80 °C for 12 h. Table 1 presents the proximate and ultimate analyses of the SL. The solvents and reagents utilized in the experimental procedures, which included Fe_2O_3 , sulfur, hydrogen, tetralin, tetrahydrofuran (THF), toluene, and n-hexane, were all commercially pure chemical compounds and were used without further purification.

Table 1. Proximate and ultimate analyses of SL.

Sample	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)			ШC	
	M _{ad}	A _d	\mathbf{V}_{daf}	FC _{daf}	C _{daf}	H _{daf}	N _{daf}	$S_{t,d}$	- п/С
SL	20.77	17.14	46.96	53.04	70.18	5.31	1.09	1.82	0.91

ad: air dry basis; d: dry basis; daf: dry ash-free basis; St,d: total sulfur on dry basis.

2.2. Liquefaction Procedure

The liquefaction kinetics test of the SL was conducted using a 200 mL high-pressure reactor. The addition of the 20 g coal sample to the reactor was followed by the addition of 30 mL of solvent, a 3% iron catalyst, and elemental sulfur (S/Fe = 1.2, atomic ratio), after which the reactor was placed in a heating furnace. Following the charging and discharging of nitrogen for three consecutive cycles, hydrogen was charged and discharged for three cycles in the reactor, which was filled with 4 MPa of hydrogen subsequently. The reactor began to stir, and once the reaction temperature was reached, it was maintained for a specified time. After the termination of the reaction, cooling water was introduced into the reactor to rapidly cool it down [13].

The liquefaction products underwent a fractionation procedure, as illustrated in Figure 1. The liquefied product in the reactor was washed with 300 mL of tetrahydrofuran, and the solid obtained was THFI after Soxhlet extraction using tetrahydrofuran. The tetrahydrofuran soluble fraction was removed via rotary evaporation and then precipitated with n-hexane, and the precipitate was extracted with n-hexane to obtain an n-hexane-soluble fraction and an n-hexane-insoluble fraction. Asphaltene (AS) and preasphaltene (PA) were obtained via Soxhlet extraction of the n-hexane-insoluble matter with toluene. THFI, AS, and PA were all dried in a vacuum at 80 °C for 12 h and then weighed, respectively. The yields of oil and gas (O + G) were calculated by subtracting the yields of AS and PA from the conversion rates. All the above yields and conversions were based on dry ash-free coal samples. The repeatability of the fractionation analyses (THFI, AS, and PA) was 1%.



Figure 1. Liquefaction product separation process.

The yields of the products were defined as follows:

$$Y_{AS} = \frac{M_{AS}}{M_{daf}} \times 100\%$$

$$Y_{PA} = \frac{M_{PA}}{M_{daf}} \times 100\%$$
Conversion = $(1 - \frac{M_{THFI} - M_{cat} - M_{ash}}{M_{daf}}) \times 100\%$

$$Y_{O+G} = Conversion - (Y_{AS} + Y_{PA})$$

where Y_{AS} , Y_{PA} , Conversion, and Y_{O+G} are the AS yield, PA yield, conversion, and oil + gas yield, respectively. M_{AS} , M_{daf} , M_{PA} , M_{cat} , M_{THFI} , and M_{ash} are the weight of the AS, SL on a dry ash-free basis, PA, catalyst, THFI, and ash in the SL, respectively.

3. Results and Discussion

3.1. Hydro-Liquefaction Experiments on the SL

Recent theoretical studies in coal science indicate that coal contains low-molecularweight compounds that interact with the macromolecular skeleton structure of coal [17–20]. During the liquefaction process, the low-molecular-weight compounds can be dissolved and extracted using a liquefaction solvent below pyrolysis temperature. It is necessary to subtract this part of the low-molecular-weight compounds when calculating the reaction kinetics parameters in the heating-up stage because these low-molecular-weight compounds are not produced by the liquefaction reaction and are, strictly speaking, thermally soluble and extracted. Therefore, this proportion of conversion should be deducted when calculating the reaction kinetics of the heating-up stage. In our early work, it was found that pyrolysis began at 598.15 K, and the temperature of the maximum weight loss rate for the SL was 699.15 K [13]. Therefore, in this paper, the non-isothermal stage was from 598.15 to 698.15 K, and the isothermal stage was 698.15 K. The liquefaction conversion products of the Shengli lignite at 598.15 K were attributed to the portion of low-molecularweight compounds, which was deducted when calculating the kinetic parameters of the heating-up stage. Figure 2 shows the heating curve of the 200 mL reactor used in the kinetic



experiment. The figure illustrates that it takes 6.4 min to raise the temperature in the reactor from 598.15 to 698.15 K. The isothermal stage begins at 33.5 min.

Figure 2. The temperature rise curve of 200 mL reactor.

Table 2 shows the conversion and product yield in the SL liquefaction experiment during the heating-up stage. The conversion rate of SL at 598.15 K was 12.11%. At this temperature, the SL primarily underwent thermal extraction of its low-molecular-weight compounds without a significant hydro-liquefaction reaction [17,19]. When the temperature was increased to 698.15 K, the liquefaction conversion of the SL reached 62.18%. The yields of O + G, AS, and PA increased almost linearly during the heating-up stage. At low liquefaction temperatures, the weak covalent and non-covalent bonds in SL are cleaved, such as the ether bridges connecting the aromatic clusters, and the generated pyrolysis radicals are stabilized by active hydrogen to form mainly asphaltene, preasphaltene, and oils [21,22]. The hydrogenation reaction of the asphaltene and preasphaltene is not obvious at these temperatures, and the distribution of the liquefaction products is mainly determined by the pyrolytic products of the SL. This perspective agrees with some researchers [6,7], who believe that oil and gas are mainly obtained from coal conversion directly but not from asphaltenes and preasphaltene during the heating-up stage. In addition, because of the high liquefaction activity of SL, the part of it that is easily reactive may not have sufficient time to be fully converted when the temperature reaches 698.15 K. As a result, the remaining easily reactive part may continue to be converted during the isothermal stage.

Table 2. Experimental results of	of SL liquefaction	during the hea	ating-up stage
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Time (min)	Temperature (K)	O + G (wt%, daf)	AS (wt%, daf)	PA (wt%, daf)	Conversion (wt%, daf)	O + G /Conversion *	(AS + PA) /Conversion *
0	598.15	9.34	2.75	0.02	12.11	/	/
1.5	623.15	10.81	3.07	2.53	16.41	0.34	0.66
3.0	648.15	14.63	8.88	5.62	29.13	0.31	0.69
4.6	673.15	21.90	5.52	14.18	41.60	0.43	0.57
6.4	698.15	29.88	15.23	17.07	62.18	0.41	0.59

*: Calculated by subtracting the value of 598.15 K, respectively.

Furthermore, on subtracting the values of 598.15 K from the conversion rate and the production rate of each product, respectively, the ratio of the O + G yield and the AS + PA yield to conversion remained relatively constant during the heating-up stage, as seen in Table 2. This result further suggests that during the heating-up stage, the liquefaction products are primarily coal pyrolysis products, and the hydrogenation of asphaltene and preasphaltene has not yet occurred significantly.

Table 3 shows the conversion and product yield in the SL liquefaction experiment during the isothermal stage over a period of 90 min. During the initial 10 min of this stage, the liquefaction conversion and the O + G yield of the SL increased rapidly, and its PA yield decreased. This indicates that both the remaining easily reactive part and the hard-to-react part of the SL underwent hydrogenation. Additionally, there was a conversion of asphaltene and preasphaltene into oil and gas. During the isothermal stage from 10 to 30 min, the increase rate of the liquefaction conversion of the SL slowed down significantly. However, the rate of the O + G yield still increased, and the AS yield and PA yield decreased. This suggests that the remaining easily reactive part of the SL was fully reacted, while the hard-to-react part was still being reacted. Additionally, the conversion of AS and PA into oil and gas occurred significantly. This indicates that as the reaction time is prolonged, the easily reactive part's pyrolysis reaction is basically completed. At this moment, the rate of the hydrogenation of asphaltene and preasphaltene, which were produced due to the cracking of the SL, exceeded the rate of production, resulting in a gradual reduction in the yield of AS and PA. During the isothermal stage from 30 to 90 min, the increase rate of the liquefaction conversion of the SL further slowed down. Additionally, the rate of the O + G yield also slowed down, while there was no significant change in the AS yield and PA yield. During this stage, it was suggested that the conversion of the hard-to-react part into asphaltene and preasphaltene and the conversion of asphaltene and preasphaltene into oil and gas took place. These two types of conversions occur at similar rates, resulting in an equilibrium state, where the rate of conversion and the rate of O + G production gradually increased, while the AS yield and PA yield remained approximately constant.

Time	Temperature	O + G	AS	PA	Conversion
(min)	(K)	(wt%, daf)	(wt%, daf)	(wt%, daf)	(wt%, daf)
0	698.15	29.88	15.23	17.07	62.18
10	698.15	59.01	12.35	12.69	84.05
20	698.15	67.48	9.69	10.30	87.47
30	698.15	71.77	8.26	9.71	89.74
40	698.15	71.95	8.38	9.76	90.09
60	698.15	75.08	8.85	9.30	93.23
90	698.15	76.78	8.64	9.18	94.61

Table 3. Experimental results on SL liquefaction during the isothermal stage.

To briefly summarize, the liquefaction process of SL can be divided into three stages. During the first stage (the heating-up stage), which involves rapid pyrolysis and hydrogenation of the lignite, large amounts of oil, gas, asphaltene, and pre-asphaltene are obtained directly. In this stage, asphaltene and pre-asphaltene are evidently basically not converted into oil and gas. During the second stage (the initial isothermal stage), the remaining easily reactive part that was not reacted during the heating-up stage continues to be converted into oil, gas, asphaltene, and preasphaltene. Additionally, asphaltene and preasphaltene are converted into oil and gas, while the hard-to-react part of the SL is converted into asphaltene and preasphaltene. During the third stage (the final isothermal stage), the remaining hard-to-react part of SL is converted into asphaltene and preasphaltene, which are then converted into oil and gas. The rates of these two conversions approach equilibrium.

3.2. Kinetic Model during the Heating-Up Stage

According to the results of the SL liquefaction experiments during the heating phase, the following assumptions were made. (1) Shengli lignite was classified into three components based on their reactivity: the easily reactive part (M_1), the hard-to-react part (M_2), and the unreactive part (M_3). It was assumed that only M_1 underwent a rapid pyrolytic hydrogenation reaction during the heating-up stage, while M_2 and M_3 did not undergo any transformation. (2) To simplify the calculation, oil, gas, and water were considered one product (O + G), and asphaltene and preasphaltene were considered one product (PAA).

(3) Asphaltene and preasphaltene were not further hydrogenated. (4) All the reaction steps were assumed to be first-order and irreversible, and the influence of mass transfer, heat transfer, and the sample particle size on the liquefaction process was ignored [23].

Based on the aforementioned hypotheses, the reaction kinetics model of SL liquefaction during the heating-up stage was established, as shown in Figure 3. The expression in the kinetic model of M_1 during the heating-up stage was provided as follows.

$$\frac{dM_1}{dt} = -k_1(T) \cdot M_1 \tag{1}$$

where the reaction rate constant $k_1(T)$ was expressed as a function of temperature using the following equation.

$$k_1(T) = k_{10}T^n \exp(-\frac{E_a}{RT})$$
 (2)

where T represented the temperature correction factor. By substituting Equation (2) into Equation (1), the following equation was obtained.

$$\frac{d\ln M_1}{dT} = -\frac{k_{10}}{\alpha} T^n \exp(-\frac{E_a}{RT})$$
(3)

where α represents the heating rate and was obtained by fitting the data linearly to temperature and time with an α value of 15.77 K/min.

The M_{10} value calculated the difference in the coal conversion rates between 698.15 and 598.15 K. The experimental determination of the M_{10} value for SL was 50.07%. The values $(k_{10} = 2.46 \times 10^5 \text{ min}^{-1}, n = 0.42, E_a = 89.7 \text{ kJ/mol})$ were obtained using numerical solutions to Equation (3) and regression analysis based on the experimental data presented in Table 2. It could be found that the activation energy of the M_1 liquefaction reaction of SL was only 89.7 kJ/mol, which is slightly lower than that of Shenhua sub-bituminous coal, which is about 93 kJ/mol during the heating-up stage [7]. Figure 4 displays a comparison between the experimental values and the model's calculated curve for the content of M_1 during the heating-up stage. The experimental values closely match the model's calculated curve, suggesting that the kinetic model of the liquefaction reaction during the warming phase is reasonable.



Figure 3. Reaction scheme of SL liquefaction during the heating-up stage.



Figure 4. The experimental value and model-calculated value of M_1 at heating-up stage.

(5)

3.3. Kinetic Model during the Isothermal Stage

Analysis of the data from the SL liquefaction experiments during the isothermal stage suggested that at the beginning of this stage, the conversion of SL increased rapidly, while the AS yield and the PA yield decreased rapidly. This indicates that during this stage, hydropyrolysis of the coal occurs alongside the conversion of asphaltene and preasphaltene. Thus, this stage's reaction is more complex, requiring consideration of multiple reaction pathways and kinetic parameters when establishing the kinetic model. It is also necessary to consider the conversion of the remaining M_1 at the beginning of the isothermal stage. Under these circumstances, the following assumptions were further made. (1) SL was classified into three components based on their reactivity: the easily reactive part (M_1) , the hard-to-react part (M_2) , and the unreactive part (M_3) . It was assumed that M_2 only generated asphaltene and preasphaltene, while M₃ did not undergo any transformation. (2) To simplify the calculation, oil, gas, and water were considered one product (O + G), and asphaltene and preasphaltene were considered one product (PAA). (3) It was considered that all the reaction steps were assumed to be first-order and irreversible, and the influence of mass transfer, heat transfer, and the sample particle size on the liquefaction process was ignored [23].

Based on these three assumptions, the reaction kinetic model of SL liquefaction during the isothermal stage was established, as shown in Figure 5. The mathematical model for the dynamics was expressed using equations in matrix form. The calculation process was as follows.

 $t=0, \vec{\alpha}=0$

$$\frac{\overrightarrow{\alpha}}{dt} = k \overrightarrow{\alpha}$$
(4)

If

where,

$$\begin{pmatrix} M_1\\ M_2 \end{pmatrix}$$

$$\vec{\alpha} = \begin{cases} M_2 \\ PAA \\ O+G \end{cases}$$
(6)

$$\vec{\alpha}_{0} = \begin{cases} M_{10} \\ M_{20} \\ PAA_{0} \\ (O+G)_{0} \end{cases}$$

$$\tag{7}$$

$$k = \begin{cases} -(k_1 + k_2) & 0 & 0 & 0\\ 0 & -k_3 & 0 & 0\\ k_2 & k_3 & -k_4 & 0\\ k_1 & 0 & k_4 & 0 \end{cases}$$
(8)

The following results could be obtained.

$$M_1 = M_{10}e^{-(k_1 + k_2)t} (9)$$

$$M_2 = M_{20}e^{-k_3t} \tag{10}$$

$$PAA = \frac{k_2 M_{10}}{k_4 - k_1 - k_2} e^{-(k_1 + k_2)t} + \frac{k_3 M_{20}}{k_4 - k_3} e^{-k_3 t} + \left(\frac{k_2 M_{10}}{k_4 - k_1 - k_2} - \frac{k_3 M_{20}}{k_4 - k_3} + PAA_0\right) e^{-k_4 t}$$
(11)

$$M_{O+G} = \frac{k_1 - k_4}{k_4 - k_1 - k_2} M_{10} e^{-(k_1 + k_2)t} + \frac{k_4 M_{20}}{k_3 - k_4} e^{-k_3 t} \\ + \left(\frac{k_3 M_{20}}{k_4 - k_3} - \frac{k_2 M_{10}}{k_4 - k_1 - k_2} - PAA_0\right) e^{-k_4 t} \\ + (O+G)_0 + PAA_0 + M_{10} + M_{20}$$
(12)

where k_1 , k_2 , k_3 , and k_4 are the apparent reaction rate constants for different steps, as shown in Figure 5. M_{10} , M_{20} , PAA_0 , and $(O + G)_0$ represent the initial values of M_1 , M_2 , PAA, and (O + G), respectively.



Figure 5. Reaction model of SL liquefaction at the isothermal stage.

Therefore, the amount of unconverted coal at time *t* is calculated as follows.

$$M = M_1 + M_2 + M_3 = M_{10}e^{-(k_1 + k_2)t} + M_{20}e^{-k_3t} + M_3$$
(13)

The equation presented below was obtained through non-linear fitting, using Equation (13) and the data from Table 2.

$$M = M_1 + M_2 + M_3 = 14.03e^{-0.020t} + 20.79e^{-0.263t} + 2.98$$
(14)

The value of R^2 was 0.997.

The other kinetic parameters obtained according to non-linear regression using Equations (11) and (12) for the isothermal stage are shown in Table 4. This shows that during the isothermal stage of SL liquefaction, the remaining easily reactive part (M_1) is 14.03%, and the hard-to-react part (M_2) is 20.79%. This suggests that the conversion of M_2 may be predominant in the isothermal stage. Meanwhile, this also indicates that the reaction paths in the isothermal stage may be quite different from those in the heating-up stage. In addition, k_3 and k_4 are significantly higher than k_1 and k_2 , further suggesting that the conversion of M_2 into PAA and the conversion of PAA into O + G were predominantly observed during the isothermal stage. Simultaneously, k_3 is higher than k_4 , indicating that the conversion rate of M_2 into PAA is faster than that of PAA into O + G. This further suggests that the conversion of PAA is the controlling step during the isothermal stage of the SL liquefaction reaction. Therefore, to improve the oil yield in the isothermal stage, it is necessary to increase the conversion rate of PAA into O + G. This can be achieved, for example, by providing a high-activity catalyst and a better hydrogen supply environment [24–26]. Furthermore, the residue yield (on a dry ash-free basis) of SL was 2.81% after 180 min of isothermal time, which was significantly longer than the time required for the kinetic analysis. The theoretic value of unreactive coal, M_3 , as shown in Table 4, is 2.98%, which closely matches the experimental value. This suggests that the kinetic model established in the isothermal stage had excellent predictive capabilities for the longer lignite liquefaction test. Figure 6 displays the experimental values and model-calculated curves for each product yield and unreacted coal yield. There are satisfactory fits between the experimental data and the theoretical curves.

Rate Constant (min ⁻¹)	Value	Components (wt%, daf)	Value
k_1	0.018	M_{10}	14.03
k_2	0.002	M_{20}	20.79
k_3	0.263	M_{30}	2.98
k_4	0.157	/	/

Table 4. Kinetic parameters of SL liquefaction during isothermal stage.



Figure 6. Comparison of experimental values and model-calculated curves during isothermal stage.

4. Conclusions

The hydro-liquefaction properties with 4 MPa of initial pressure and a kinetic model of SL were investigated. The liquefaction performance of the SL was excellent. When the temperature rose to just 698.15 k, the liquefaction conversion, and the O + G yield were 62.18% and 29.88%, respectively. After one hour of reaction at this temperature, the conversion, and the O + G yield were 94.61% and 76.78%, respectively.

The liquefaction reaction of SL with 4 MPa of initial pressure was divided into two stages: the heating-up stage and the isothermal stage. SL was classified into three components based on their differences in reactivity: the easily reactive part, the hard-to-react part, and the non-reactive part. Kinetic models were established for each stage, and the calculated values were in excellent agreement with the experimental data. During the heating-up stage, the easily reactive part of SL was 50.07%, and it was converted directly into oil, gas, asphaltene (AS), and preasphaltene (PA) simultaneously, without significant secondary hydrogenation conversion of the AS and PA products. During the isothermal stage, the remaining easily reactive part continued to react completely, while the hard-to-react part was converted into AS and PA. Meanwhile, AS and PA were subsequently converted into hydrocarbons significantly. The conversion of AS and PA into oil and gas was a rate-controlling step in the isothermal stage.

The weight percent of unreacted coal estimated using the model calculated in the isothermal stage was 2.98%, which was significantly consistent with the experimental value of 2.81%, indicating the feasibility of the model in estimating the maximum conversion rate for lignite hydro-liquefaction under mild conditions.

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Nomenclature

- DCL Direct coal liquefaction
- SL Shengli lignite
- THF Tetrahydrofuran
- O + G Oil and gas
- AS Asphaltene
- PA Preasphaltene
- THFI Tetrahydrofuran insoluble
- PAA Preasphaltene and asphaltene

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