

Kinetics of coal liquefaction during heating-up and isothermal stages

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Abstract

Direct liquefaction of Shenhua bituminous coal was carried out in a 500 ml autoclave with iron catalyst and coal liquefaction cycle-oil as solvent at initial hydrogen of 8.0 MPa, residence time of 0–90 min. To investigate the liquefaction kinetics, a model for heating-up and isothermal stages was developed to estimate the rate constants of both stages. In the model, the coal was divided into three parts, easy reactive part, hard reactive part and unreactive part, and four kinetic constants were used to describe the reaction mechanism. The results showed that the model is valid for both heating-up and isothermal stages of liquefaction perfectly. The rate-controlled process for coal liquefaction is the reaction of preasphaltene plus asphaltene (PAA) to oil plus gas ($O + G$). The upper-limiting conversion of isothermal stage was estimated by the kinetic calculation.

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1. Introduction

Coal is the most abundant fossil fuel known in the world, and also a vital global energy source. Today, the main consumption of coal is pulverized coal combustion for power generation which leads to many environment pollution and waste. Direct coal liquefaction is an advantageous approach for the clean and effective utilization of coal, but also a complex combination of physical and chemical process. It includes removing of extractable material from coal, cracking of larger molecule and stabilizing the resulting free radical by hydrogen [1,2]. The efficiency of direct coal liquefaction depends not only on its origin and coalification degree, but also on the petrographic composition within the same type of coals, the content and nature of mineral components. The mechanism and kinetics studies of coal liquefaction play an important role for reactors design and process optimization.

Kinetics of coal liquefaction is very complex due to the formation of numerous compounds. The approach of

kinetic studies is to separate these compounds into “kinetically similar” classes based on some separation technique. Most familiar separation method is depending on solubility of liquefaction product in various solvents [3]. Coal liquefaction is usually regarded as series and parallel reaction process. Up to now, many works have been carried out for the mechanism and kinetics study of coal liquefaction, and various kinetic models have been advanced. Weller et al. [4,5] proposed that the conversion of coal to oil passes through the formation of asphaltenes, which is still accepted today. Francesco et al. [6] investigated the hydro-liquefaction of coal in a stirred batch reactor at a constant temperature (430 °C) in the presence of tetralin/naphthalene mixtures, and the analytic equations they obtained from the model by regressing the experimental data seem to fit the data satisfactorily. Ikeda et al. [7] investigated the procedure of coal liquefaction in a flow reactor of 1 t/d process supporting unit (PSU) for the NEDOL Process. They established a reaction kinetic model of coal liquefaction with retrogressive reaction and elucidated the mechanism. Ding et al. [8] made a kinetic study of both thermal and catalytic (Fe impregnated on coal) liquefaction of DECS-6 coal with plastic-derived liquids as solvent. Xu

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et al. [9] divided the liquefaction reaction into two stages: prior to the onset of extensive bond cleavage and following the onset of extensive bond cleavage. Both stages were considered to be multiple parallel, independent, irreversible, first-order reactions with a Gaussian distribution of activation energies. The obtained activation energy is between 35 and 80 kJ mol⁻¹ for the first stage, between 124 and 238 kJ mol⁻¹ for the second stage. Simsek et al. [10] proposed five reaction mechanisms based on a series of irreversible and pseudo first-order reactions through the liquefaction investigation of six Turkish coals with microwave heating. And the best fit between experimental and model value was the model which suggested the oils, asphaltenes, and preasphaltenes were formed directly from coal. Singh et al. [11] established a kinetic model which is applicable to the liquefaction of widely different coals catalyzed by iron-sulfur catalysts in the coal minerals and/or iron pyrite catalysts. They found that the source of the iron-sulfur catalyst has no effect, whereas H₂S has a strong inhibitive effect on the hydrogenation reactions.

In liquefaction with batch reactor, it usually requires long heating-up and cooling-down time, during which significant reactions will occur. The liquefaction reaction at low temperature stage and high temperature stage are different, so the kinetic studies of heating-up stage are important and attract many researchers' attentions. Govindan et al. [3] studied the kinetics of Illinois No. 6 coal liquefaction in a batch reactor under non-isothermal conditions from 330 °C to 450 °C at total pressures up to 7.0 MPa and the reaction times from 5 to 60 min. They found that several kinetic models could predict concentration-time profiles satisfactorily. Takeshl et al. [12] used a non-isothermal method of kinetic analysis to study coal hydrogenation, and found that the kinetic parameters obtained by this technique compare favorably with those obtained by a conventional approach. Edward et al. [13] studied the liquefaction kinetics of Kentucky No. 6 coal under non-isothermal conditions in a solution of tetralin and decalin at a total pressure up to 7.5 MPa. The non-isothermal method provided a means of obtaining reaction rate data for the complex initial stage of the coal liquefaction process.

Different rank, different petrographic composition and different mineral components of coal mean different kinetic model and mechanism at the same liquefaction conditions [14]. In this work, Shenhua bituminous coal, loaded with iron catalyst, was liquefied in a 500 ml autoclave with coal liquefaction cycle-oil, from 1 t/d pilot plant in Beijing Institute of Coal Chemical Engineering (BICCE), as solvent.

Overall process was considered as first-order irreversible reactions. Kinetic model was developed for heating-up and isothermal stages, and the reaction rate constants at two stages were estimated. The results displayed perfectly coherence between experimental and predicted values. In addition, the upper-limiting conversion of isothermal stage was estimated by the kinetic calculation.

2. Experimental

2.1. Materials

The Shenhua coal sample was ground to particles less than 100 mesh, and dried under vacuum at 100 °C for 10 h. The proximate, ultimate and petrographical analysis results of sample are shown in Table 1.

2.2. Experimental procedure

The experiments were carried out in a 500 ml autoclave with magnetic stirrer. In each run, about 21 g coal sample was added to the reactor, the solvent, coal liquefaction cycle-oil, was added in solvent/coal ratio of 55/45, the catalyst is 1 wt%Fe of coal and sulfur in molar ratio of sulfur/Fe being 2. After the reactants were loaded into the reactor, the reactor was sealed and flushed three times with hydrogen before pressurizing to the desired initial hydrogen pressure of 8.0 MPa. Afterwards the reactor was heated to the desired temperature at 5 °C/min by a furnace outside the reactor and maintained at that temperature for the desired time (for the runs of heating-up stage, the isothermal time being zero) under stirring with rate of 400 rpm. Upon completion of experiment, the reactor was taken out from furnace and cooled with fan to below 200 °C within 15 min.

2.3. Product separation and analyses

The liquid and solid products from the reactor were separated into oil (*n*-hexane soluble), asphaltene (toluene soluble but *n*-hexane insoluble), preasphaltene (THF soluble but toluene insoluble), and residues (THF insoluble) by Soxhlet extraction with *n*-hexane, toluene, and THF, respectively, as shown in Fig. 1. The conversion was defined as the percentage of coal into preasphaltene, asphaltene, oil and gas during the liquefaction.

The pyrolysis of original coal and liquefaction residues were performed in a thermogravimetric analyzer (Mettler Toledo TGA/SDTA851^e) to check the effect of coal pyrolysis during liquefaction, with coal sample of 20 mg in N₂

Table 1
The property and petrographical analyses of Shenhua coal sample

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)					Petrographical analysis (wt%, daf)			
<i>M</i> _{ad}	<i>A</i> _d	<i>V</i> _{daf}	C	H	O	N	S	Vitrinite	Inertinite	Exinite	Mineral
9.34	5.52	38.24	80.13	4.88	13.51	1.06	0.42	62.8	34.0	1.8	1.4

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