

θ_c = time at which the ash layer begins to form
 λ = position at time θ , of the reaction interface separating the fully and partly reacted portions of the solid
 ψ = cumulative concentration defined as $\int_0^\theta a \, d\theta$
 ψ_1 = cumulative concentration at the interior collocation point

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Novel Kinetic Analysis of Coal Liquefaction

Takeshi Okutani* and Neil R. Foster

CSIRO Division of Fossil Fuels, PO Box 136, North Ryde, NSW, Australia 2113

The application of a nonisothermal method of kinetic analysis to the study of coal hydrogenation is described. Kinetic parameters obtained by this technique compare favorably with those obtained with a conventional approach. The nonisothermal method is convenient and provides a means of obtaining reaction rate data for the complex initial stages of the coal liquefaction process.

Introduction

Kinetic parameters for the coal hydrogenation process, although of a purely empirical nature due to the complex chemical structure of coal and its hydrogenation products, are essential in order to design reactors and to facilitate process optimization. Kinetic analysis of coal hydrogenation is usually carried out in batch autoclaves, which enables the measurement of the conversion of coal with time at a constant temperature, and is referred to in this paper as the conventional approach. However, this method is laborious, and because of the excessive heat-up times required in standard autoclaves it is impossible to determine reaction rates at the initial stages of hydrogenation.

In the area of solid-state chemistry, Kubo et al. (1966) proposed a method of nonisothermal analysis whereby kinetic data are estimated from the relationship between a conversion, measured at a constant heating rate, and temperature. This method is as accurate and much simpler than the conventional approach. If the method is applicable to studies of coal liquefaction it will provide a valuable tool for kinetic analysis of this complex reaction. When combined with rapid quenching of the products the method will also provide a potential means of obtaining accurate reaction rate data for the initial stages of the liquefaction process.

The results obtained by the application of Kubo's nonisothermal method to coal liquefaction using Wandoan coal (Australia) and an α -Fe₂O₃-S catalyst (5% Fe₂O₃ + 2% S, based on coal) are reported in this paper. The kinetic parameters obtained are compared with those determined by conventional analysis.

Experimental Section

Materials. Proximate, ultimate, and maceral analyses of Wandoan coal (-100 mesh) are presented in Table I. The coal samples were dried for 12 h at 107 ± 5 °C under

Table I. Proximate, Ultimate, and Maceral Analyses of Wandoan Coal

Proximate Analysis (wt %, Air Dry Basis)	
moisture	7.7
ash	22.1
volatile matter	37.1
fixed carbon	33.1
Ultimate Analysis (wt %, daf)	
carbon	75.5
hydrogen	6.2
nitrogen	1.0
sulfur	0.3
oxygen (diff.)	17.0
Maceral Analysis (wt %)	
vitritinite	84
exinite	9
inertinite	7

vacuum. Analytical grade α -Fe₂O₃ (Merck) was used as catalyst without purification; the sulfur has been described previously (Okutani et al., 1979). Both the α -Fe₂O₃ and sulfur were in powder form (-300 mesh). Tetralin (purity greater than 99.5%, Ajax Chemicals, Australia) was used as a vehicle oil without further purification. Commercial hydrogen gas was of analytical grade.

Apparatus and Sample Preparation. The batch-type 115-mL unstirred autoclave (Hastelloy C) has previously been described (Okutani et al., 1979). In order to maintain contact between coal particles and hydrogen, a method was used (Yokoyama et al., 1979) in which α -Al₂O₃ particles were mixed with coal particles; 10 g of coal powder, 0.5 g of α -Fe₂O₃, 0.2 g of S, and 10 g of α -Al₂O₃ (80 mesh spheres) were mixed. Yokoyama et al. (1979) have shown that mass transfer resistances, as reflected by lack of hydrogen availability, are negligible when this method of sample preparation is adopted. α -Al₂O₃ was prepared by calcination of γ -Al₂O₃ (analytical grade, Merck) for 1 h at 1150 °C. For experiments using Tetralin as vehicle oil, the sample was wetted by adding 6 g of Tetralin to a mixed solid sample of 4 g of coal, 0.2 g of α -Fe₂O₃, 0.08 g of S, and 10 g of α -Al₂O₃.

* The Government Industrial Development Laboratory, Hokkaido, 2-17 Tsukisamu-Higashi, Toyohira-ku, Sapporo, 061-01, Japan

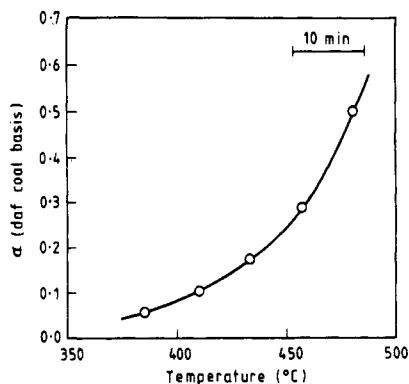


Figure 1. Nonisothermal conversion curve ($3^{\circ}\text{C min}^{-1}$) for Wandoan coal liquefaction (coal- $\alpha\text{-Fe}_2\text{O}_3\text{-S}$).

Procedure for Nonisothermal Experiments. Prepared samples were placed in the autoclave which was pressurized with hydrogen to 100 kg cm^{-2} (9.8 MPa) and heated at a constant heating rate of $3^{\circ}\text{C min}^{-1}$ to 350, 375, 400, 425, or 450°C . Temperatures were measured at the center of the sample. After reaching the desired reaction temperature, the autoclave was cooled to room temperature at a constant rate of $12^{\circ}\text{C min}^{-1}$. Conversion (α) was determined on the basis of benzene-insoluble material (residue of benzene Soxhlet extraction corrected for FeS produced from the $\alpha\text{-Fe}_2\text{O}_3\text{-S}$ catalyst, and coal ash).

The nonisothermal method resulted in greater temperature differences between the autoclave surface and the center of the sample than for the conventional approach. Separate measurements revealed that the temperature distribution in the autoclave could be described by the relationship

$$T = ar^2 + T_1 \quad (1)$$

where r is the internal radius of the autoclave and T is the temperature in $^{\circ}\text{C}$.

By regarding the sample volume as a cylinder of radius, r , and height, h , the mean temperature, \bar{T} , can be determined as

$$\bar{T} = \frac{\int_0^r 2\pi rh f(T) dr}{\int_0^r 2\pi rh dr} \quad (2)$$

so

$$\bar{T} = 0.5(T_2 - T_1) + T_1 \quad (3)$$

where T_1 is the sample center temperature and T_2 is the temperature at the inner surface of the autoclave. For all experiments the reaction temperatures were considered to be the calculated mean temperatures.

Procedure for Conventional Experiments. Samples and hydrogen gas were charged to the autoclave in a manner similar to that adopted for the nonisothermal experiments. The autoclave was heated to the desired temperature at $7^{\circ}\text{C min}^{-1}$. Experiments were performed for reaction times of 0, 15, 30, 45, 60, 90, and 120 min at center-of-sample temperatures of 406 and 430°C . These conditions were equivalent to mean reaction temperatures of 414 and 438°C , respectively. In the experiment using Tetralin, the reaction temperature was 410°C . The remainder of the procedure was as for the nonisothermal studies.

Results and Discussion

Kinetic Analysis by use of Nonisothermal Reaction Data. The nonisothermal reaction data for the liquefac-

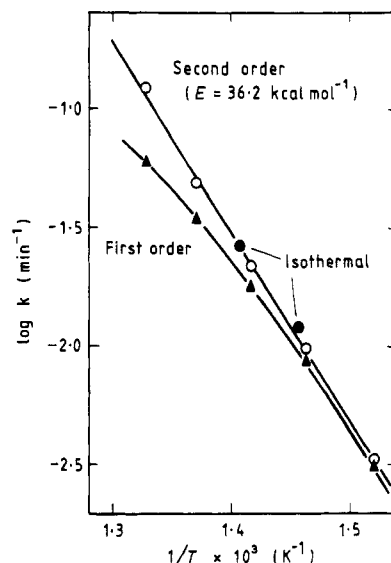


Figure 2. Arrhenius plots of rate constants for Wandoan coal liquefaction (coal- $\alpha\text{-Fe}_2\text{O}_3\text{-S}$; heating rate $3^{\circ}\text{C min}^{-1}$).

tion of Wandoan coal, in the absence of vehicle oil, are presented in Figure 1. The reaction rate ($d\alpha/dt$) at a particular temperature and conversion is determined from the slope of the tangent to the conversion curve at that temperature. Because of the nature of rate data obtained in this manner, the classical method of evaluating proposed rate equations by comparing predicted and observed conversions cannot be adopted. However, the suitability of proposed rate equations can be determined from nonisothermal data by evaluating the rate constant at each temperature and α , and determining whether or not these constants display straight-line Arrhenius behavior. This procedure is based on the assumption that the activation energy (E) is constant over the temperature and conversion ranges studied.

Ordinarily, coal liquefaction is treated as a first-order reaction, the rate of which is described as

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (4)$$

$$k = \frac{1}{(1 - \alpha)} \frac{d\alpha}{dt} \quad (5)$$

The Arrhenius plot of rate constant (k) values for the liquefaction of Wandoan coal, determined using the first-order reaction rate equation, is shown in Figure 2. Clearly, the relationship is nonlinear in the high reaction temperature region.

A second-order rate equation is now proposed, where

$$\frac{d\alpha}{dt} = k(1 - \alpha)^2 \quad (6)$$

$$k = \frac{1}{(1 - \alpha)^2} \frac{d\alpha}{dt} \quad (7)$$

The rate constants obtained with this relationship are also plotted in Figure 2. The data display linear Arrhenius behavior over the whole temperature range studied, indicating that the liquefaction of Wandoan coal can be adequately described by second-order reaction kinetics.

The results obtained when Tetralin was used as a vehicle oil are shown in Figures 3 and 4. Considerable deviation from straight-line Arrhenius behavior is apparent at high temperatures when first-order kinetics are used to describe the rate of reaction. However, as with the experiments without vehicle oil, second-order kinetics provide a good description of the rate of conversion over the entire range

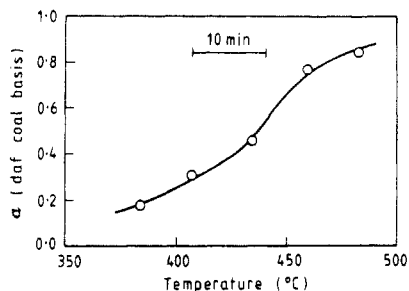


Figure 3. Nonisothermal conversion curve ($3\text{ }^{\circ}\text{C min}^{-1}$) for Wandoan coal liquefaction (coal- α - Fe_2O_3 -S-Tetralin).

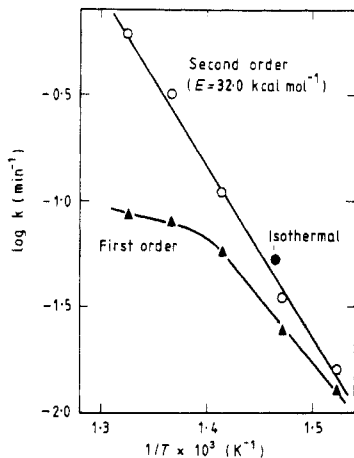


Figure 4. Arrhenius plots of rate constants for Wandoan coal liquefaction (coal- α - Fe_2O_3 -S-Tetralin; heating rate $3\text{ }^{\circ}\text{C min}^{-1}$).

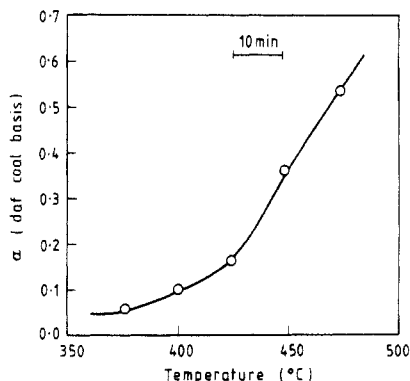


Figure 5. Nonisothermal conversion curve ($2\text{ }^{\circ}\text{C min}^{-1}$) for Wandoan coal liquefaction (coal- α - Fe_2O_3 -S).

of temperatures and conversions studied ($\alpha = 0.2$ to 0.85).

Influence of Heating Rate on Nonisothermal Analysis. Although the rate of reaction is expected to be influenced by the heating rate, the kinetic parameters determined by the nonisothermal method should be constant, as the slope of the tangent to the nonisothermal conversion curve is always equivalent to the reaction rate $d\alpha/dt$ (min^{-1}) at a particular temperature and conversion. In order to investigate this aspect, an additional conversion curve was obtained at a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$. The data obtained are shown in Figure 5. Comparison of this curve with that obtained at a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$ (Figure 1) clearly shows the expected shift to higher conversions at each temperature with the slower heating rate. However, the second-order Arrhenius plots show good agreement for the two heating rates (Figures 2 and 6). The derived activation energies are 36.2 and $34.8\text{ kcal mol}^{-1}$ for heating rates of 3 and $2\text{ }^{\circ}\text{C min}^{-1}$, respectively.

Kinetic Analysis with Conventional Reaction Data. Experiments were performed at reaction temperatures of 414 and $438\text{ }^{\circ}\text{C}$ without vehicle oil and at $410\text{ }^{\circ}\text{C}$ with

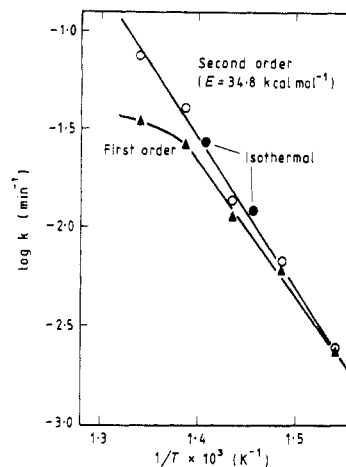


Figure 6. Arrhenius plots of rate constants for Wandoan coal liquefaction (coal- α - Fe_2O_3 -S; heating rate $2\text{ }^{\circ}\text{C min}^{-1}$).

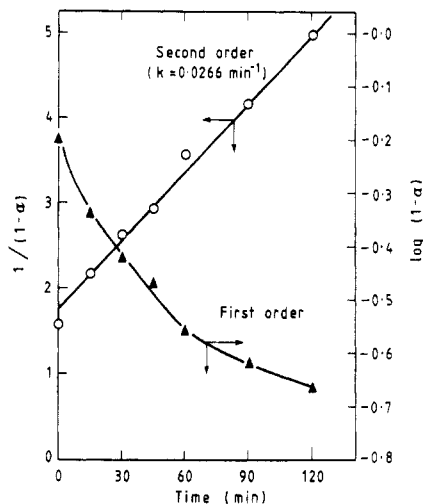


Figure 7. Kinetic data obtained from conventional analysis: first- and second-order plots for Wandoan coal liquefaction performed at $438\text{ }^{\circ}\text{C}$ (coal- α - Fe_2O_3 -S).

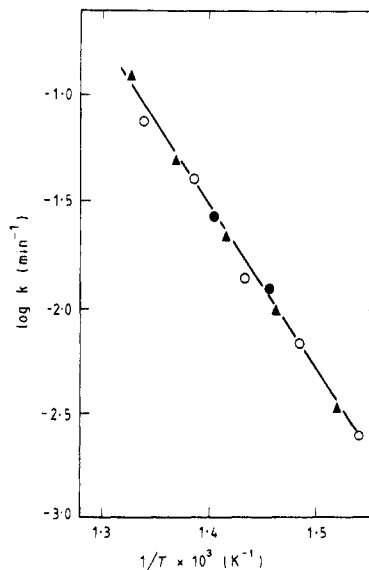


Figure 8. Comparison of second-order rate constants derived from nonisothermal method (\blacktriangle , $2\text{ }^{\circ}\text{C min}^{-1}$; \circ , $3\text{ }^{\circ}\text{C min}^{-1}$) and conventional method (\bullet).

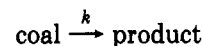
vehicle oil. The results obtained at $438\text{ }^{\circ}\text{C}$ without vehicle oil, plotted on the basis of both first- and second-order reaction kinetics, are shown in Figure 7. The data clearly show that the liquefaction of Wandoan coal can be described by second-order kinetics. The k values calculated

for the three temperatures are plotted in Figures 2 and 6 for the experiments without vehicle oil and in Figure 4 for the experiments with vehicle oil. The excellent agreement between the kinetic parameters derived from the non-isothermal method at two heating rates and the conventional method is more clearly illustrated in Figure 8.

Conclusions

The data presented clearly show that the nonisothermal method of kinetic analysis developed by Kubo et al. (1966) can be applied to studies of coal liquefaction, thereby providing a rapid and convenient means of obtaining empirical expressions to describe the rate of conversion of coal.

The liquefaction of coal has previously been considered to be a first-order reaction with respect to coal (Weller et al., 1951a,b; Falkum and Glem, 1952; Ishii et al., 1965). However, the results presented in this paper show the liquefaction of Wandoan coal to be most suitably described by second-order kinetics over the entire range of reaction conditions studied. Therefore, when coal is regarded as a single reactant, the coal liquefaction process may be represented as



where the reaction product is a general term which includes gas, water, oil, and asphaltenes.

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Registry No. Fe_2O_3 , 1309-37-1; S, 7704-34-9.

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Binary and Ternary Ion-Exchange Equilibria with a Perfluorosulfonic Acid Membrane

Marcia J. Manning* and Stephen S. Melsheimer

Department of Chemical Engineering, Clemson University, Clemson, South Carolina 29631

Binary and ternary ion-exchange equilibrium data were obtained for the Du Pont Nafion 120 perfluorosulfonic acid membrane for several exchange systems. The total concentration of the external solution and the ionic content of the membrane were varied. The resulting binary selectivity coefficients indicated that potassium is the most preferred of the counterions studied. The sequence of increasing preference is $\text{H}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{K}^+$. The binary selectivities proved to be only moderately dependent upon the total concentration and ionic ratio of the external solution. Ternary equilibrium data were taken for combinations of the metal ions with hydrogen. It was found that binary selectivity data could be successfully used to predict the ternary ion-exchange equilibria. Exchanger phase composition in the Nafion membrane was predicted with an average error of 7% as compared to an average error of 39% when the assumption of ideal solutions (that is, the binary selectivity coefficients taken as unity) was used. While not highly accurate, this simple technique may be adequate for many applications.

Background

A continuing area of study in ion exchange has been the development of continuous ion-exchange schemes in order to avoid the cyclic, intermittent operation of traditional packed column systems. One such process, termed Donnan dialysis (Wallace, 1967), uses countercurrent flow of the feed and regenerant streams in channels separated by an ion-exchange membrane.

In recent studies (Lake and Melsheimer, 1978; Yazar et al., 1978) a mathematical model of mass transfer in Donnan dialysis has been developed for binary (two counterion) systems. This model utilized the Donnan equilibrium relation, written in terms of concentrations rather than activities, to represent the equilibrium between the solution and the membrane

$$\left(\frac{C_A}{\bar{C}_A} \right)^{1/z_A} = \left(\frac{C_B}{\bar{C}_B} \right)^{1/z_B} \quad (1)$$

This implies the assumption of ideal solution behavior for both phases, and thus an ionic selectivity of unity for the membrane.

While this simplistic assumption gave acceptable results in binary exchange systems, ionic selectivity effects were expected to be of paramount importance in multicomponent systems. Investigations of ternary systems (Yazar et al., 1978) verified this expectation, leading to the requirement for reliable selectivity coefficient data for the membrane-electrolyte systems of interest. As no data were found in the literature for the membrane used in the dialyzer studies (Du Pont Nafion 120 perfluorosulfonic acid membrane), this investigation was undertaken to acquire the needed data. Another purpose of the study was to explore the feasibility of predicting ternary exchange

* Amoco Research Center, Naperville, IL.