

Kinetics and activation energy of solvent swelling of coal altered by an ultrasonication-enhanced process

Zhaoting Pu, Jie Mi[†], Jian Kang, and Shuaiguo Zhang

Key Laboratory of Coal Science and Technology of Shanxi Province and Ministry of Education,
Taiyuan University of Technology, Taiyuan 030024, P. R. China
(Received 17 October 2013 • accepted 9 July 2014)

Abstract—We studied the kinetics and activation energy of solvent swelling in Qinyuan and Xiongshan coal in perchloroethylene (PCE) using conventional and ultrasonication-enhanced treatment conditions. Kinetic parameters suggested that both coal types exhibited anomalous diffusion regardless of treatment conditions. However, the kinetic parameter n , an exponent that crudely indicates the nature of the solvent diffusion process, decreased with the addition of ultrasound in both coal types. We suggest this change is due to the greater diffusion of PCE into coal during ultrasonication based on greater relaxation of the coal macromolecular network and microscopic agitation of the liquid solvent. Activation energy of coal solvent swelling decreased for both coal types with the addition of sonication, indicating that the energy barrier for the process was reduced in the presence of ultrasound.

Keywords: Ultrasonication, Ultrasound, Coal Solvent Swelling, Kinetics, Activation Energy

INTRODUCTION

Coal is one of the world's most abundant fossil fuel resources and the primary energy source used in China. It is known to have a highly complex, three-dimensional macromolecular network structure consisting of polyaromatic units. These units are linked by both covalent and non-covalent bonds, including hydrogen bonds, van der Waals interactions, electrostatic interactions, and π - π interactions [1-3]. The network structure also contains appreciable amounts of small, weakly bound molecular species varying in mobility [1,4]. Pretreatment with a solvent, such as pyridine, produces swelling in coal and allows more weakly bound species to be released. Carrying out such pre-swelling treatments at room temperature has been shown to increase coal extraction yield and liquefaction conversion yield by selectively disrupting hydrogen bonds and increasing the mobility of small molecules associated with the coal macromolecular network [5-8].

Solvent swelling has been extensively used to study the structure of coal macromolecular networks by determining the average molecular weight between cross-links and solubility parameters [9,10]. While various methods have been utilized to study coal solvent swelling, the two major methods for collecting swelling-related data have been volumetric measurement using packed beds and gravimetric measurement using solvent sorption from the vapor phase [11-14]. The volumetric method is most commonly used to measure the average bulk swelling of powdered coal [15,16]. In many studies, individual coal particles have been used to study coal swelling behavior. However, many studies have found anisotropic solvent swelling in coals upon first exposure to solvents [15-17]. The complex het-

erogeneity of coal can also lead to variations in particle behavior and swelling anisotropy within a single coal sample [16,17]. For example, the value of n (a number that crudely indicates the nature of the solvent diffusion, see Eq. (1)) is sensitive to the coal particle shape [16]. Applying swelling methods to bulk coal is preferred due to the relatively uniform swelling produced in this approach.

Ultrasonication has been widely used in chemical, food and other industries. When ultrasound is applied to the swelled coal slurry, two mechanisms take place: (1) physical breakage, at both the macro scale and at the scale of noncovalent bonds between coal molecules or between coal molecules and other molecules, and (2) leaching, which removes some of the small molecule compounds by mass transfer [18-20]. In conventional methods of coal solvent swelling, the main focus is on surface reaction; little solvent penetration into the interior of the coal matrix is expected during a short treatment period [16]. Ultrasonic swelling of coal can help address this limitation of the conventional method, because physical breakage can help the solvent reach the interior of the coal matrix and reduce the amount of time necessary for treatment [21]. Studying the mechanism of coal solvent swelling during ultrasonication-enhanced methods can therefore contribute to both research on coal macromolecular structure and development of technologies for effective and clean conversion of coal into clean coal.

To gain a greater understanding of the effects of ultrasound on solvent swelling of coal, we investigated the swelling behavior and kinetics of Qinyuan (QY) and Xiongshan (XS) coal treated with perchloroethylene (PCE). We also experimentally measured the kinetic parameters and activation energy of conventional and ultrasonic swelling for these coal types.

EXPERIMENT

QY and XS coal samples were collected in Changzhi, Shanxi prov-

[†]To whom correspondence should be addressed.

E-mail: mijie111@163.com

Copyright by The Korean Institute of Chemical Engineers.

Table 1. Proximate and ultimate analysis of coals

| Coal | Proximate analysis (wt%) | | | Ultimate analysis (wt%, daf) | | | | |
|------|--------------------------|-------|-------|------------------------------|------|------|------|------|
| | Mad | Ad | Vdaf | C | H | O | N | S |
| QY | 0.70 | 16.41 | 18.27 | 71.05 | 3.31 | 4.82 | 0.91 | 2.80 |
| XS | 0.65 | 18.39 | 17.71 | 68.83 | 3.29 | 3.11 | 0.97 | 4.76 |

ince, China. Each coal sample was ground to particles ranging from 124 to 150 μ m diameter using grinder, then dried at 100 °C for 12 hours. The proximate analysis and ultimate analysis of the samples are summarized in Table 1. The two coals were low-ranked bituminous coals similar to the brown and subbituminous coals in swelling behavior [22]. Intermediate radicals attack neighboring aromatics randomly because of many oxygen-containing functionalities on aromatics, so that this results in forming somewhat entanglement structure: highly entangled structure makes the coal less soluble to organic solvents [22]. Analytical reagent PCE (Shanxi Hangke Science Co. Ltd.) was used as a solvent.

The ultrasonication system employed in this study (JXD-09, 20 kHz, 560 W, Beijing Jinxing Ultrasonic Equipment & Technology Co. Ltd.) consists of an ultrasonic vibration-generating tank and power supply system. The temperature of the water can be adjusted to within 1 °C of a desired target by a water circulation system. Solvent swelling experiments of ground QY and XS coal were conducted under atmospheric pressure and at five different temperatures (8, 18, 28, 38, 48 °C). For each experiment, 0.5 g of ground coal was packed into a glass tube and centrifuged at 2,000 rpm for 20 min. The height of coal was measured as h_0 . About 2 mL solvent was then added and mixed. The sample was left for a certain period of time and then again centrifuged, and the height was measured as h_t . The swelling ratio (Q) of the coals was determined as $Q = h_t/h_0$. The tube was then placed into a temperature-controlled volume of water in either a glass beaker, representing a conventional treatment, or in the ultrasonication tank. Each coal treatment was subsampled at intervals of 10, 20, 30, 40, 50, and 60 min during swelling, and the data at the stable equilibrium state was subsampled after 24 h.

The resulting data were processed according to the method reported by Ritger and Peppas [23]. The kinetics of coal solvent swelling can be described using the following empirical equation (Eq. (1)):

$$\frac{Q_t - 1}{Q_e - 1} = kT^n \quad (1)$$

where t is the solvent uptake time. In addition, Q_e , determined by dividing the average volume of the coal sample during swelling by its average volume prior to swelling, is the volumetric swelling ratio at time t ; Q_e , defined by dividing the average volume of swollen coal at equilibrium by its average volume prior to swelling, indicates the volumetric swelling ratio of coal at the equilibrium state. Finally, k is a swelling rate constant, and n is the diffusion exponent, which crudely indicates the nature of diffusion in the sample [24–26].

The values of the kinetic parameters, n and k , can be calculated by first constructing a graph of time-course volumetric swelling data, plotting $\ln[(Q_t - 1)/(Q_e - 1)]$ versus $\ln(t)$, then determining its slope and intercept (Eq. (2)):

$$\ln\left(\frac{Q_t - 1}{Q_e - 1}\right) = \ln(k) + n \ln(t) \quad (2)$$

The activation energy of coal solvent swelling can be calculated by constructing a graph of volumetric swelling, plotting $\ln(k)$ versus the inverse of treatment temperature in Kelvins based on the Arrhenius equation (Eqs. (3) and (4)):

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad (3)$$

$$E_a = -R \left[\frac{d(\ln(t))}{d(1/T)} \right] \quad (4)$$

Table 2. Equilibrium swelling ratio Q_e , rate constant k and diffusion exponent n for QY and XS coal in PCE at different temperatures

| Temperature (°C) | Traditional | | | Ultrasonic | | |
|------------------|---------------|--------|---------|---------------|--------|---------|
| | Q_e | n | k | Q_e | n | k |
| QY | | | | | | |
| 8 | 1.1820±0.0034 | 0.6838 | 0.04622 | 1.2052±0.0025 | 0.6794 | 0.05726 |
| 18 | 1.2011±0.0039 | 0.7056 | 0.05113 | 1.2312±0.0026 | 0.6786 | 0.06260 |
| 28 | 1.2370±0.0031 | 0.6892 | 0.05781 | 1.2796±0.0033 | 0.6641 | 0.06766 |
| 38 | 1.2799±0.0028 | 0.6882 | 0.06188 | 1.3062±0.0031 | 0.6546 | 0.07421 |
| 48 | 1.3406±0.0034 | 0.6634 | 0.06927 | 1.3521±0.0027 | 0.6347 | 0.07962 |
| XS | | | | | | |
| 8 | 1.0531±0.0033 | 0.8084 | 0.03328 | 1.0572±0.0028 | 0.7844 | 0.03951 |
| 18 | 1.0542±0.0044 | 0.7932 | 0.03998 | 1.0628±0.0029 | 0.7698 | 0.04656 |
| 28 | 1.0568±0.0025 | 0.7691 | 0.04683 | 1.0702±0.0027 | 0.7472 | 0.05024 |
| 38 | 1.0598±0.0035 | 0.7529 | 0.05101 | 1.0813±0.0033 | 0.7299 | 0.05370 |
| 48 | 1.0830±0.0032 | 0.7338 | 0.05275 | 1.0960±0.0026 | 0.7149 | 0.05887 |

The value of $d[\ln(k)]/d(1/T)$, which indicates the dependence of $\ln(k)$ for the swelling process on temperature, can thereby be obtained from the slope of the plots of $\ln(k)$ versus $1/T$.

RESULTS AND DISCUSSION

Swelling experiments of QY and XS coal were conducted in PCE at a series of temperatures under conventional and ultrasonic conditions. Table 2 shows the values of Q_e , n , and k for QY and XS coal swelled in PCE at different temperatures. These results indicate that both coal types had higher swelling ratios under the ultrasonication treatment than under the conventional treatment. In particular, Q_e was up to 3.44% and 2.03% greater for QY and XS coal, respectively, in the ultrasonication treatment. Graphs of Q_t against

time at 28 °C are shown for QY and XS coal in Fig. 1 and Fig. 2, respectively. It is clear that the swelling rate for both coal types in PCE increased at a certain degree with the use of ultrasonication.

The observed change in swelling rate is probably due to increased accessibility of the coal structure to the solvent created during ultrasonication. Non-covalent coal-coal bonds have been shown to be broken by acoustic cavitation ultrasound waves cause during such swelling treatments [16,27,28]. This leads to relaxation of the coal macromolecular network, thereby providing more space for non-polar solvent molecules to penetrate the network and come in contact with a greater surface area of the coal. The swelling process was also improved by continual application of ultrasonic waves, which cause rapid penetration of solvent into the coal pores and macromolecular network via acoustic streaming. That is, the swelling ratio

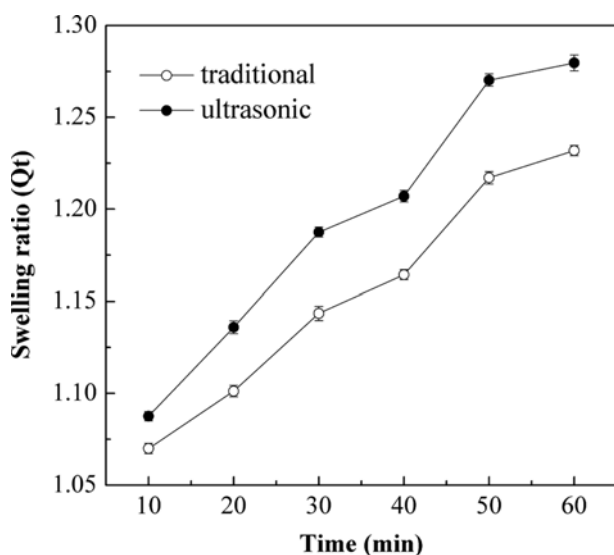


Fig. 1. Swelling ratio Q_t with time for the swelling of QY coal in PCE at 28 °C.

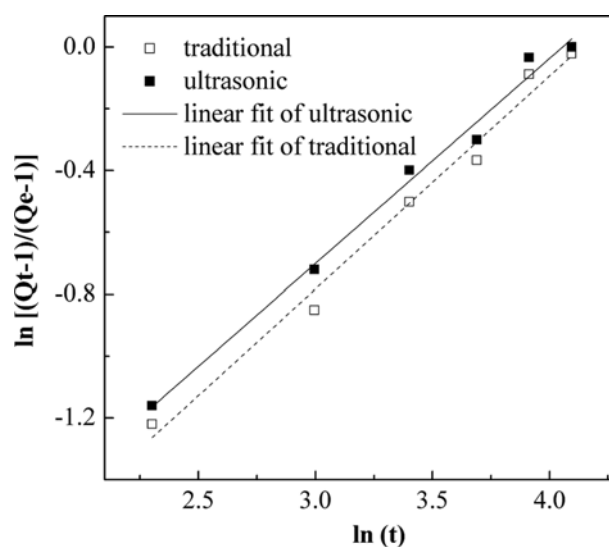


Fig. 3. $\ln[(Q_t-1)/(Q_e-1)]$ by $\ln(t)$ from the swelling of QY coal in PCE at 28 °C.

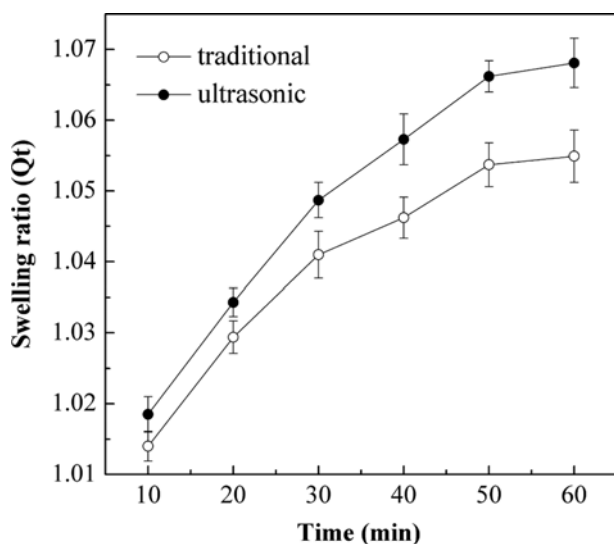


Fig. 2. Swelling ratio Q_t with time for the swelling of XS coal in PCE at 28 °C.

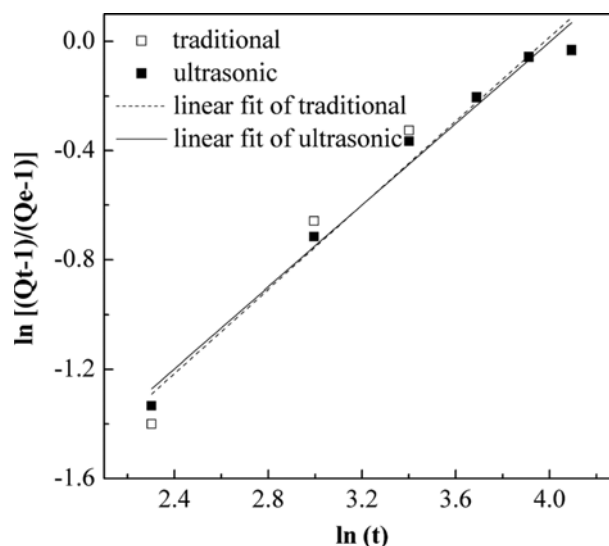


Fig. 4. $\ln[(Q_t-1)/(Q_e-1)]$ by $\ln(t)$ from the swelling of XS coal in PCE at 28 °C.

at equilibrium as well as swelling rate increased in ultrasonicated, PCE-swelled QY and XS coal due to the effects of both acoustic cavitation and acoustic streaming.

Graphs used to determine the values of k and n during PCE-swelling with and without ultrasonication are shown for QY coal in Fig. 3 and for XS coal in Fig. 4. It is clear that, as previously observed for coal swelling [12,24,25], the maximal swelling rate of both coal types in PCE obeyed a first-order rate law.

The solvent transport mechanism, determined using the diffusion exponent (n), can be classified into four categories. Values of n in the range 0.43-0.50 indicate Fickian diffusion, values of 0.50-0.84 indicate anomalous diffusion; case-II diffusion is indicated by values in the range 0.85-1.0, and super case-II diffusion produces $n > 1.0$ [23,26,29]. The Fickian diffusion process is controlled primarily by the concentration gradient of the particles, while the case-

II process is controlled mainly by the relaxation of the macromolecular structure. The anomalous process is intermediate between Fickian and case-II, indicating that both processes are involved. The diffusion of PCE into QY coal produced n for conventional and ultrasonic conditions, respectively (Table 2), indicating that anomalous diffusion prevailed regardless of treatment type. As shown in Fig. 5, the value of n decreased with when ultrasonication was added. This suggests that QY coal swelling likely moved towards a diffusion process having a greater influence of particle concentration gradient with the application of ultrasonic waves. This trend was also observed for XS coal, as shown in Fig. 6 and Table 2.

The observed changes in n may be attributed to the ultrasonic enhancement in mass transfer between liquid and solid parts of the coal swelling system due to acoustic cavitation and acoustic streaming [19,20,30]. Ultrasonication influences mass transfer in liquid-solid systems in several ways: erosion of or collisions at the solid surface, or the microscopic agitation of liquid [19,20,30]. Ultrasonication overall improves diffusion rates not only by producing collisions and erosion of solid particles in ground coal, but also by creating small, imploding cavitation bubbles on the surface of coal particles [19,20,30]. The rapid creation and collapse of these cavitation bubbles can produce numerous tiny liquid masses, resulting in microscopic agitation of the liquid solvent. Therefore, the solvent molecules can contact a greater surface area of the coal macromolecules. Furthermore, the transmission of ultrasonic shock waves within the acoustic field through the liquid solvent would be expected to induce microvibration of solvent molecules, thereby increasing the average translational energy of these small molecules. This, in turn, would allow accelerated diffusion of small solvent molecules into the relaxed coal network. The accessibility of the coal macromolecular network to the solvent also increases as the ultrasonication increases mass transfer. Since the relaxation of the macromolecular structure controls case-II diffusion, the value of n decreases when swelling methods add an ultrasonic treatment [19, 20,30].

We also determined the dependence of $\ln(k)$ for coal solvent

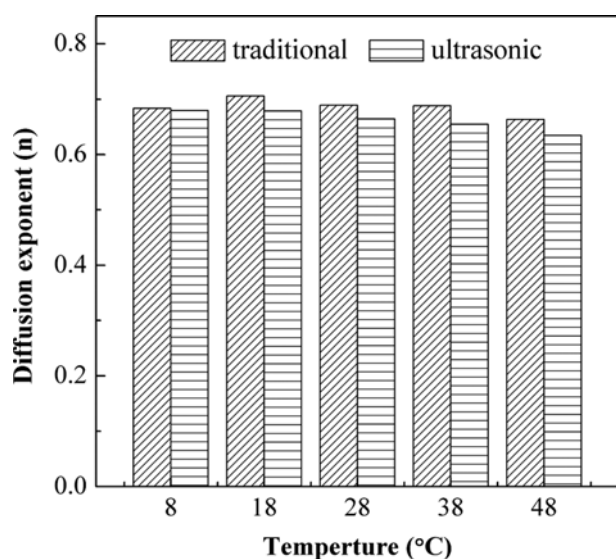


Fig. 5. Change of kinetic parameter n for QY coal in PCE.

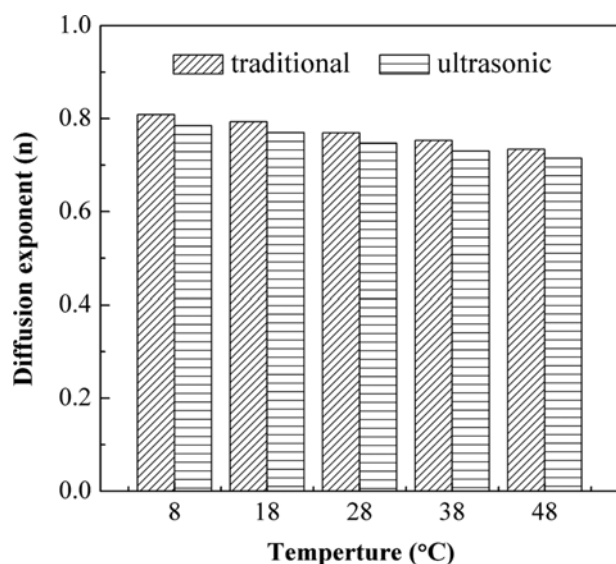


Fig. 6. Change of kinetic parameter n for XS coal in PCE.

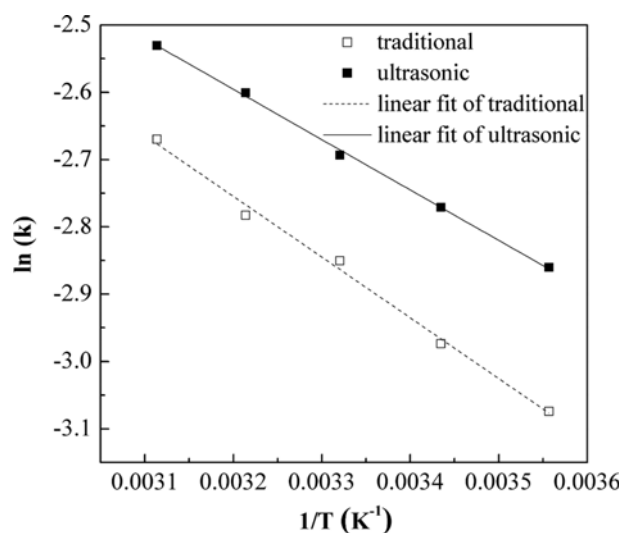


Fig. 7. Variation of $\ln(k)$ with $1/T$ for the swelling of QY coal in PCE.

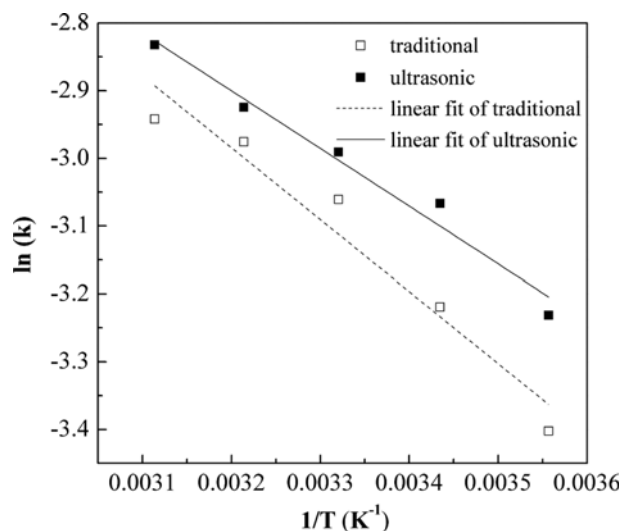


Fig. 8. Variation of $\ln(k)$ with $1/T$ for the swelling of XS coal in PCE.

swelling on temperature (i.e., $d[\ln(k)]/d[1/T]$) for QY and XS coal under both swelling treatments, shown in Fig. 7 and Fig. 8, respectively. For QY coal, swelling activation energy was calculated to be -902.89 and -748.89 under conventional and ultrasonication treatments, respectively. For XS coal, the values were -1061.7 and -852.73 , respectively.

Based on the above values and Eq. (4), the apparent activation energy of solvent swelling of coal in PCE was calculated for each coal and treatment type. The swelling activation energy of QY coal in PCE decreased from $7.5071 \text{ kJ}\cdot\text{mol}^{-1}$ to $6.2266 \text{ kJ}\cdot\text{mol}^{-1}$ when ultrasound was added to the treatment, while that of XS coal decreased from $8.8275 \text{ kJ}\cdot\text{mol}^{-1}$ to $7.0900 \text{ kJ}\cdot\text{mol}^{-1}$. This indicates the presence of an energy barrier for the swelling process, and that ultrasonication reduces this barrier. The reduced apparent activation energy can help further explain why the observed swelling rate for both coals increased in ultrasonicated samples. This also supports the idea that the observed decrease in n can be attributed to ultrasonic enhancement of mass transfer in the liquid-solid system.

CONCLUSIONS

We studied the kinetics of solvent swelling in two different coal types in PCE under conventional and ultrasonication treatment conditions. Kinetic parameters indicated that both coal types exhibited anomalous diffusion under both treatment conditions. However, the values of the kinetic parameter n decreased in ultrasonicated samples compared to conventional treatment in both cases. This is likely due to increased diffusion caused by ultrasonic mass transfer effects, including liquid agitation and relaxation of coal macromolecular network. The apparent activation energy of coal solvent swelling decreased by 17.06% in QY coal and by 19.68% in XS coal when ultrasonication was added. This indicated an energy barrier for the swelling process is reduced by the application of ultrasound, likely due to macromolecular network relaxation effects. In summary, ultrasonication is clearly a factor that can improve the sol-

vent swelling kinetics of coal.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (51272170/21276172) and the Key Programs for Science and Technology Development of Shanxi Province (No. 20080322035). Suggestions from Dr. Mengmeng Wu of Taiyuan University of Technology have been much appreciated.

REFERENCES

1. F. Castro-Marciano and J. P. Mathews, *Energy Fuels*, **25**, 845 (2011).
2. C. Chen, J. Gao and Y. Yan, *Energy Fuels*, **12**, 1328 (1998).
3. J. W. Larsen, T. K. Green and J. Kovac, *J. Org. Chem.*, **50**, 4729 (1985).
4. A. M. Mastral, M. T. Izquierdo and B. Rubio, *Fuel*, **70**, 139 (1991).
5. H. F. Shui, Z. C. Wang and M. X. Cao, *Fuel*, **87**, 2908 (2008).
6. Ö. Sönmez and E. S. Giray, *Energy Source. Part A*, **33**, 1901 (2011).
7. T. Takanohashi, X. Fengjuan, I. Sanokawa and M. Iino, *Fuel*, **79**, 955 (2000).
8. V. Zubkova and A. Strojwas, *Energy Source. Part A*, **34**, 609 (2012).
9. C. P. Painter, *Energy Fuels*, **4**, 379 (1990).
10. C. P. Painter, J. Graf and M. M. Coleman, *Energy Fuels*, **4**, 393 (1990).
11. T. Aida and T. G. Squires, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.*, **30**, 95 (1985).
12. L. Chen, J. L. Yang and M. X. Liu, *Ind. Eng. Chem. Res.*, **50**, 2562 (2011).
13. S. T. Hsieh and J. L. Duda, *Fuel*, **66**, 170 (1987).
14. J. R. Nelson, O. P. Mahajan and P. L. Walker, *Fuel*, **59**, 831 (1980).
15. H. Gao, L. Artok, K. Kidena, S. Murata, M. Miura and M. Nomura, *Energy Fuels*, **12**, 881 (1998).
16. D. V. Niekerk, P. M. Halleck and J. P. Mathews, *Fuel*, **89**, 19 (2010).
17. G. D. Cody, J. W. Larsen and M. Siskin, *Energy Fuels*, **2**, 340 (1988).
18. B. Ambedkar, R. Nagarajan and S. Jayanti, *Ultrason. Sonochem.*, **18**, 718 (2011).
19. W. C. Xia, J. G. Yang and C. Liang, *Powder Technol.*, **237**, 1 (2013).
20. K. W. Ze, X. H. Xin and C. J. Tao, *J. Chin. Univ. Min. Technol.*, **17**, 358 (2007).
21. J. Garcia-Noguera, F. I. P. Oliveira, M. I. Gallão, C. L. Weller, S. Rodrigues and F. A. N. Fernandes, *Dry. Technol.*, **28**, 294 (2010).
22. K. Kidena, S. Murata and M. Nomura, *Fuel Process. Technol.*, **89**, 424 (2008).
23. P. L. Ritger and N. A. Peppas, *Fuel*, **66**, 815 (1987).
24. F. E. Ndaji and K. M. Thomas, *Fuel*, **72**, 1525 (1993).
25. F. E. Ndaji and K. M. Thomas, *Fuel*, **72**, 1531 (1993).
26. Y. Otake and E. M. Suuberg, *Energy Fuels*, **11**, 1155 (1997).
27. M. V. Kondrin, E. L. Gromnitskaya, A. A. Pronin, A. G. Iyapin, V. V. Brazhkin and A. A. Volkov, *J. Chem. Phys.*, **137**, 084502 (2012).
28. J. B. Milligan, K. M. Thomas and J. C. Crelling, *Energy Fuels*, **11**, 364 (1997).
29. S. Mazumder, F. Vermolen and J. Bruining, *SPE J.*, **16**, 856 (2011).
30. M. A. Margulis, *Ultrason. Sonochem.*, **1**, 87 (1994).