LETTERS TO THE EDITOR

To the Editor:

Referring to the paper by A.H. Mamaghani, J.K. Beddow, and A.F. Vetter entitled "Chemical Comminution of Coal" [**33**(2), p. 319, Feb., 1987], we would like to bring the following information to your attention.

Molecular size of the reagent is suggested as a possible explanation for the rate of coal comminution. This is based on the argument that smaller molecules diffuse faster and thus they should lead to higher comminution rates. For the alcohols considered in their study, the authors' conclusion appears to be valid. However, when the data of Table 2 of the paper are reordered according to descending comminution rate as shown in Table 1 it becomes clear that there is not a direct correlation between the comminution rate and the molecular size in general. This is due to the fact that the mechanism of reagent transfer into the porous media is dominantly a flow phenomena and less a diffusion process. The characteristics of the reagent flow through porous media are determined by the fluid and porous media properties. Thus, for a given porous media, the dimensionless capillary imbibition number

$$N_c^I = \gamma \rho \, L / \mu^2 \qquad (1)$$

correlates consistently as suggested by Civan et al. (1985) with the comminution rate as shown in Table 1. This feature has been shown previously by Civan et al using experimental data for NH_3, CF_3CO_2H, HNO_3, H_2SO_4 and CH_3SO_3H as reagents for Croweburg bituminous coal of Oklahoma.

Table 1. Comminution Rate vs. Molecular Size and Imbibition Number at 25°C

Reagent	Comminut. Rate, mg/cm^2 · h	Molec. Size, Å	Capillary Imbib. No. $N_c^I = \gamma\rho L/\mu^2$*
Acetone	19.6	30.78	178
NaOH (2% wt. in Water)**	3.9	19.53	61
Methanol	3.6	25.20	50
Ethanol	3.1	28.50	18
Propanol	3.0	30.96	6
Butanol	2.8	33.11	4
Hexanol	2.1	36.79	0.7

*γ = surface tension; ρ = density; μ = viscosity; and L = length of flow path occupied by the liquid for $L = 1$ cm.

**Estimated by interpolation from a plot of the comminution rate vs. the capillary imbibition number.

Table 2. Variation of Capillary Imbibition Number with NaOH Concentration

NaOH wt. % in Water	Capillary Imbib. No. $N_C^I = \gamma\rho L/\mu^2$*
0	88
5	44
10	25
15	13

*For $L = 1$ cm.

Table 2 shows the effect of NaOH concentration on the capillary imbibition number. As indicated by Table 2 increasing NaOH concentrations lead to decreasing capillary imbibition numbers. Hence the comminution rates are lower for higher NaOH concentrations. This too is confirmed by the authors' finding that scouting experiments with higher concentrations of sodium hydroxide led to poor comminution rates.

In view of the above discussion it appears that the capillary imbibition number given by Eq. 1 should be used as a measure of the relative effectiveness when evaluating reagents for coal comminution.

Literature Cited

Civan, F., R. M. Knapp, A. P. Hagen, and M-K Wang. "Solvent Selection for Coal Comminution," Int. Conf. on Alternative Energy Sources, Miami Beach, FL (Dec. 9–11, 1985); *Alternative Energy Sources VII, Hydrocarbons/Energy Transfer,* T. Veziroğlu, Ed., Vol. 5, 71, Hemisphere Publishing, (1987).

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Reply:

In response to Dr. Faruk Civan and Dr. Roy M. Knapp's letter to the editor, I must agree that their imbibition number data does correlate with the comminution rate as presented in Table 1. However I find it difficult to conclude that the higher the capillary imbibition number, the higher the comminution rate will be. This is supported by the fact that when the comminution rates were measured as a function of caustic concentration in a methanol- NaOH system, the higher rates were achieved at around 6–8% caustic concentration; refer to Figure 3 in the article entitled "Chemical Comminution of Coal" [**33**(2), p. 319, Feb., 1987]. This contradicts Dr. Civan and Dr. Knapp's conclusion as shown in their Table 2, where it is suggested that an increase in the caustic concentration reduces the capillary imbibition number and therefore the comminution rates are decreased.

I believe the mechanism for the chemical comminution of coal is more complex than suggested by my dear colleagues. A series of detailed experiments with different types of coal have indicated that comminution rates are effected by applied pressure on coal (Mamaghani et al., 1986), solvent flow rates, size of the coal sample, and types of coal with similar porosity. Clearly there are other factors such as the electrical repulsive forces that are generated within the coal matrix by the comminuting reagent which effect and control the comminution rates.

Literature cited

A. H. Mamaghani, J. K. Beddow, A. F. Vetter, "Chemical Comminution of Coal in Simulated Stress Fields," *Powder Technology*, **45**(2), p. 191 (Jan. 1986).

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To the Editor:

In Table 5 of a recent paper by Sorrentino et al. entitled "Activity Coefficients of Aroma Compounds in Model Food Systems" [32(12) p. 1988, Dec., 1986], infinite dilution activity coefficient, γ, determined experimentally is compared to that predicted with UNIFAC. The systems studied involve lower alcohols, ketones, esters and aldehydes in water, i.e. systems where proven models such as ASOG and UNIFAC may be expected to perform reasonably well.

To our surprise, the authors find a mean error of 260% between experimental values and those predicted by UNIFAC. We would like to comment on the UNIFAC predictions and the experimental values.

For the systems studied, the authors report a mean deviation between the experimental activity coefficients and those predicted by UNIFAC of 260%. The UNIFAC parameter tables have continuously been revised and extended, and it is not clear which of the revised versions the authors have used. We have, however, checked the calculations using all published versions of the parameter tables, and in all cases (except for propanol-water, where there were some problems with early versions of the tables) we obtained a mean deviation of 40%. Using the parameter table published by Gmehling et al. (1982) we obtained the results shown in Table 1. (Compare with Table 5 of the paper by Sorrentino et al.) It should be noted that the values predicted by UNIFAC tend to be larger than those measured by Sorrentino et al.

Table 1. Infinite Activity Coefficients of Solutes in Water

Solutes	γ exp*	γ UNIFAC*	γ UNIFAC**
Methanol	1.64	2.24	2.25
Ethanol	3.55	6.15	7.62
Propanol	11.2	29.1	20
2-Propanone	7.7	18.4	11.4
2-Butanone	29.5	83.9	31.7
Ethyl acetate	77.0	35	84.7
Propyl acetate	450.0	163	242
Ethanal	4.43	41	3.47
Propanal	15.6	189	9.7

*Values obtained by Sorrentino et al. (1986).

**Values obtained using the UNIFAC model and the parameter table of Gmehling et al. (1982). Mean deviation: 40%.

We have compared the experimental values by Sorrentino et al. with the extensive data bank of infinite dilution activity coefficients (Gmehling and Onken, 1977; Gmehling, 1985). It appears by comparison that many of the values reported by Sorrentino et al. are about 30% lower than generally accepted values. For example the γ value for ethanol in water is in the normal temperature range on the order of 6.0. This may be verified by the very many correlations of VLE data for the ethanol-water system shown by Gmehling and Onken, 1977. Sorrentino et al. obtained a value of 3.55.

Literature cited

Gmehling J., P. Rasmussen and Aa. Fredenslund, "VLE by UNIFAC Group Contribution," *Ind. Eng. Chem. Process Des. Dev.* **21** 118 (1982).
Gmehling J. and U. Onken, "Vapor-Liquid Equilibrium Data Collection," *Dechema Chemistry Data Series*, Frankfurt (1977).
Gmehling J., "Thermodynamic Databases," CODATA Bulletin 58, 56f, (November 1985).
Sorrentino F., A. Vorlley and D. Richon, AIChE J., **32** 1988 (1986).

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Reply:

We confirm that the values reported in the third column of Table 1 of the letter by Fredenslund and his coauthors were obtained with the parameters given in the monograph, "Vapor-Liquid Equilibria using UNIFAC," (Fredenslund, 1977). By using the parameters from Gmehling et al. (1982), we also confirm the data given in the fourth column of Table 1 in their letter.

The reliability of measurements through the stripping technique has been proven by several tests. The activity coefficient for hexane in *n*-hexadecane has been compared to various literature data (Leroi et al., 1977; Antoine et al. 1980). Results on water-alcohols (especially water-ethanol) have been compared satisfactorily to calculated data of thermodynamic models from vapor-liquid equilibrium data of several authors (Lebert and Richon, 1984). In the case of the mixture water-2-propanone, measurements have been performed with different stripping flows (Richon et al., 1985) leading to the same value of the activity coefficient within 1%. Furthermore, no significant difference can be found on activity coefficient values obtained with another operator or another cell.

By comparing the infinite dilution activity coefficients measured by Sorrentino et al. and γ^∞ calculated by UNIFAC plus parameters from the table (Gmehling et al., 1982), we may note that experimental γ^∞ are higher than calculated γ^∞ for alcohols and 2-propanone, slightly lower for 2-butanone and lower for acetates and aldehydes.

Literature cited

Fredenslund, A., J. Gmehling, and P. Rasmussen, "Vapor-Liquid Equilibria Using UNIFAC," Elsevier, Amsterdam (1977).
Gmehling, J., P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem. Process. Des. Dev.*, "VLE by UNIFAC Group Contribution," **21**, 118 (1982).
Lebert, A., and D. Richon, *J. Agri. and Food Chem.*, **32**, 1156 (1984).
Leroi, J. C., J. C. Masson, H. Renon, J. F. Fabries, and H. Sannier, *Ind. Eng. Chem. Process. Des. Dev.*, **16**, 139 (1977).
Richon, D., P. Antoine, and H. Renon, *Ind. Eng. Chem. Process. Des. Dev.*, **19**, 144 (1980).
Richon, D., F. Sorrentino, and A. Voilley, *Ind. Eng. Chem. Process. Des. Dev.*, **24**, 1160 (1985).
Sorrentino, F., A. Voilley, and D. Richon, *AIChEJ.*, **32**, 1988 (1986).

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