

# A LABORATORY EXPERIMENT ON COMBINED MASS TRANSFER AND KINETICS

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**T**HIS ARTICLE DESCRIBES a senior-level undergraduate laboratory experiment on combined mass transfer and kinetics. Specifically, the increase of pH in an aqueous solution of acetic acid (such as vinegar) is followed with a digital pH meter during neutralization with commercial antacid tablets. This experiment was successfully implemented into the chemical engineering laboratory curriculum at Georgia Tech during the winter quarter of 1988, at a total cost of \$600. The reagents can be purchased cheaply at a local supermarket.

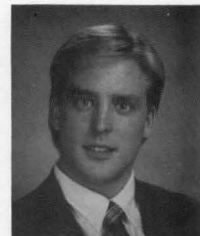
## BACKGROUND

The development of meaningful yet inexpensive engineering laboratory experiments on chemical kinetics is a difficult task. The incorporation of mass transfer concepts into such experiments renders this task even more formidable.

The pH values of the gastric contents of human stomachs can typically vary from 1.0 to 3.0. Similarly, the pH values for many foods, specifically fruits (apples, apricots, grapefruit, oranges, peaches, pears, strawberries), are in the range of 3.0-4.0. Thus, dilute acetic acid (such as vinegar) with a pH of around 3.0 is a reasonably effective and inexpensive representative of the weak organic acids present in a human body. This acid may then be employed for simple laboratory simulation of the biochemical processes associated with neutralization by commercial over-the-counter antacids to relieve gastric distress.

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**Stuart A. Sanders** received his bachelor's degree in chemical engineering in June of 1988 from the Georgia Institute of Technology. He developed the laboratory experiment described in this article during his senior year. He is currently employed as a composites engineer with Pratt-Whitney in West Palm Beach, Florida.



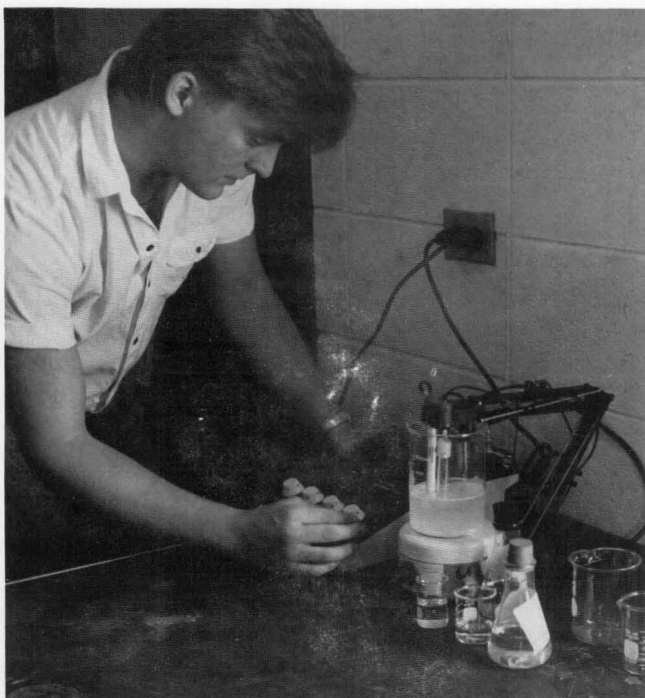
**Jude T. Sommerfeld** is a professor in the School of Chemical Engineering at Georgia Tech. He received his BChE from the University of Detroit and his MSE and PhD degrees, also in chemical engineering, from the University of Michigan. His 25 years of industrial and academic experience have been primarily in the area of computer-aided design, and he has published over eighty articles in this and other areas.



## EQUIPMENT

The principal piece of equipment needed for this laboratory experiment is a pH meter and electrode with a reasonably rapid response time, *e.g.*, 5-10 seconds. For this purpose, an Accumet Model 910 pH meter with digital readout was purchased from Fisher Scientific for about \$500. A glass-body combination electrode (with automatic temperature compensation) was also purchased from the same company (Catalog No. 13-639-285), as well as two buffer solutions (pH = 1.0 and 7.0) for 2-point standardization of the pH meter. Total cost of these latter items was less than \$100.

Most of the remaining required equipment items are standard laboratory supplies, such as beakers, graduated cylinders, and reagent bottles. A magnetic stirrer and stirring bar are required, as well as a timer. A set of vernier calipers is also needed for the students to measure the dimensions of the antacid tablets studied. A photograph of the experimental setup is shown as Figure 1.



**FIGURE 1.** Experimental setup to study neutralization of vinegar with antacid tablets.

#### PRELIMINARY TESTS

Some initial tests were performed on the neutralization of distilled white vinegar with granulated or powdered antacids. As one might expect, the neutralization was completed within less than a minute. This time frame is, of course, unacceptable for two reasons: 1) response time considerations of the electrode and 2) duration of the experiment for data acquisition. It was also found that very little vinegar was required if one wished to avoid excessive consumption of the antacid.

Thus, in all further experiments the distilled white vinegar was diluted with distilled water in the ratio of 1:20. It was also decided to use antacid tablets as the neutralization agents. Two such commercial products were chosen, and they are denoted as R and T throughout this article. The various properties and physical characteristics of these antacid tablets are given in Table 1.

#### PROCEDURE

Following is a summary of the procedure for this laboratory experiment, as distributed to the students.

The protective tip is removed from the pH electrode, and the latter is rinsed well with distilled water to remove any residue which may have formed on the

electrode tip. The 2-point standardization of the pH meter is then performed with the two buffer solutions in accordance with the procedure given in the manufacturer's instruction manual. A copy of the latter is provided (loaned) to the students at the beginning of the experiment.

A fresh acid solution is prepared by mixing 25 ml of distilled white vinegar and 500 ml of distilled water in a 1-liter reagent bottle. From the latter, 250 ml of this fresh acid solution are transferred to a 500-ml beaker, which is placed on a magnetic stirrer. This beaker is then positioned below the electrode assembly, and the latter is lowered into the acid solution. Care is taken to ensure that the stirring bar will not hit the electrode tip during operation. The initial pH of the acid solution is recorded (typically 3.09).

The thickness ( $H$ ) and diameter ( $D$ ) of a tablet of the test antacid are measured with the vernier calipers. At time = 0, the suggested number of tablets ( $m = 5$  for brand R, 3 for brand T) are dropped into the acid solution and the timer is started. The stirring speed is adjusted to achieve a fair degree of homogeneity, and so that the tablets are just barely lifted off of the bottom of the beaker. The pH values for the solution are recorded at 30-second intervals for the first five minutes, at 1-minute intervals for the next 15 minutes, and at 2-minute intervals for the remainder of the run—until the tablets are completely dissolved and the solution pH has levelled off at a constant value (typically 40-50 minutes total).

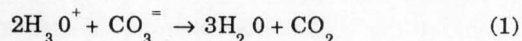
The above procedure is then repeated for the second antacid (R or T) to be investigated. Typical experimental data from such an investigation of brand T are presented in Table 2.

**TABLE 1**  
Characteristics of Antacid Tablets Studied

Property	Antacid Brand	
	R	T
Active (alkaline) ingredient	Dihydroxylaluminum sodium carbonate	Calcium carbonate
Typical mass of tablet, g	1.42	1.33
Mass of active ingredient, mg	335	500
Mass fraction active ingredient ( $x_B$ )	0.236	0.376
Mol. wt. of active ingredient ( $M_B$ )	144.0	100.09
Typical thickness of tablet ( $H$ ), cm	0.520	0.377
Typical diameter of tablet ( $D$ ), cm	1.610	1.610
Aspect ratio ( $\alpha = H/R$ )	0.646	0.468
Density of tablet ( $\rho$ ), g/cm <sup>3</sup>	1.341	1.733
No. of tablets used in an experiment ( $m$ )	5	3

## THEORY

Very simply, the overall ionic reaction for this system is:



It is assumed that the instantaneous rate of the overall reaction, measured as the rate of disappearance of the hydronium ion, is proportional to the product of the instantaneous remaining surface area of the tablets and the hydronium ion concentration, with the order for the latter as yet unspecified. Thus

$$\frac{1}{V} \frac{dN_A}{dt} = -k\alpha C_A^n \quad (2)$$

Now, the area of a given tablet (disc) is the sum of its two faces plus its edge, or  $2\pi r^2 + 2\pi rh$ . Assuming that the aspect ratio ( $\alpha = \text{height}/\text{radius}$ ) of a given tablet remains constant throughout the dissolution process, the instantaneous surface area of a tablet is  $2\pi r^2(1 + \alpha)$ . Eq. (2) then becomes, after assuming constant reaction volume ( $V$ )

$$\frac{dC_A}{dt} = -2\pi kmr^2(1 + \alpha)C_A^n \quad (3)$$

It is necessary to relate  $C_A$  and  $r$  in the above equation. From the stoichiometry of Eq. (1)

$$\frac{dN_A}{dt} = 2 \frac{dN_B}{dt} \quad (4)$$

Eq. (3) then becomes

$$\frac{1}{V} \frac{dN_B}{dt} = -\pi kmr^2(1 + \alpha)C_A^n \quad (5)$$

We further assume that the composition of an antacid tablet remains constant throughout the process. Thus

$$N_B = \frac{\pi m r^2 h \rho x_B}{M_B} = \frac{\alpha \pi m \rho x_B r^3}{M_B} \quad (6)$$

Eq. (5) then becomes

$$\frac{dr}{dt} = \frac{-k(1 + \alpha)M_B V}{3\alpha \rho x_B} C_A^n \quad (7)$$

From an overall material balance

$$C_A = C_A^0 - \frac{2\alpha \pi m \rho x_B}{M_B V} (R^3 - r^3) \quad (8)$$

The final differential equation to be integrated, in

**TABLE 2**  
Experimental Data on the  
Neutralization of Vinegar with Antacid Brand T

t, min	pH	t, min	pH	t, min	pH
0.0	3.09	8.0	4.47	29.0	5.63
1.0	3.19	9.5	4.70	31.0	5.67
1.5	3.43	10.0	4.74	33.0	5.70
2.0	3.57	11.0	4.82	35.0	5.74
2.5	3.69	12.0	4.90	37.0	5.77
3.0	3.80	13.0	4.97	39.0	5.80
3.5	3.90	14.0	5.09	41.0	5.84
4.0	3.98	15.0	5.20	42.0	5.85
4.5	4.06	21.0	5.44	43.0	5.87
5.0	4.12	23.0	5.49	44.0	5.88
6.0	4.24	25.0	5.53	45.0	5.90
7.0	4.35	27.0	5.58		

terms of the single dependent variable  $r$ , is then obtained after substitution of Eq. (8) into Eq. (7).

## REACTION ORDER

In the case of  $n = 1$  (process is first-order with respect to the acid concentration), the substitution of Eq. (8) into Eq. (7) yields

$$\frac{dr}{dt} = -k(\gamma^3 + \beta^3 r^3) \quad (9)$$

where

$$\gamma^3 = \frac{(1 + \alpha)M_B C_A^0 V}{3\alpha \rho x_B} - \frac{2\pi m(1 + \alpha)R^3}{3} \quad (10)$$

and

$$\beta^3 = \frac{2\pi m(1 + \alpha)}{3} \quad (11)$$

Eq. (9) can then be integrated between the limits of  $r = R$  at  $t = 0$  and  $r$  at  $t$  to yield

$$\frac{l}{3\gamma^3} \left\{ \frac{1}{2} \ln \frac{(l+r)^2(l^2 - lR + R^2)}{(l+R)^2(l^2 - lr + r^2)} + \sqrt{3} \left[ \text{TAN}^{-1} \left( \frac{2r-l}{l\sqrt{3}} \right) - \text{TAN}^{-1} \left( \frac{2R-l}{l\sqrt{3}} \right) \right] \right\} = kt \quad (12)$$

where

$$l = \frac{\gamma}{\beta} \quad (13)$$

Thus, a plot of the left-hand side of Eq. (12), denoted as  $f(r)$ , versus time ( $t$ ) would yield a straight line if  $n$  were equal to unity. The slope of this straight line would be the combined mass transfer and kinetic rate constant,  $k$ . The function  $f(r)$  is computed at each experimental data point by calculating  $r$  from rearrangement of Eq. (8)

$$r = \sqrt[3]{R^3 - \frac{M_B V}{2\alpha\pi m \rho x_B} (C_A^0 - C_A)} \quad (14)$$

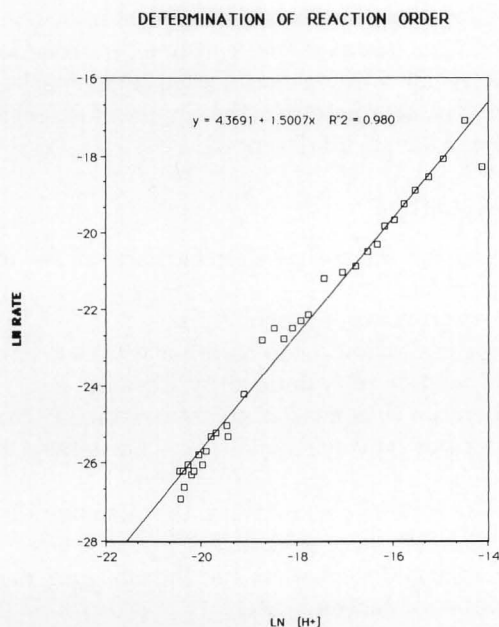
and invoking the definition of pH

$$\text{pH} = -\log(C_A) \quad (15)$$

When the data of Table 2 were converted and plotted in the indicated fashion, however, the results were disappointing. Instead of a straight line, a smooth curve with a monotonically decreasing slope was obtained, indicating that  $n \neq 1$ .

A differential analysis of the experimental data of Table 2 was next performed. For this purpose, the pH data of Table 2 were converted to  $C_A$ , numerically differentiated with respect to time, and the resulting rate normalized with respect to the instantaneous total surface area of the tablets. The latter is computed as

$$a = 2\pi m r^2 (1 + \alpha) \quad (16)$$



**FIGURE 2.** Plot of reaction rate, normalized to the instantaneous surface area of the tablets, versus the hydronium ion concentration, in log-log coordinates.

where  $r$  is again computed from Eq. (14), averaged over the time increment selected.

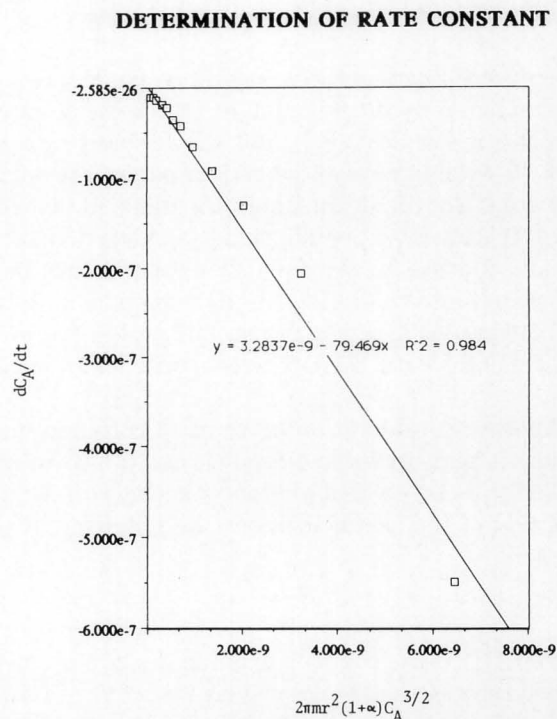
The logarithm of the normalized rate

$$\ln \left[ -\frac{1}{a} \cdot \frac{dC_A}{dt} \right]$$

was then plotted versus the logarithm of the hydronium ion concentration. The result of this procedure is shown in Figure 2. As Eq. (2) indicates, the slope of this straight line in log-log coordinates should be equal to the reaction order ( $n$ ) with respect to the hydronium ion concentration. Least-squares regression analysis of these data for the T tablets yielded a slope of  $n = 1.5007$ , with a correlation coefficient of 0.980. Similar results, *i.e.*,  $n \cong 3/2$ , were obtained from experimental data on neutralization with brand R tablets.

#### DATA ANALYSIS

Thus, in the laboratory instructions to the students, they are given the value of  $n = 3/2$  in Eq. (2), and then asked to experimentally determine the value of the combined mass transfer and kinetic rate constant,  $k$ . This is accomplished by again numerically differentiating the data to obtain  $dC_A/dt$ , and plotting this result versus the product of  $2\pi m r^2 (1 + \alpha) C_A^{3/2}$



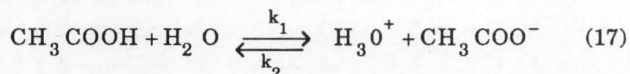
**FIGURE 3.** Plot of reaction rate to obtain rate constant from Eq. (3).

[see Eq. (3)];  $r$  is again calculated from Eq. (14). The result of this procedure is shown in Figure 3 for the data of Table 2 on brand T tablets. Least-squares regression analysis of the data in this case yielded a value of the slope for this straight line (equal to  $k$ ) of 79.5 (liter/gmole)<sup>1/2</sup>/(cm<sup>2</sup> min).

## DISCUSSION

No reasons for the apparent process order with respect to the hydronium ion concentration of  $n = 3/2$  are provided to the students. They are not expected to come up with an explanation, either. The development of a more complete and accurate mechanism for this process would certainly be an interesting exercise, but is beyond the scope of a single undergraduate laboratory experiment (one of four during a 10-week quarter).

Thus, in addition to the single heterogeneous term of Eq. (2), incorporation of the homogeneous aqueous dissociation of acetic acid

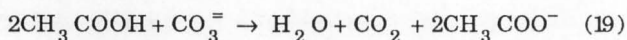


would be a more complete representation for the rate of hydronium ion disappearance. In this case, Eq. (2) would become

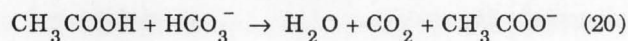
$$\frac{1}{V} \cdot \frac{dN_A}{dt} = k_A C_A^n - k_1 C_{\text{HAc}} + k_2 C_A C_{\text{Ac}^-} \quad (18)$$

The reverse reaction rate constant ( $k_2$ ) in Eq. (18) can be eliminated by introduction of the dissociation constant for acetic acid ( $K_A$ ), but the forward rate constant ( $k_1$ ) would have to be estimated or determined. In writing Eq. (2), it was implicitly assumed that reaction (17) is always at equilibrium, and thus its net rate is equal to zero. In principle, this reaction can be incorporated into the model through usage of appropriate material balance equations, but processing of the experimental data then becomes practically intractable.

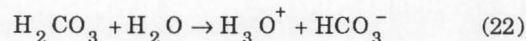
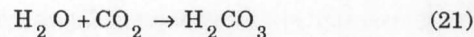
Another consideration pertains to consumption of the acetic acid. In writing Eqs. (1) and (4), it was also implicitly assumed that the only mechanism for consumption of the acetic acid was the following overall reaction



where  $\text{CO}_3^{=}$  is the common anion in the two brands of antacid tablets studied. However, since  $\text{CO}_2$  is formed as a product of reaction (19), the following additional reaction



may also be postulated for consumption of the acetic acid. The bicarbonate ion, of course, is formed from the ionic dissociation of  $\text{CO}_2$



There are two implicit assumptions underlying reaction (19) as the sole consumption sink for the acetic acid: 1) most or all of the  $\text{CO}_2$  is evolved as gas from the reaction solution; 2) the amount of  $\text{HCO}_3^-$  formed from any residual  $\text{CO}_2$  present in solution is negligible. Indeed, some gas evolution is observed during the experiment. The ionization constant for carbonic acid ( $K_c$  equal to  $4.3 \cdot 10^{-7}$  at room temperature) may be used to estimate the amount of bicarbonate ion present, *i.e.*

$$\frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_c \quad (23)$$

Thus, at the beginning of the reaction (when very little  $\text{CO}_2$  should be present in the first place) when the pH is 3.09, from Eq. (23) the ratio of the concentrations of bicarbonate ion to carbonic acid is about  $4 \cdot 10^{-4}$ , and hence the former is truly negligible. At the final pH of 5.90, however, this ratio is equal to 0.34. Reaction (20) may thus have an impact on the overall process under these conditions. The fact that this latter reaction is unimolecular in acetic acid, whereas the assumed sole consumption reaction (19) is bimolecular with respect to the same species, may conceivably be related to the apparent intermediate reaction order of 3/2 observed.

## NOMENCLATURE

- $a$  = instantaneous total surface area of the antacid tablets, cm<sup>2</sup>
- $C$  = concentration, gmole/liter
- $D$  = initial diameter of an antacid tablet, cm
- $f(r)$  = function of  $r$ , defined by Eq. (12)
- $H$  = initial thickness of an antacid tablet, cm
- $h$  = instantaneous thickness of an antacid tablet, cm
- $K_A$  = ionization constant for the aqueous dissociation of acetic acid
- $K_C$  = ionization constant for the aqueous dissociation of carbonic acid
- $k$  = combined mass transfer and kinetic rate constant, (liter/gm mole)<sup>1/2</sup>/(cm<sup>2</sup> min)
- $k_1$  = forward reaction rate constant for the aqueous dissociation of acetic acid

- $k_2$  = reverse reaction rate constant for the aqueous dissociation of acetic acid  
 $l$  = constant ( $= \gamma/\beta$ ), cm  
 $M$  = molecular weight, g/gmole  
 $m$  = number of antacid tablets present  
 $N$  = moles of a substance, gmole  
 $n$  = order of process with respect to hydronium ion concentration  
 $\text{pH}$  =  $-\log(C_A)$   
 $R$  = initial radius of an antacid tablet, cm  
 $r$  = instantaneous radius of an antacid tablet, cm  
 $t$  = time, min  
 $V$  = volume of reaction solution, liters  
 $x$  = mass fraction  
 $\alpha$  = aspect ratio of an antacid tablet ( $= H/R$ )  
 $\beta$  = constant defined by Eq. (11)  
 $\gamma$  = constant defined by Eq. (10), cm  
 $\rho$  = density of a tablet, g/cm<sup>3</sup>  
 $[ ]$  = concentration of, gmole/liter

#### Subscripts

- $A$  = acid ( $\text{H}_3\text{O}^+$ )  
 $B$  = base ( $\text{CO}_3^-$ )

#### Superscript

- $O$  = initial condition ( $t = 0$ )  $\square$

## ChE book reviews

### COAL LIQUID MIXTURES: Proceedings of the Third European Conference

edited by T. J. Pierce, et al

Hemisphere Publishing Corp., 79 Madison Ave., New York, NY; 409 pages, \$82.50 (1988)

Reviewed by Alex E. S. Green  
University of Florida

Published by the European Federation of Chemical Engineers (EFCE Publication Series No. 64, EFCE Event No. 372), this book is a report on a two day symposium held in Malmo, Sweden, 14-15 Oct 1987 (ISB No. 85295 2139). CLM-2 the 2nd European conference on this topic held in London (1985) reflected optimism on the future of CLM as well as a consolidation of works on the stability, atomization, and combustion characteristic of slurry technology. On the other hand, CLM-3 recognizes that the 1986 fall of world oil prices has generally delayed the commercial realization of CLM. The papers presented provide mostly an update of technological developments on coal water mixtures (CWM). They cover slurry preparation at pilot and commercial scales, slurry atom-

ization including an analysis of droplet mechanisms and influence of dispersants, and slurry combustion including an assessment of mineral matter transformation and reaction kinetics. Most of the CWM combustion programs in Europe are carried out on converted utility and industrial boiler plants. Whereas most USA CLM programs have emphasized the use of premium grades of coal, the European program gives considerable emphasis to the use of low-grade fuels of high ash content where local economic factors are favorable including coal washery fines. Commercial application of slurry to steam generation, to aggregate cement kiln firing and to open hearth furnaces are discussed in considerable detail reflecting the technological maturity of the use of CWM.

Economic and marketing aspects of coal liquid mixtures are nicely summarized in Chapter 27 by N. Lood on "Coal Water Fuel (CWF) in a Changing Market." He points to the increases of oil prices in 1973 and in 1979 which focused attention on the need to develop alternatives to oil and to the recent emergence of CWF as the leading candidate. He discusses CWM fuels advantages in terms of high coal reserves, market stability, the preservation of the fluid infrastructure, the safety and environmental cleanliness, and the fact that existing oil boilers could be utilized with minimal changes and low retrofit costs.

The oil price collapse of 1986 from the \$30 per barrel range to the \$10 per barrel range had a major impact on CWF. The reaction in the USA where market forces are predominant was almost immediate, and most development projects were shelved or drastically scaled down. This conference proceedings suggests that Europeans have taken a longer range perspective and are giving somewhat greater attention to the security of energy supply upon the stability of European economies *vis-a-vis* actions of the OPEC cartel. Of the member states in the European Economic Community, Italy is making the greatest progress in the use of CWF. From the continued advancement of CWM technology in Europe it would appear that the technological lead which the US had in 1985 might have been transferred abroad. The recent Clean Coal Technology program might, however, restore the US position.

This reviewer finds it difficult to understand why co-combustion of coal water fuel with natural gas has received practically no attention in Europe. Natural gas is available from the USSR, Northern Africa, and the North Sea, and its price tends to track the price of oil. Co-combustion of coal water fuel with natural gas (CWG fuel) provides advantages in the form of emission reduction, energy enhancement, flame stabilization, and other technological benefits (see *An Alternative to Oil: Burning Coal with Gas*, University Presses of Florida, 1981, and *Co-Combustion ASME FACT*, Vol 4, 1988, H00443). In this reviewer's opinion, when oil prices climb above \$20 per barrel again, CWG fuel will be the most competitive alternative to oil from environmental, energy, and economic standpoints.  $\square$