

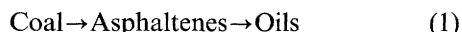
LETTER TO THE EDITOR

REMARKS ON RATE ANALYSIS OF COAL LIQUEFACTION USING KINETIC MODELS INVOLVING MULTIMOLECULAR REACTION PATHS

Dear Sir:

Recent kinetic analyses of coal liquefaction have been based on a more sophisticated reaction scheme than the conventional analyses. A paper¹⁾ in which the intramass transfer effect was discussed regarding solid catalytic liquefaction can be mentioned as such an analysis. That paper, however, reaches suspect findings that need further discussion. They are responsible for ambiguous recognition of the stoichiometric equations depicting the scheme.

Conventional schemes have been composed of networks of unimolecular reaction paths such as



Without any conflict, the above equation can be taken as both on the mass basis and on the mole basis. However, since the molecular weight of coal cannot be determined, workers have implicitly understood the equation in terms of mass basis such that unit mass

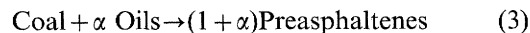
of coal converts into unit mass of asphaltenes and then into unit mass of oils. Thus, which kind of basis should be applied has been a trivial question.

The paper applied a multimolecular reaction path such as



Unlike the case of Eq. (1), which kind of the basis to apply Eq. (2) is not a trivial question. The mass basis cannot be permitted, because the mass conservation law fails: α times unit mass is missing after the reaction.

Thus, Eq. (2) must be corrected with proper stoichiometric coefficients so that mass may be conserved as follows:



It is demonstrated how the validity of the stoichiometric equations affects system simulation. The published results were compared with those obtained on the basis of the correct stoichiometric equations using the same values of rate parameters as reported in the paper. **Figure 1** shows an example of the comparison. It reveals that the former exhibits a better fit with experimental results than the latter, but fails mass balance whereas the latter does. Thus, if the valid stoichiometric equations have been applied in the

* Received October 23, 1989. Correspondence concerning this article should be addressed to S. Sato.

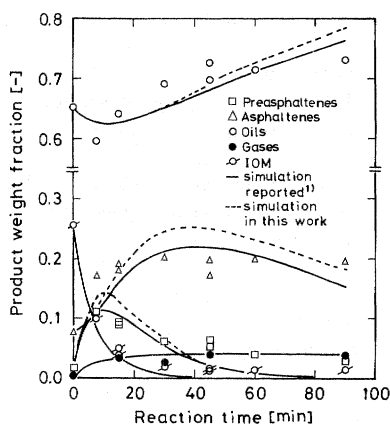


Fig. 1. Comparison of experimental liquefaction course¹⁾ and theoretical one¹⁾ simulated on the basis of invalid stoichiometric equations with that simulated on the basis of valid ones

paper, different optimal rate parameter values should have been estimated.

Therefore, the values were estimated on the basis of the correct stoichiometric equation with a computer program²⁾ using the Marquardt method.

According to the procedure outlined in the paper, α 's value was first estimated. Figure 2 shows the changes in sum of square of errors along with α . The sum in this work, differing from that in the paper, varies monotonously with α and levels off in the region of 0 to 0.1 of α . From the result the scheme without consideration of solvent effects ($\alpha=0$) is found to be more reasonable than the others ($\alpha \neq 0$) from the

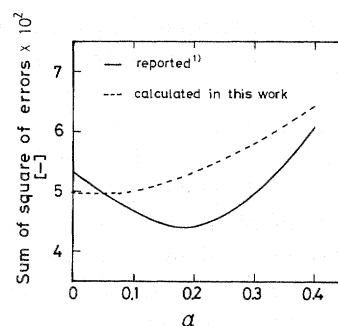


Fig. 2. Comparison of sum of square of errors¹⁾ calculated on the basis of invalid stoichiometric equations with that on the basis of valid ones

viewpoint of the model fit and of simplicity. It indicates that the scheme was not appropriate to express experimental properties, despite the proposer's expectation.

Consequently, the reported kinetic findings must to reexamined, using a more reasonable scheme.

Literature Cited

- 1) Gollakota, S. V., J. A. Guin and C. W. Curtis: *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1148 (1985).
- 2) Sato, S., T. Hashimoto and M. Morita: *Nenryo Kyokai-shi*, **59**, 103 (1980).

Shimio SATO

Department of Chemical Engineering,
Yamagata University,
Yonezawa, Yamagata 992