Comments on the Note by Edelson and Allara

L. F. ALBRIGHT

School of Chemical Engineering
Purdue University, West Lafayette, Indiana 47907

Edelson and Allara have correctly pointed out some of the problems concerned with the modeling of pyrolysis data, but we believe the problems are even more complicated than indicated by their paper. In developing a highly accurate (and theoretical) model, problems occur both in choosing all the reaction steps of importance to include in the model and also in selecting accurate parameters (energies of activation and pre-exponential terms) for each reaction step.

Considering first the reaction steps in the models, it is currently difficult to identify all important reaction steps occurring during pyrolysis. Most of the many reactions occur in the gas phase, but some reactions also occur at the walls of the reactor. Recent work in our chemical engineering laboratories at Purdue University has shown that at least six types of reactions occur on the walls of tubular reactors. Yet no known models have included terms for such surface reactions.

Considering now the energies of activation to be used in modeling the gas-phase free-radical steps for the pyrolysis, the values reported in the literature may be in error by at least 1 kcal/g-mole. Such an error may have a large effect on the predicted rate values for at least some of the reactions. Furthermore as suggested earlier by Herriott et al. (1972), the energies of activation vary to at least some extent with temperature. Values to be used at 750° to 900°C may be different than values determined experimentally at much lower temperatures. In addition, the exact mechanism of some of these specific reaction steps that may involve hot or activated radicals, or molecules may change somewhat as temperature is increased.

As additional information is being obtained so that theoretical models can be developed, semiempirical (or even semitheoretical depending on one's state of optimism) models have proven reasonably successful. The model developed by Herriott et al. using 15 free-radical gas-phase reaction steps is obviously not truly theoretical, but it does seem to be a step in the right direction. Herriott et al. recognized there were limitations to the model and emphasized the need for expanded models in the future. Of interest, energies of activation in this model did generally agree fairly well with relatively well accepted values that in some cases had been obtained independently at lower temperatures. However we agree completely with Drs. Edelson and Allara that the energies of activation of this model are not necessarily accurate values. They are probably reasonable approximations that should only be used with caution in making any theoretical predictions.

Drs. Edelson and Allara are definitely moving in the right direction when they use an expanded model containing more reaction steps than that used by Herriott et al. It is most encouraging that their model fits the experimental data of Leathard and Purnell, who operated at extremely mild (for pyrolysis) conditions, namely low temperatures, low pressures, low conversions, in the absence of steam, and in a quartz reactor operated batchwise. Side reactions were presumably minimal, and surface reactions in the quartz reactor were probably much different and were of relatively lesser importance as compared to those in commercial reactors. As a side note, batch data for free-radical reactions are difficult to interpret since the contributions of wall reactions often are quite different than those in flow reactors.

We agree with Drs. Edelson and Allara that theoretical models for pyrolysis made at much more severe conditions such as obtained by Herriott et al. will be considerably more complicated than those made at mild conditions. We plan, however, to test the expanded propane model proposed by Edelson and Allara when it is published and hence becomes available; we would like to determine how use of somewhat modified parameters predict data obtained at more severe conditions. Eventually we hope to incorporate terms for the surface reactions into our pyrolysis models.

LITERATURE CITED

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2. Leathard, D. A., and J. H. Purnell, "The Self-Inhibited Pyrolysis of Propane at Small Extents of Reaction," *Proc. Roy. Soc.*, **A 305**, 517 (1968).

Effect of Transport Processes on Conversion in a Trickle-Bed Reactor

NICHOLAS D. SYLVESTER and PUNYA PITAYAGULSARN

Department of Chemical Engineering
University of Tulsa, Tulsa, Oklahoma 74104

Reactors containing three phases (gas, liquid, and solid) are becoming more important not only for pollution control but also to the petroleum, plastics, and chemical industries for the production of new and better products. The trickle-bed reactor, as the term is used here, is one in which a liquid-and a gas-phase flow concurrently downward through a fixed bed of catalyst particles. Trickle-bed reactors are used in the petroleum