formance measure by which schedules are assessed. The run is completed in 2.4 CPU min.

The optimal solution is given in Figure 5. All due dates are met with the exception of the first order for the first saleable product (nodes 4 and 6) which is 16 time units late. Note that 57.5% (N_{41} = 11.5) of the first customer order of 20 batches for the first saleable product is allocated to the first reaction pathway compared to 55% (N_{42} = 16.5) of the second order of 30 batches. These unusual splits result because production run levels of products 4 and 5 (the intermediate in the second path) are set so that the finishing times of their respective runs coincide. Once processor 1 is relieved of product 4 production, a production run of product 6 immediately begins using the batches of its precursor (product 5) just yielded by the reactor series comprised of processors 2 and 3.

Conclusion

Several extensions to the mixed (binary) integer programming model in Rich and Prokopakis (1986) for scheduling batch operations in a multipurpose plant have been presented. The model is now capable of handling alternate production routings with or without alternate reaction pathways. That is, a product may be produced in different processor sets via the same or different reaction pathways. This permits the simultaneous production of a product in two or more locations in the plant, giving greater flexibility to a plant manager with respect to routing of processes in the plant and assigning products to processors. Two test problems have been solved with reasonable computational effort.

We have also demonstrated how the model can be further modified to allow for preventive maintenance by placing limitations on start times of production. Other occurrences, such as shortages of raw materials or time lags between steps due to quality control tests, can be dealt with in a similar fashion.

Nomenclature

A = set of indexes corresponding to saleable products
B_i = processor (reactor) batch size for product i
B_{in} = number of binary variables used in formulation
D_{ik} = due date for kth order of saleable product i
f_{ij} = stoichiometric factor: number of units of product i required to produce one unit of immediate successor product j
F_{ik} = finishing time of production run k of product i
I_{i0} = initial inventory for product i
M = number of processors
N = number of products
N' = total number of nodes in the precedence network, $N' \geq N$; the strict inequality holds if the precedence network is other than an assembly structure
$N_{arc,i}$ = number of arcs in digraph associated with saleable product i
N_{ik} = number of batches of product i produced in production run k (decision variable)
N_{ik}^j = number of batches of product i produced in production run k via jth reaction path or by jth set of processors (decision variable)
$p(i)$ = number of reaction paths through which saleable product i can be synthesized
$R(i)$ = number of customer orders for saleable product i
$s(i)$ = number of processor sets capable of producing product i
S_{ik} = start time of production of kth run of product i (decision variable)
t_i = cycle time for a processor (or processor set) required by product i
T_{ik} = tardiness of kth order of saleable product i (decision variable)
U_p = the set of products which require processor p
W = large number relative to any task duration
w_{ik} = objective function weight for kth order of saleable product i
X_{ik} = production requirement for product i (expressed in the same units as B_i); size of kth customer order if i is saleable; product demand due to order k if i is intermediate
$y_{ikjk'}$ = binary variable used to resolve potential conflict between product i/run k and product j/run k'
Z_{in} = latest completion time of the nth run of product i taking all $s(i)$ processor sets (or all $p(i)$ reaction paths) into consideration

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CORRESPONDENCE

Comments on "Structure of Complex Catalytic Reactions: Thermodynamic Constraints in Kinetic Modeling and Catalyst Evaluation"

Sir: The article by Shinnar and Feng looks considerably like the results published earlier by Gorban and co-authors (Bykov and Gorban, 1984, 1985; Gorban, 1979a–c, 1980; Gorban and Bykov, 1980; Gorban and Yablonskii, 1980, 1981; Gorban et al., 1980). To avoid further duplications and to inform the readers, I report that in the above-cited articles, a new concept for qualitative analysis of chemical kinetics equations has been developed. In Gorban (1979a), the algorithm for the definition of regions of accessible composition for a given reaction mechanism and the location of the equilibrium and original compositions has been proposed. In Gorban (1979b), many thermodynamically allowed paths of reaction have been studied. In Gorban et al. (1980), this method has been extended to open catalytic systems. The developed methods allow one to create a new procedure for planning unsteady kinetic experiments (Gorban and Yablonskii, 1980). These results are partially reflected in a survey by Gorban et al. (1980). By use of these results, the problem on boundary equilibriums has been solved (Gorban, 1980). In Gorban

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(1979c), the size of the region where the linear estimation can be applied has been evaluated. The connection between the times of relaxation to equilibrium and equilibrium flows has been found in Bykov and Gorban (1984, 1985), Gorban (1979c), and Gorban and Yablonskii (1981). The enumerated results have found further development in the books by Gorban (1984), Gorban and Bykov (1986), and Yablonskii et al. (1983, 1984). The ones by Yablonskii et al. are going to be published in English by Elsevier. The book by Gorban (1984) is devoted to chemical kinetics equations and their thermodynamic analysis.

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Response to Comments on "Structure of Complex Catalytic Reactions: Thermodynamic Constraints in Kinetic Modeling and Catalyst Evaluation"

Sir: I was very gratified to hear that Professor Gorban's important work in chemical kinetics will soon be available in English in a more accessible form, and we are looking forward to the publication of his book. We became aware of Gorban's work through the review article in *International Chemical Engineering*, and we properly referenced Gorban's work in our latest paper. However, Dr. Bykov's comment that we duplicated Gorban's results is rather strange. As much as we could ascertain from the papers available, the majority of our work and results have no direct parallel to Gorban's work.

It is true that some of the ideas of geometric representation of the accessible space are similar. However, the use made of these methods is different. Gorban's emphasis is on reactions for which mass action kinetics apply. Our work emphasized catalytic reactions of arbitrary complexity. The overall observed reaction in the latter case is a sum of a large number of individual steps with intermediates which do not appear in the overall reaction rate and for which one frequently cannot apply mass action kinetics. It is important to understand the properties of such overall rate equations, as these are the only ones measurable. This led us to the definition of an independent reaction and also to the concept of coupling between reactions due to joint intermediates.

Furthermore, Gorban seems to be more interested in the mathematical structure of a system of equations comprised of individual reactions following mass action kinetics and the way they approach equilibrium, whereas we were more interested in how the thermodynamic constraints imposed by specific catalyst properties affect the reachable space. What especially concerned us were the implications of these constraints for process design, catalyst development, and catalyst testing. Therefore, our emphasis was not just in understanding the contraints imposed by specific catalyst properties but also in finding ways to overcome them, such as nonisothermal reaction trajectories, enlargement of the component space, and embedding of the catalyst site in a selective membrane. The latter is important both in enzyme kinetics and in shape selective catalysis. Thus, our approach allows one to evaluate the impact of shape selectivity on the reachable space. Space selectivity obviously cannot affect the second law, but it can strongly modify the permissible trajectories for a specific catalyst.

The use of thermodynamic analysis in chemical reactor design, catalyst design, and chemical process development can be a very powerful tool that has, until now, been underutilized and also not well understood. We see our paper as well as Gorban's work as the first steps toward making these tools and methods more widely available. There are still many existing unsolved problems in this field.

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