# 203c A New Look at Competing Reversible Reactions Leading to Optimal Operting Policies

*Derek W. Griffin, Jeffrey D. Ward, Duncan A. Mellichamp, and Michael F. Doherty*

Current research in the field of plantwide design and operation addresses issues such as the choice of an appropriate control structure (design) for available control degrees of freedom, process configuration and controller selection, appropriate equipment sizing, and capacity based operation of an already built chemical plant. For a given plant and operating policy one must choose the most appropriate control system configuration; a centralized control structure, with perhaps optimal set-point regulation or a decentralized, perhaps self-optimizing one. Several authors have investigated the case of a plant with reactor, separation system, and recycle stream. Operating policies that have been suggested to handle production rate changes include maintaining constant recycle loop flow rates (Luyben 1994), operating the reactor at maximum holdup (Larson & Skogestad, 2000; Larson et al., 2003), or allowing both the reactor holdup and recycle flows to vary (Wu & Yu, 1996; Wu et al., 2002). A more recent and general approach to this problem considers different classes of irreversible process chemistries, using recycle flow rates as design variables and allowing reactor holdup to vary (Ward et. al, 2004). It is found, depending on the specific underlying chemistry, that the plant should be operated either on the reactor volume constraint or to scale the reactor holdup and recycle flow rates linearly with production rate subject to constraints. However, when one or more of the competing reactions is reversible, the predicted operating policy can change, as discussed below.

Processes involving reversible reactions can be difficult to design and/or operate because of chemical equilibrium conversion limitations. Studies have been made on various series-parallel reactor network configurations that yield the largest attainable region for reversible reactions (Hopley et al., 1996; Glasser and Hildebrandt, 1997). A method for overcoming equilibrium conversion is the use of reactive distillation; many recent studies compare such a unit operation to the conventional reactor, separator, recycle process (Ung and Doherty, 1995; Gadewar et al., 2004). For conventional processes that involve competing reversible reactions alternative control structures that achieve desired production rates and that reject disturbances have been identified for optimal control configuration (Kapilakarn & Luyben, 2003). Most recently published research considers the design of systems specifically for reversible chemistries; the work described here focuses on the operation of a conventional plant that incorporates equilibrium reactions.

The methodology developed by Ward et al. classifies irreversible chemistries into one of two groups. If at least one reactant has a rate dependence stronger in an undesired reaction than the desired one, then the chemistry is considered to be “bounded” and the optimal policy is to operate the reactor completely full at all times. The other class, “non-bounded” chemistries, operates optimally away from the physical constraints of the system. If reaction reversibility is introduced into the rate laws the operating policy can change. For example, if only the undesired reaction(s) are reversible; the operating policy predicted by Ward et al. remains the same for either class of chemistries. But if the main reaction is strongly reversible, i.e. has a low equilibrium constant, the optimal operating policy for a bounded chemistry can actually be away from the reactor volume constraint, similar to that predicted for a non-bounded chemistry. As the equilibrium constant becomes larger (as the reaction becomes nearly irreversible) the optimal operating policy for such a chemistry moves back against the reactor volume constraint in line with the original irreversible bounded chemistry. Systems having an operating policy away from all constraints are expected to be better handled by a centralized control structure, while decentralized control is easier to design for a system that always operates on constraints. The results described can be extended to any system of competing reactions that can be classified as bounded or non-bounded. This extension is important to the process systems community because all chemistries are inherently reversible to some degree.

Gadewar, S. B., L. Tao, M. F. Malone, and M.F. Doherty, “Process Alternatives for Coupling Reaction and Distillation,” Chem. Eng. Res. & Des., 82(A2), 140, (2004).

Glasser, D. and D. Hildebrandt, “Reactor and Process Synthesis,” Comput. Chem. Eng., 21, S775 (1997).

Hopley, F., D. Glasser, and D. Hildebrandt, “Optimal Reactor Structures for Exothermic Reversible Reactions with Complex Kinetics,” Chem. Eng. Sci., 51, 2399 (1996).

Kapilakarn, K., and Luyben W. L., “Plantwide Control of Continuous Multiproduct Processes: Two-Product Process,” Ind. Eng. Chem. Res., 42, 1890 (2003).

Larsson, T., M. S. Govatsmark, S. Skogestad and C.-C. Yu, “Control Structure Selection for Reactor, Separator and Recycle Processes,” Ind. Eng. Chem. Res., 42, 1225 (2003).

Larsson, T. and S. Skogestad. “Plantwide Control---A Review and a New Design Procedure,” Model Ident. Control, 21, 209 (2000).

Luyben, W. L., “Snowball Effects in Reactor/Separator Processes with Recycle,” Ind. Eng. Chem. Res., 33, 299 (1994).

Ung, S. and M. F. Doherty, “Synthesis of Reactive Systems with Multiple Equilibrium Chemical Reactions,” Ind. Eng. Chem. Res., 34, 2555 (1995).

Ward, J. D., D. A. Mellichamp and M. F. Doherty. “The Importance of Process Chemistry in Selecting the Operating Policy for Plants with Recycle,” Ind. Eng. Chem. Res. 43, 3957 (2004).

Wu, K.-L. and C.-C. Yu, “Reactor/Separator Processes with Recycle---1. Candidate Control Structures for Operability,” Comput. Chem. Eng., 20, 1291 (1996).

Wu, K.-L. C.-C. Yu, W. L. Luyben, and S. Skogestad, “Reactor/Separator Processes with Recycle---2. Design for Composition Control,” Comput. Chem. Eng., 27, 401 (2002).