Semicontinuous Reactive Distillation for Specialty Chemicals Production: Economic Comparison with Batch and Continuous Processing

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ABSTRACT

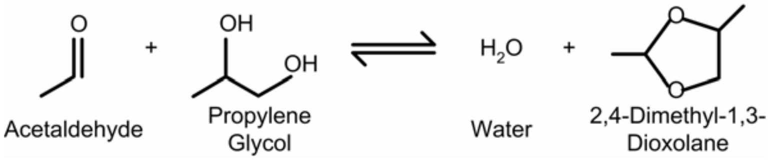
Semicontinuous reactive distillation (SRD) has been introduced as a novel means of integrating reaction and separation operations using a forced-cyclic strategy. Rigorous simulations of equivalent batch, continuous, and semicontinuous designs were analyzed and compared over a range of production capacities. In the case study examined, the SRD design requires significantly less capital costs than both batch and continuous strategies, and requires about the same amount of manufacturing costs as batch. As a result, the SRD strategy is the economically optimal choice for a wide range of intermediate production rates.

INTRODUCTION

With the increasing demand for specialty and fine chemicals, manufacturers seek to design processes that operate at intermediate capacities. At these intermediate production rates, neither batch nor continuous strategies stand out as the clear choice. Instead, a new process is proposed. For systems that require both reactions and separations, semicontinuous reactive distillation (SRD) integrates these two methods using a reactive middle vessel [1], and uses a forced-cyclic strategy based on semicontinuous distillation [2-7]. In addition to the reactive middle vessel, SRD uses an auxiliary tank and requires only one distillation column, which is used for multiple purposes during different phases of the cycle. SRD operates in a continuous cycle, and is not down for the cleaning, warm-up, or shutdown stages that are often required in batch operation.

SIMULATIONS

The exothermic, reversible reaction



is used as the case study to compare the SRD to batch and continuous equivalents. The two products, 2,4-dimethyl-1,3-dioxolane (24DMD) and water, form a low-boiling azeotrope. The two reagents are the lowest and highest boilers (acetaldehyde at T_{NBP}=21^{o}C, propylene glycol at T_{NBP}=181^{o}C), leaving the products and the azeotrope in the middle. This makes ordinary continuous reactive distillation difficult, since complete separation of the two products in the distillate and bottoms streams is rendered impossible by the azeotrope. Moreover, the kinetics in the column would be thermodynamically limited by this temperature difference. *Kaymak* [8] has shown that for some exothermic, reversible $A + B \rightleftharpoons C + D$ reactions, such as this one, it is preferable to perform the reaction outside of the column.

Processes that create equimolar amounts of 24DMD and water were simulated using the continuous, batch, and semicontinuous design strategies. In each process, up to 1.6 mol% of impurities were permitted in the products. The reaction kinetics were based on rate equations presented in *Broekhius* [9], equilibrium data were taken from *Dhale* [10], and UNIQUAC constants describing VLLE data were taken from *Chopade* [11]. The continuous process was simulated using ASPEN PLUS 2004, the batch process was simulated with ASPEN BATCHSEP 2004, and the SRD process was simulated by integration of the dynamic MESH equations [12], with physical property calculations performed using the ASPEN PROPERTIES 2004 engine. All capital costs were estimated with the ASPEN ICARUS PROCESS EVALUATOR 2004, and include the cost of materials, construction, labor, wiring, paint, and other considerations. Utility costs were based on the industrial values given in *Seider et al*. [13].

The continuous process (see Figure 1) uses an external CSTR for 24DMD production. Fresh acetaldehyde and propylene glycol are fed to the CSTR in equimolar amounts. The reactor product, leaving at near chemical equilibrium conditions (about 80% product and 20% reactant) enters the first distillation column. In this column, acetaldehyde is recovered in the distillate and recycled to the CSTR. The remaining three species are removed at the bottom. The bottoms stream is sent to a second distillation column. In this column, propylene glycol is removed in the bottoms product and recycled to the CSTR. At the top of the column, 24DMD and water is collected in equimolar amounts and sent downstream. Several parameters, including the CSTR temperature, CSTR volume, the pressure in each column, the feed locations, the feed qualities, and the reflux and reboil ratios, were adjusted to minimize the total costs of the system. The process was analyzed over a wide range of capacities, and detailed economic costs were calculated.

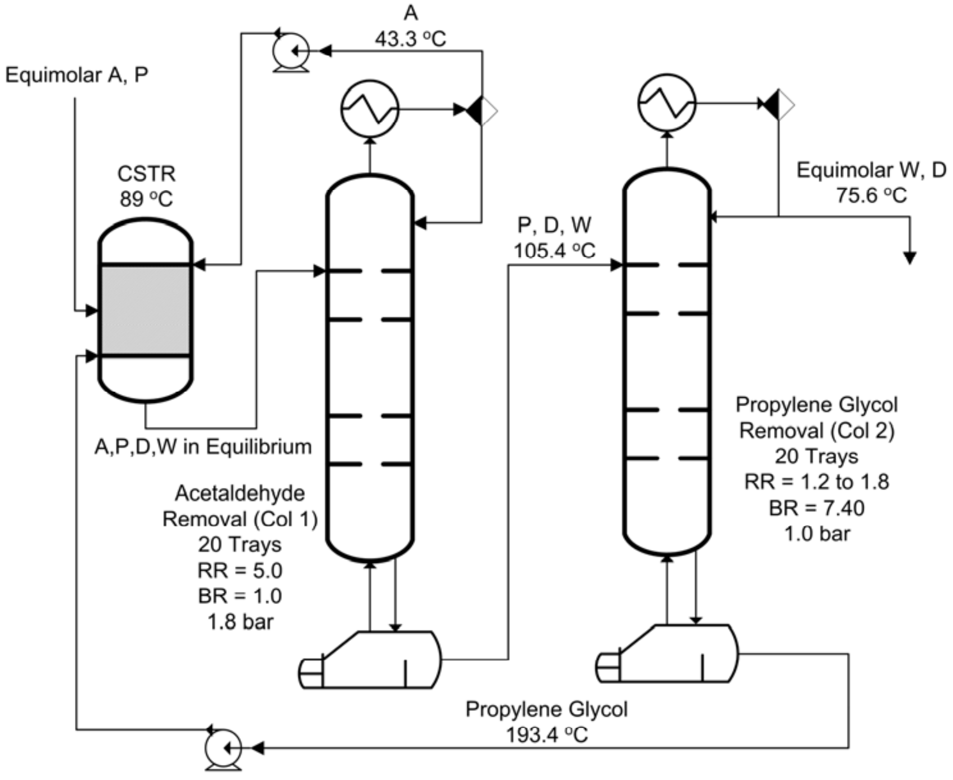


Figure 1. Continuous process. (A) = acetaldehyde, (P) = propylene glycol, (D) = 24DMD, and (W) = water.

The batch process uses a fed-batch reactor (FBR) in parallel with a batch distillation column, as shown in Figure 2. At the beginning of the cycle, the still of the empty distillation column receives the product of the FBR, consisting of the four chemical species in chemical equilibrium. After a heating and warm-up period, acetaldehyde is collected in the distillate and sent to the FBR. Once this species has been removed, water and 24DMD are collected together in a receiving tank. When this has completed, the heating is shut down, and the liquid on the trays in the column drains into the still. The still contents, consisting of nearly all propylene glycol, are then emptied into the FBR. A nitrogen purge and cool-down process prepares the column for the next batch, ending the cycle.

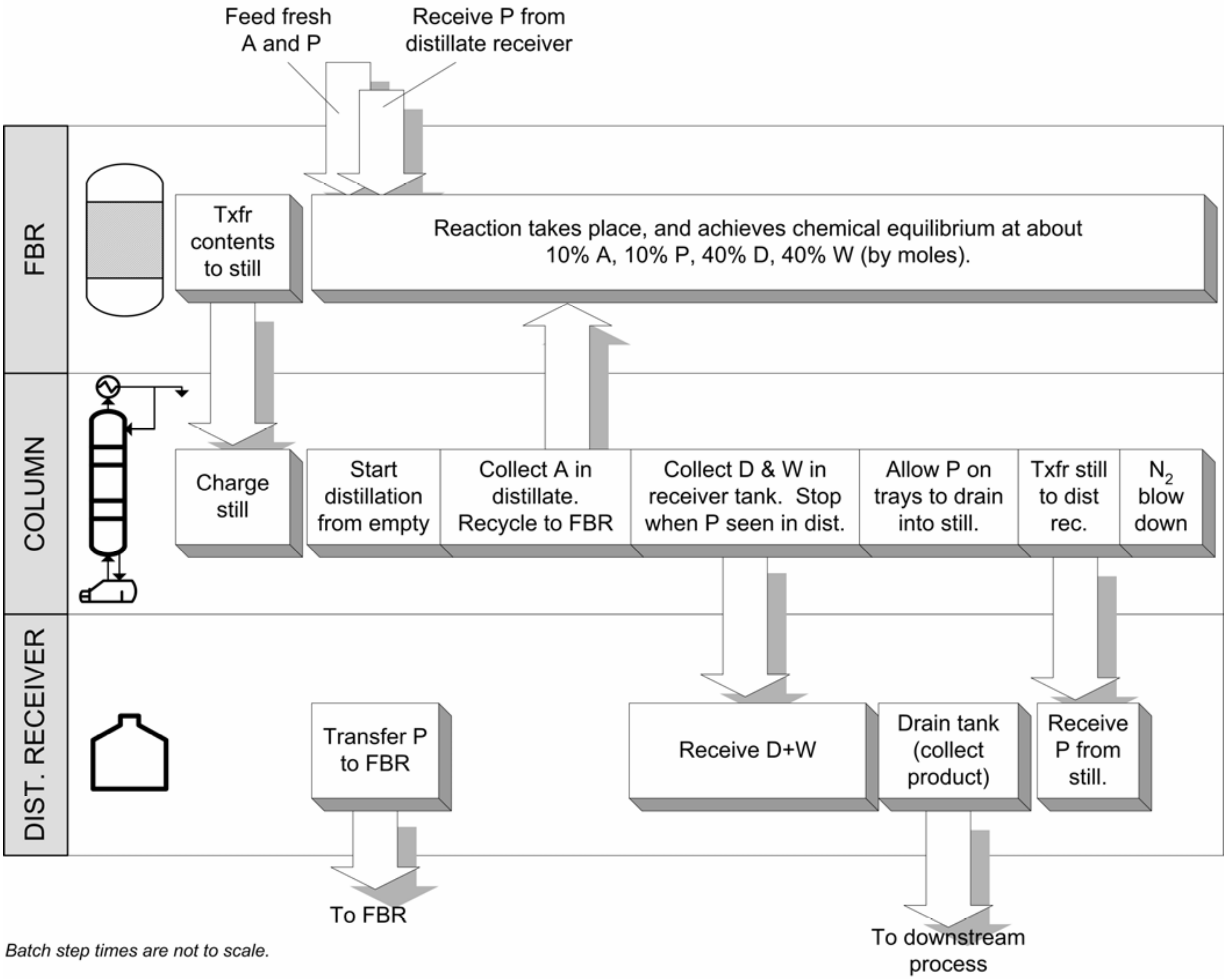


Figure 2. Batch recipe. (A) = acetaldehyde, (P) = propylene glycol, (D) = 24DMD, and (W) = water.

The semicontinuous reactive distillation process consists of an FBR, a distillation column, and an auxiliary tank, as shown in Figure 3. Each cycle consists of two phases with three modes each. In the beginning of the first phase, the FBR begins with the four species in chemical equilibrium. This is fed to the column, where acetaldehyde is removed in the distillate, and the other three species exit through the bottoms product. The acetaldehyde is recycled to the FBR, and the bottoms product is collected in the auxiliary tank. When the

24DMD has been removed from the FBR, the feed is stopped, and no more bottoms product is collected. Acetaldehyde left in the column is purged through the distillate and collected in the FBR, while the FBR is simultaneously charged with a fresh feed supply. After this, the liquid in the auxiliary tank is fed to the column, the distillate is recycled to the auxiliary tank, and no bottoms product is collected. This shifts the column profile to be rich in 24DMD and water at the top, and rich in propylene glycol at the bottom. As the second phase of operation begins, the feed from the auxiliary tank continues, 24DMD and water is recycled to the auxiliary tank, and the bottoms product, rich in propylene glycol, is sent to the FBR. Once the propylene glycol has been removed from the auxiliary tank, the feed to the column stops, and no more bottoms product is collected. The 24DMD and water remaining in the column is purged through the top and collected in the auxiliary tank. The column is then fed with the liquid in the FBR, the distillate is recycled to the FBR, and no bottoms product is taken, preparing the column for the next cycle. The product in the auxiliary tank is drained and collected, ending the cycle.

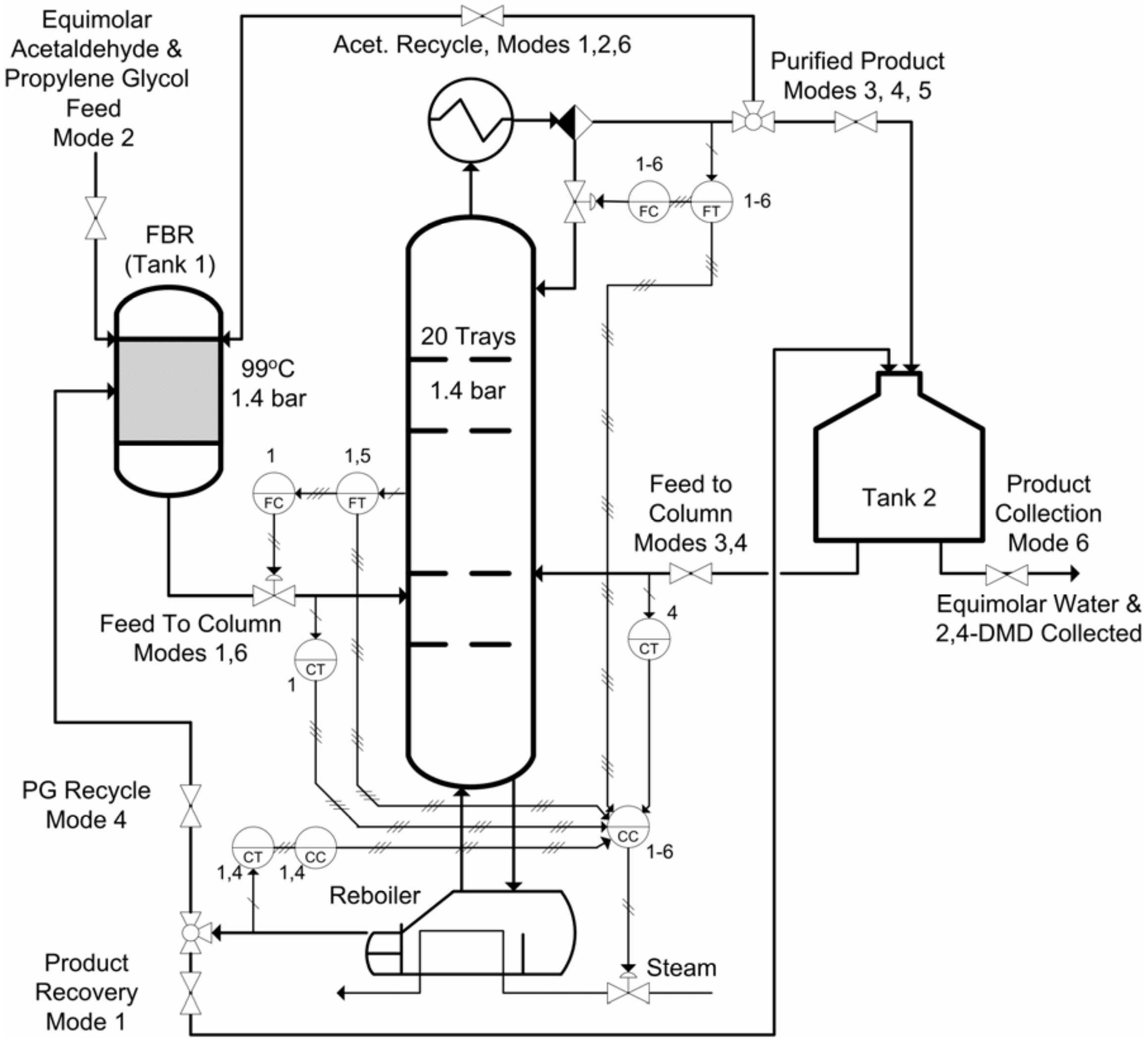


Figure 3. SRD process. FCs (flow controllers) and CCs (composition controllers) are used, with FTs (flow transmitters) and CTs (composition transmitters). The annotated numbers indicate the modes during which the devices are active. The behavior and functionality of each controller changes throughout the cycle.

RESULTS

The three processes were simulated over a range of production rates. The production rate for the continuous system was altered by changing the feed rate of reactants to the system. For the batch and SRD processes, other parameters affected the production rate, such as the size of each batch and the feed rate to the column. Using a three-year lifetime and an effective interest rate of 33%, the processes were compared based on their total annualized cost, including all costs from capital, labor, utilities, taxes, land, maintenance, operations, and other considerations. For the batch and semicontinuous designs, each batch followed immediately after the end of the previous batch without any down time. The reader is encouraged to view a video of the SRD process, available on the web [14].

The batch process was found to have the lowest total capital costs for production rates below about 1.0 MMkg/yr of 24DMD, with the SRD process having the lowest capital costs for rates above that value, as shown in Figure 4a. The relatively low capital costs of the SRD system for intermediate and large production rates are due to only one column required (as compared with the continuous process), and the smaller size of the tanks required (as compared to the batch process). The annual manufacturing costs for the SRD and Batch processes are approximately equivalent, as shown in Figure 4b. As expected, the continuous process requires less annual manufacturing expenses due to lower energy costs at higher production rates and economies of scale. The overall expenses of the three systems are compared based on the total annualized cost, as shown in Figure 5. Based on this comparison, the batch process is the best choice for production rates below 1.0 MMkg/yr, the continuous process is best at rates above about 4.5 MMkg/yr, and the SRD process is the optimal choice for production rates in between.

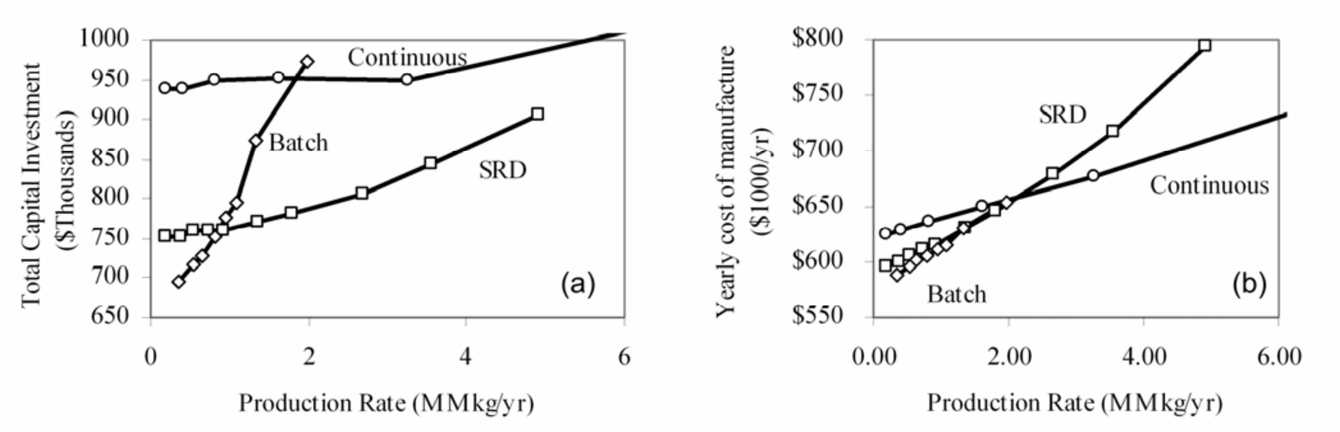


Figure 4. Cost comparisons of the continuous, batch, and SRD processes. (a) The total capital investment of each process. (b) The annual cost of manufacture of each process. Production rates are based on the amount of 24DMD produced in MMkg/yr.

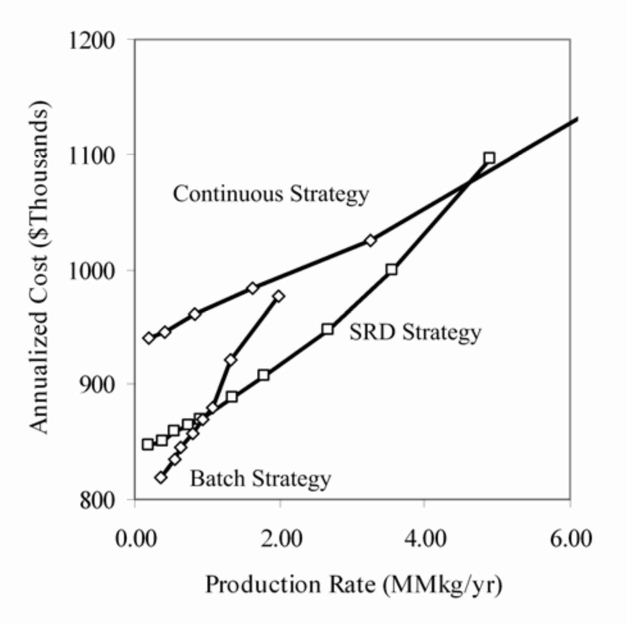


Figure 5. Overall economic comparison of the continuous, batch, and SRD processes, based on annualized cost.

CONCLUSIONS

The semicontinuous reactive distillation process is the most cost-effective way of producing 24DMD at intermediate production rates. Because an increasing amount of fine and specialty chemicals are produced at intermediate rates, an SRD design should be considered for processes where integrated separations and reactions are needed, particularly those where conventional reactive distillation is undesirable.

ACKNOWLEDGEMENT

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