The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu) or Mark A. Burns (e-mail: maburns@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

AN INTRODUCTION TO PROCESS FLEXIBILITY

Part 2: Recycle Loop with Reactor

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An earlier article[1] discussed teaching flexibility via a simple heat-exchange problem. Heat exchange is a convenient starting point for flexibility teaching because the equations and resulting calculations are easy to handle. Other process operations can rapidly become complex and a rigorous treatment very demanding.[2] Hence it is pleasing to find that a potentially complex recycle loop with reactor can be simplified to provide a thought-provoking, process-flowsheet-based exercise that emphasizes understanding of the system's operation.

It is important to stress, even with simplification, that the recycle loop is still a much broader example than that for heat exchange, making the exercise more suitable as a basis for project work or a discussion question. One of the authors first became interested in the problem when attempting to explain the operating bounds of an ammonia or methanol synthesis loop during the course of final-year design projects. The reactor used in this exercise is a simpler design than commonly found in ammonia and methanol plants, but the exercise still illustrates many of the issues that make design and operation of such process systems so interesting.

BACKGROUND

The exercise considers a reversible exothermic reaction taking place in the gas phase over a catalyst in an adiabatic reactor. The reactor is part of a recycle loop where product is separated from the reactor effluent and unreacted feed is recycled (see Figure 1). It is well known that when designing recycle loops, an economic optimum exists for reactor conversion that balances reactor size against the combination of product separation load and circulation rate.

Having chosen the design conversion, the circulation rate is an immediate consequence in order to meet the required

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production. The choice of reactor operating temperature is also important and may be optimized by the designer as part of the reactor size-separation load/circulation rate trade-off.

In the case of reversible exothermic reactions, selection of a relatively low temperature permits a higher conversion, but this must be balanced against a slower rate of reaction leading to a large catalyst inventory. The design conversion for reversible exothermic reactions often approaches quite closely the upper bound imposed by thermodynamics.

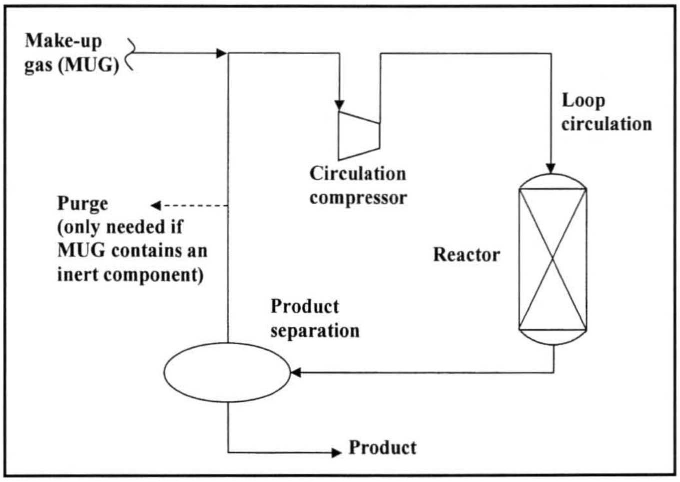

Figure 1.

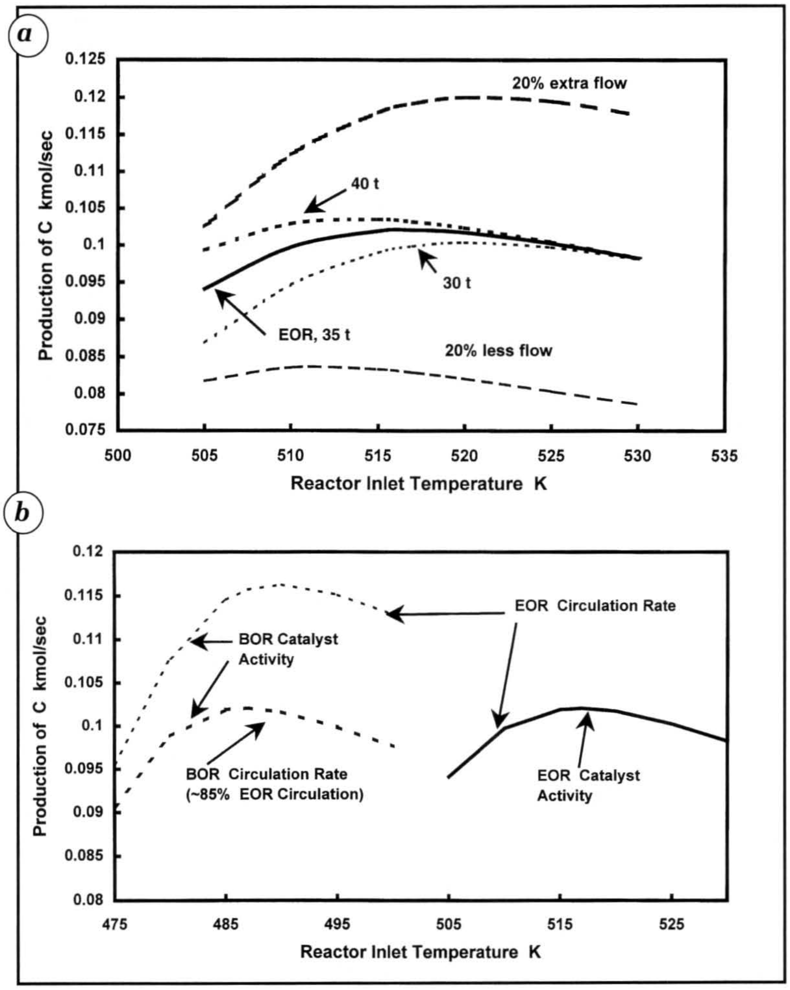

Figure 2.

Finally, the temperature will increase through the catalyst bed, but a single temperature value is needed to characterize operation; for this we will use inlet temperature. It is assumed that reactor inlet temperature can be adjusted independently.[1]

For a flexibility study, the catalyst inventory and other equipment will be fixed; we are interested in investigating how the plant will perform under alternative operating conditions.

From the earlier discussion, two obvious parameters to characterize operation are circulation rate and reactor inlet temperature. As noted before, the reactor inlet temperatures can be adjusted to maximize production for fixed circulation rate (illustrated in Figure 2a.[3]).

To the left of the maximum, increasing inlet temperature improves the rate of reaction, leading to more production. But as the temperature increases, the deteriorating equilibrium conversion imposed by thermodynamics "bites," and production peaks. Operation at the optimum inlet temperature ensures that the minimum circulation rate to meet production is being used; we assume the optimum temperature to be selected in each case.

A typical industrial example is more complex and involves four additional considerations:

- Catalyst deactivation
- Producing circulation around the loop
- Loop pressure
- Presence of an inert component in the make-up gas

The catalyst can be deactivated in several ways.[4] Here, we are more interested in the overall effects of deactivation than we are in the details of one particular mechanism, so we adopt a simple model—namely, uniform deactivation throughout the catalyst inventory. The normal response to loss of production through catalyst deactivation is to raise the reaction rate by increasing the inlet temperature. For reversible exothermic reactions, however, this action further limits the conversion, and unless the circulation rate is also increased, the production target will not be met.

The effects of catalyst deactivation are demonstrated in Figure 2b, which compares performance at beginning-of-run (BOR) and end-of-run (EOR). Note particularly that the BOR circulation rate is

Parts 1 and 2 of this paper introduce flexibility by providing exercises that force the student to consider how the system will actually operate—this is an important first step for developing a robust design. Further, a wide-ranging knowledge of basic chemical engineering is required, making these exercises (particularly Part 2) ideal as the basis for project work.

15% less than that for EOR; if the EOR circulation rate were implemented at BOR, overproduction would result.

Normal design practice would be to set the loop process parameters for EOR operation, but producing a design sufficiently flexible to operate at BOR is clearly very desirable. Loop circulation is normally produced using a variable speed centrifugal compressor, so compressor characteristics become important in meeting process flexibility.

Centrifugal compressor characteristics are represented by a head-capacity curve and, for recycle systems (where the loop pressure drop is 10% or less of the nominal operating pressure) the loop can be treated as one of constant density, and the compressor characteristics will have roughly the same shape as those obtained for centrifugal pumps.

Figure 3 shows the operating point to be defined where the system curve intersects the compressor characteristic; for a recycle loop the system curve is based solely on friction losses because the discharge returns to the suction.

Also shown in Figure 3 is the implementation of reduced circulation rate via compressor speed reduction. The affinity laws[5] can be applied to relate compressor performance at different speeds. Sometimes the speed reduction required is quite large, taking the compressor close to a critical speed, which induces synchronous whirling of the shaft; this condition must be avoided and hence places a lower bound on operation.

Typically, critical speeds are found in the range of 60 to 80% of normal running speed. Two other constraints that arise from compressor operation are

- *Maintenance of sufficient volumetric flowrate through the machine to avoid surge; for a low-head compressor (as considered here) this constraint will lie well to the left on the head-capacity curve (around 50% of normal capacity) and hence will not be influential.*
- *Overspeed trip, typically set at 10 to 15% above the normal running speed; this constraint obviously "bites" for operating modes requiring higher circulation rates.*

The constraints imposed by compressor operation lead to the third parameter that required further consideration—namely, loop pressure. Varying loop pressure is helpful when matching compressor operation to process requirements because

- *A reduction in loop pressure increases the circulating gas specific volume; hence, circulating the same quantity of gas would require a faster compressor speed to cope with the larger volumetric flowrate, i.e., moving operation away from the critical speed.*
- *If the reaction is one where there is volume reduction as the reaction proceeds, pressure reduction will give a lower, thermodynamic limited, conversion, and this will lead to a larger circulation rate and a move away from the critical speed.*

The loop pressure cannot be set independently, however. In a simple example where the feed contains no inert component, the rate of reactant consumption (in the reactor) must balance the rate of make-up gas (MUG) flow into the loop in order for the pressure to remain steady. In other words, at steady-state, the reactor inlet temperature and circulation rate (combined with the pressure) must give a reaction rate that just balances the MUG rate. If the circulation rate, say, were smaller, the loop would equilibrate at a higher pressure with the extent of the pressure increase being limited by the relief valve setting on the loop.

Finally, we need to consider an inert component in the MUG. In many industrial examples, the MUG to the synthesis loop is not pure reactant, but contains 1 to 2% by volume of an inert component. Unless the inert is removed, it will accumulate in the loop and slow the rate of reaction. In a pressurized loop, some inert will dissolve in the product, but

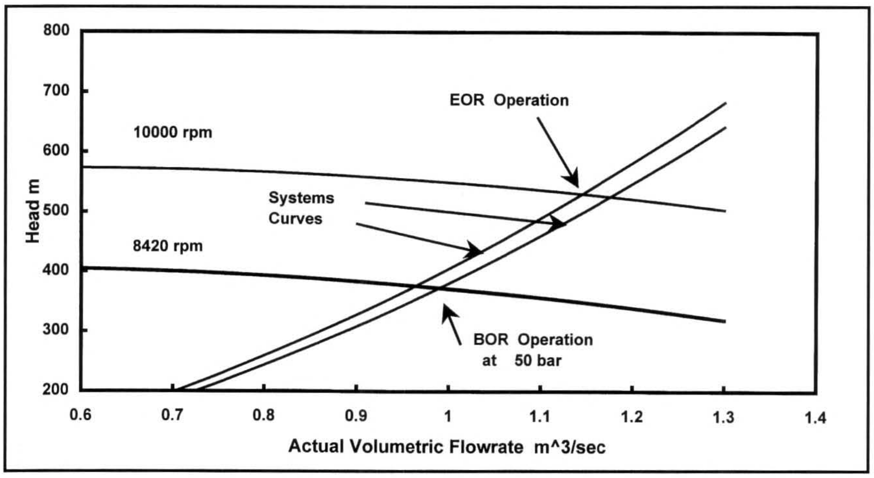

Figure 3.

most has to be purged from the loop (see Figure 1). A relatively high purge rate ensures the inert composition in the recycle loop is low and the rate of reaction high for the pressure because the inert has only a small diluting effect. A high purge rate, however, results in a large reactant loss and, in design mode, setting the purge rate is an economic optimization that adds the third dimension of MUG rate to the reactor size- separation load/circulation-rate balance already discussed.

From a flexibility viewpoint, recycle loops with purge can fully exploit the interacting trio of parameters (circulation rate, reactor inlet temperature, and pressure) because pressure can now be set independently via the purge rate rather than being a consequence, as previously noted.

To illustrate, if the loop is initially at steady state, reducing the purge rate causes the inert composition to increase, so the loop pressure must increase to restore the reactant partial pressures. There will be a compensating reduction in MUG demand. If the circulation rate is also increased, it will limit the change in pressure needed.

In view of the complexity added by considering an inert in the MUG, the main part of the exercise concentrates on pure MUG; handling an inert in the MUG is considered at the end of the exercise.

PROBLEM STATEMENT

The reversible exothermic chemical reaction

$$A + B \Leftrightarrow C$$

takes place in the gas phase over a fixed catalyst bed in a reactor operated adiabatically. The reaction data are summarized in Table 1. The reactor forms part of a recycle loop (shown in Figure 1) where C is totally separated from the reactor effluent. For the first three parts of the exercise, you may assume the make-up gas contains only A and B in stoichiometric proportions (mixture RMM=50); hence the recycle stream also contains only A and B, and the purge flowrate will be zero.

TABLE 1
Reaction Data for the Exercise

Heat of reaction = -14000 kJ per kmol of C formed

Rate of production of C by the forward reaction = $k_F P_A P_B$

where

k_F = BOR rate constant, kmol sec^{-1} bar^{-2} (kg of catalyst)$^{-1}$

k_F = 100 exp(-94000/8.314 T)

Rate of destruction of C by the reverse reaction = $k_B P_C$

where

k_B = BOR rate constant, kmol sec^{-1} bar^{-1} (kg of catalyst)$^{-1}$

k_B = 525000 exp(-108000/8.314 T)

P_A, P_B, P_C = partial pressures of A, B, and C, bar

T = absolute temperature of the reacting mixture, K

Specific heat capacities: C_{PA}, C_{PB}, C_{PC} = 30, 40, 70 kJ $kmol^{-1}$ K^{-1}

The recycle loop at end-of-run (EOR) is designed to operate at a nominal pressure of 50 bar, with a circulation rate through the reactor of 2.2 kmol sec^{-1}. The EOR loop pressure drop is 5 bar; this comprises 4 bar for all equipment excluding the reactor and 1 bar for the reactor. The EOR reactor pressure drop may be further decomposed:

- *Pressure drop (based on EOR circulation rate) for reactor if catalyst were in good mechanical condition: 0.7 bar*
- *Allowance (based on experience) for catalyst particle breakdown and loss of voidage: 0.3 bar*

Circulation through the reactor is provided by a single-stage centrifugal compressor whose head (H_C, m) - capacity (Q, m^3 sec^{-1}) characteristic at 10,000 rpm is represented by

$$H_C = 530.5 + 149.52\,Q - 130.585\,Q^2$$

The exercises below examine the process flexibility requirements for the synthesis loop as the catalyst inventory of 35000 kg slowly deactivates. Catalyst deactivation is modeled by assuming EOR k_F and k_B values are only 30% of those applying at BOR (see Table 1).

You may assume the heat exchanger arrangements on the reactor feed have sufficient flexibility to produce a wide range of reactor feed temperatures and the compressor suction operates at 40°C. Also, assume the reactants A and B have negligible solubility in the product.

1) Determine the maximum production of C achievable at EOR conditions by varying the reactor inlet temperature.

2) You wish to achieve the same production rate of C as that calculated in (1), but using BOR catalyst.
   a) Calculate the circulation rate required if the loop pressure remains at 50 bar.
   b) If the circulation rate is maintained at 2.2 kmol sec^{-1}, at what pressure would the loop need to operate?
   c) Use the insight you have gained from solving 2(a) and (b) to explain the interrelationship between loop pressure, circulation rate, and reactor inlet temperature. How might you exploit this flexibility to deal with variation of catalyst activity?

3) a) Confirm the compressor speed of 10,000 rpm will satisfy EOR operating conditions.
   b) Determine the compressor speed for 2(a).
   c) Determine the compressor speed for 2(b).
   d) Comment on your answer to 2(c) in light of the compressor speeds you have just calculated.

4) The MUG to the synthesis loop contains 2% of an inert compound, I, in addition to equal proportions of A and B. If the circulation rate is 2.4 kmol sec^{-1} and the purge rate is 0.05091 kmol sec^{-1}, determine the loop operating pressure to meet the production target from part 1. What would happen if the purge rate were reduced further, and how would you mitigate the consequences?

SOLUTION

The solution of this problem requires a model for the chemical reactor, which is easily generated by integrating the differential mass and energy balances through the reactor:

$$\frac{dFc}{dw} = q\left(k_F P_A P_B - k_B P_C\right)$$

$$\frac{dT}{dw} = \frac{q\,14000\left(k_F P_A P_B - k_B P_C\right)}{\left(F_A C_{PA} + F_B C_{PB} + F_C C_{PC}\right)}$$

where w is the mass of catalyst and q is the multiplying factor to account for catalyst deactivation.

At the reactor inlet, the flowrates and temperatures are $F_A=F_{A0}$, $F_B=F_{B0}$, $F_C=0$, $T=T_0$, and at any subsequent point, $F_A=F_{A0} - F_C$, $F_B=F_{B0}-F_C$. Ideal gas behavior is assumed to calculate the partial pressures, *e.g.*, $P_A=P_TF_A/(F_A+F_B+F_C)$, where P_T is the nominal loop pressure. Any one of a number of numerical integration packages can be used.

1. Setting $F_{A0}=F_{B0}=1.1$ kmol sec^{-1}, q=0.3, and $P_T=50$ bar, the model is run for a range of inlet temperatures T_0. F_C is noted after integration through 35 tons of catalyst and the results recorded as a plot of F_C against T_0 (see the middle curve in Figure 2a). The peak indicates a maximum production of 0.10206 kmol sec^{-1} for C at an inlet temperature of 517K. (Note the sensitivity to circulation rate changes, but relative lack of sensitivity to catalyst inventory changes as indicated by the other curves in Figure 2a.)

2(a). For BOR catalyst q=1.0 and $P_T=50$ bar, the problem requires a trial-and-error solution to find F_{A0} and F_{B0} that give the required production of F_C. A solution is found for $F_{A0}=F_{B0}=0.951$ kmol sec^{-1} with a reactor inlet temperature of 487K (see Figure 2b). (Note: maintaining the EOR circulation rate gives a large overproduction.)

2(b). For BOR catalyst q=1.0 and $F_{A0}=F_{B0}=1.1$ kmol sec^{-1}, the problem requires a trial-and-error solution to find P_T that gives the required production of F_C. A solution is found for $P_T=43.64$ bar with a reactor inlet temperature of 495K.

2(c). By performing the calculations in 2(a) and 2(b), students should be aware that there are three important variables. Reactor inlet temperature can and should be optimized for all situations, but circulation rate and loop pressure are related and cannot be set independently. The above exercises take the two extreme positions of maintaining loop pressure or maintaining circulation rate; the corresponding maximum reduction in circulation rate or loop pressure is then calculated. In practice, an operator would use a smaller change in circulation rate and allow the loop pressure to equilibrate with a reduction somewhat less than the maximum change previously calculated.

3(a.) Plotting the head-capacity curve using the given equation produces the 10,000 rpm line in Figure 3. The EOR circulation rate is 2.2 kmol sec^{-1} or a compressor suction flowrate of [(2.2)(0.08314)(313)]/50=1.145 m^3 sec^{-1}, and as may be seen from the curve or equation, this implies that a H_C of 530.5m will be thrown up. If the loop pressure drop is 5 bar, this is equivalent to an H_S of $(5)(10^{5)}/[(9.81)(96.07)]=530.5$m, *i.e.,* $H_S=H_C$ and the compressor speed of 10,000 rpm will satisfy EOR operating conditions (96.07 kg m^{-3} is the gas density at the compressor suction and is calculated from the ideal gas law).

3(b). In this case, the system head will be proportional to the (circulation rate)^2 because the loop pressure is maintained at 50 bar and thus the gas density can be assumed constant. We neglect the effect of minor composition and reactor exit temperature changes. Thus the system curve passes through the volumetric flowrate [(2)(0.951)(1.145)]/2.2=0.9899 m^3sec^{-1} at a head of $[(4.7)(530.5)(0.951\{2/2.2\})^2]/5=372.7$m. Stable operation requires the compressor speed to be reduced such that the head-capacity curve also passes through this point. Let N be the new compressor speed and the stable operating point must map back onto the 10,000 rpm head-capacity curve. Thus

$$372.7\left(\frac{10,000^2}{N}\right) = 530.5 + \left((149.52)(0.9899)\left(\frac{10,000}{N}\right)\right) - \left((130.585)\left(0.9899^2\right)\left(\frac{10,000}{N}\right)^2\right)$$

Solving the quadratic gives N=8420 rpm; this is shown as the second compressor curve in Figure 3. (This is quite a large speed reduction and may bring the compressor quite close to the critical speed.)

3(c). In this case, the system head will be proportional to the

$$\left(\frac{\text{circulation rate}}{\text{loop pressure}}\right)^2$$

because dropping the loop pressure has a strong effect on gas density. The required point on the system curve is defined by $[(1.145)(50)]/43.64=1.3119 m^3 sec^{-1}$ at a head of $[(4.7)(530.5)(\{50/43.64\}^2)]=654.6 m$. Using the same approach as that applied in 3(b), but this time anticipating a speed increase, we solve the quadratic to give N=11,160 rpm. (This is quite a large speed increase and may bring the machine close to overspeed trip.)

3(d). Answer 2(c) advocates a middle path—some reduction in circulation rate and a corresponding loop pressure reduction. The answers to section 3(b) and (c) show that if loop pressure or circulation rate is maintained, the extremes of compressor speed are also approached, *i.e.,* 2(a) takes operation close the critical speed and 2(b) results in operation near overspeed trip. Hence, the middle path requires a steadier machine speed, closer to normal running speed.

4. The equations representing the reactor must be modified to include the presence of the inert. Two changes are needed:

1. Inclusion of the inert component flowrate, F_I, in the circulation rate $(F_A+F_B+F_C+F_I)$; this reduces the partial pressure of any reactant.
2. Inclusion of the inert component heat capacity, F_IC_{PI}, in the heat capacity $(F_AC_{PA}+F_BC_{PB}+F_CC_{PC}+F_IC_{PI})$; this provides a greater heat sink and so reduces the temperature rise across the reactor.

Before the reactor simulation can be used, the effect of the inert component on the recycle loop material balance must be established. In particular we need the reactor feed composition. Figure 4 shows all the information easily derivable from the problem statements, but two important unknowns remain; namely 1) flowrates of A or B in the reactor feed, X, and 2) MUG flowrate, M. Writing component mass balances for a reactant and the inert at the mixing point just before the compressor gives

$$X=0.49M+(X-0.10206)\left(\frac{2.14497}{2.19588}\right)$$
$$2.4-2X=0.02M+(2.4-2X)\left(\frac{2.14497}{2.19588}\right)$$

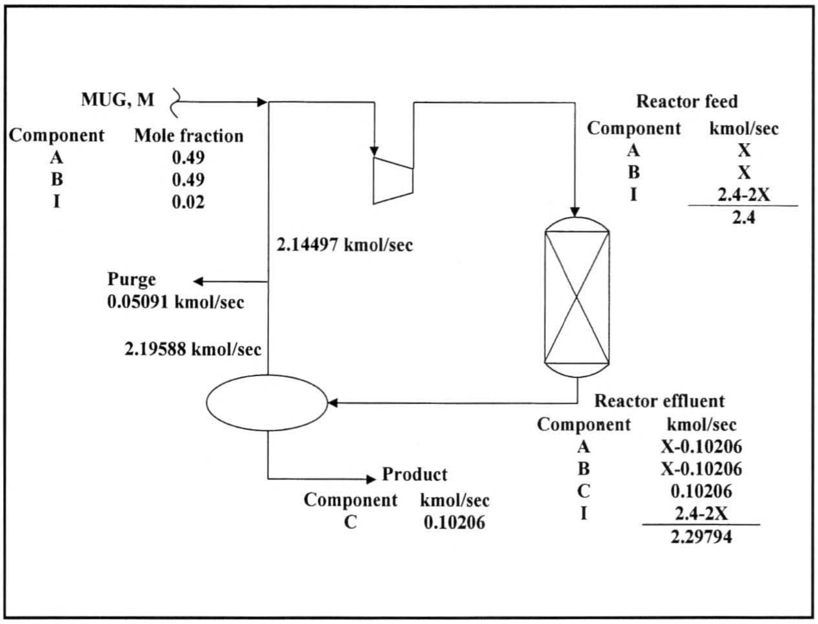

Figure 4.

Solving for X and M gives X=1.089976 kmol sec^{-1} and M=0.255028 kmol sec^{-1}, and hence the reactor feed for the simulation is A and B, 1.089976 kmol sec^{-1} and I is 0.220048 kmol sec^{-1}. Note particularly that the MUG rate has increased by 24.9%, compared to an inert free MUG, to account for the reactants lost in the purge. Solving for the loop pressure in this part of the exercise is also by trial and error. A loop operating pressure of 55.62 bar will ensure the target production is met if the reactor inlet temperature is optimized at 517K.

Reducing the purge will increase the inerts composition of the gas in the loop. At constant circulation rate, the change must cause the loop pressure to increase in order to restore the reactant partial pressures. For high-pressure systems, the relief valve is typically set at 10% above normal running pressure; hence the calculated loop pressure of 55.62 is probably unacceptable if 50 bar is viewed as normal operation. A further reduction in purge flow would certainly cause the relief valve to lift. To limit the pressure increase, the best tactic would be to increase the loop circulation rate.

SUMMARY

Parts 1 and 2 of this paper introduce flexibility by providing exercises that force the student to consider how the system will actually operate—this is an important first step to developing a robust design. Further, a wide-ranging knowledge of basic chemical engineering is required, making these exercises (particularly Part 2) ideal as the basis for project work.

REFERENCES

1. Jones, W.E., and J.A. Wilson, "An Introduction to Process Flexibility: Part 1," *Chem. Eng. Ed.,* **31**(3), 172 (1997)
2. Swaney, R.E., and I.E. Grossmann, "An Index for Operational Flexibility in Chemical Process Design," *AIChE J.,* **31**(4), 621 (1985)
3. Froment, G.F., and K.B. Bischoff, *Chemical Reactor Analysis,* 2nd ed., John Wiley, New York, NY, p. 425 (1990)
4. Ibid. p. 219
5. Aerstin, F., and G. Street, *Applied Chemical Process Design,* Plenum Press, New York, NY, p. 237 (1978) ❐