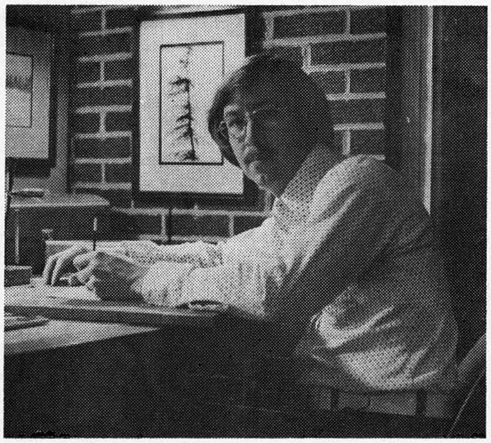
ChE classroom

MATERIAL BALANCE CALCULATIONS WITH REACTION

Steady-State Flow Processes

JAMES W. LACKSONEN
University of Toledo
Toledo, Ohio 43606



James Lacksonen received his B.Sc. and M.Sc. (1959) and Ph.D. (1964) degrees in ChE from the Ohio State University. He has worked industrially as a research engineer and a project engineer for Battelle Memorial Institute, the Pittsburgh Plate Glass Co. and the General Tire & Rubber Co. before going to the University of Toledo in 1967. He is an active consultant for Owens-Illinois, Inc. After serving as Assistant Dean of the College of Engineering for 5 years, he returned to full-time teaching and research and is now active in doing research on accelerated aging of paper, with particular reference to problems in art. He also is a professional watercolor artist and is an avid cross-country skier and jogger.

MANY BEGINNING chemical engineering students have difficulty with recycle calculations, particularly for reacting systems. After several years of attempting various methods to explain these calculations in introductory courses, I have developed the following approach. Since the greatest difficulty occurs with reacting processes, the method presented here will be for these kinds of problems.

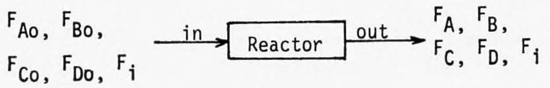
Basis for solution: At steady-state we can write for each component the following molar balance:

- **Reactants: moles out = moles in — moles of what reacts**
- **Products: moles out = moles in + moles of what forms**
- **Inerts: moles out = moles in**

Since we are concerned with reacting systems, it is more direct to use moles rather than mass since the stoichiometry is in terms of moles. Also note that, although the above statements are classically written as: 0 = in − out ± reaction, the suggested re-arrangement has been found to be psychologically more appealing to students.

Consider the following general chemical reaction: $aA + bB \rightarrow cC + dD$ and define species A as the limiting reactant. Let F_{Yo} be the molar flow rate of specie Y into the process, F_y be the molar flow rate of Y out, and F_i be the molar flow rate of inerts.

NON-RECYCLE PROCESS



Define degree of conversion of limiting reactant A, $X_A = (F_{Ao} - F_A)/F_{Ao}$ which is also known as the overall degree of conversion, as then we have:

$$F_A = F_{Ao} - F_{Ao} X_A \qquad F_C = F_{Co} + F_{Ao} X_A\, c/a$$
$$F_B = F_{Bo} - F_{Ao} X_A\, b/a \quad F_D = F_{Do} + F_{Ao} X_A\, d/a$$
$$F_i = F_i$$

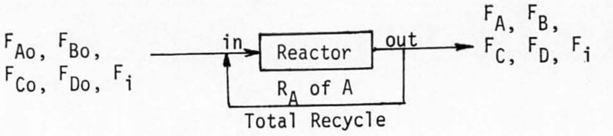
Summing these equations:

Total molar flow rate out $= F_i + F_{Ao} + F_{Bo} + F_{Co} + F_{Do} + (F_{Ao} X_A \Delta n)/a$
where: $\Delta n = (c + d) - (a + b)$.

Note that the term $(F_{Ao} X_A \Delta n)/a$ determines whether the number of moles out is greater or less than the number of moles in.

RECYCLE PROCESS

Let R be the total molar flow rate of the recycle stream and R_A be the molar flow rate of the limiting reactant A in the recycle.



Define once-through degree of conversion of limiting reactant A, $X_A = (F_{Ao} - F_A) / (F_{Ao} + R_A)$, and then we have:

$$\begin{aligned} F_A &= F_{Ao} - [F_{Ao} + R_A]\, X_A \\ F_B &= F_{Bo} - [F_{Ao} + R_A]\, X_A\, b/a \\ F_C &= F_{Co} + [F_{Ao} + R_A]\, X_A\, c/a \\ F_D &= F_{Do} + [F_{Ao} + R_A]\, X_A\, d/a \\ F_i &= F_i \end{aligned}$$

Summing these equations:

Total molar flow rate out $= F_i + F_{Ao} + F_{Bo} + F_{Co} + F_{Do} + [(F_{Ao} + R_A)\ X_A\ \Delta n]/a$
where: $\Delta n = (c+d) - (a+b)$ as before.

The term $(F_{Ao} + R_A)\ X_A\ \Delta n/a$ represents the increase or decrease in the molar flow rate out compared to in. Note that the expression $[F_{Ao} + R_A]\ X_A$ is a repeating element in the calculations.

EXAMPLE 1

The reaction $2A + 5B \rightarrow 3C + 6D$ is conducted at steady-state in a recycle reactor. The fresh feed is A and B. A is 30% excess. The once-through conversion of B is 60% and its overall conversion is 95%. After coming out of the reactor, a portion of pure B is separated and recycled. Find the recycle ratio R/F (molar basis) where F = fresh feed rate $= F_{Ao} + F_{Bo}$.

SOLUTION

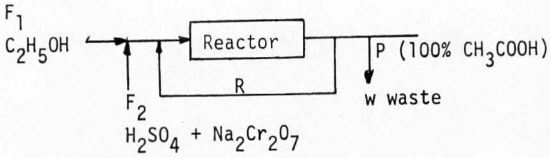
Basis: $F_{Ao} = (2)(1.3)$ moles A/time and $F_{Bo} = 5$ moles B/time
Balance on limiting reactant B:
$F_B = F_{Bo} - [F_{Bo} + R_B]\ X_B$ (from once-through conversion definition)
But: $[F_{Bo} - F_B]/F_{Bo} = 0.95$ from over-all conversion definition. Noting that $R_B = R$ = total recycle stream: $0.05\ F_{Bo} = F_{Bo} - [F_{Bo} + R]\ X_B$; $(0.05)(5) = 5 - (5 + R)(0.6)$
Solving for R: $R = 2.92$ moles B/time recycled.
Thus: $R/F = R/(F_{Ao} + F_{Bo}) = 2.92/7.6 = 0.38$

EXAMPLE 2

The following steady-state process is conducted in a recycle reactor:

$$3\ C_2H_5OH + 2\ Na_2Cr_2O_7 + 8\ H_2SO_4 \rightarrow$$
$$3\ CH_3COOH + 2\ Cr_2(SO_4)_3 + 2\ Na_2SO_4 + 11\ H_2O$$

The process flow diagram is:



Information about process:

- 90% over-all conversion of C_2H_5OH.
- 85% once-through conversion of limiting reactant C_2H_5OH.
- On an over-all molar basis, H_2SO_4 is 20% excess and $Na_2Cr_2O_7$ is 10% excess.
- All the CH_3COOH formed comes out stream P.
- R contains C_2H_5OH and H_2SO_4 only.
- $R/F_1 = 1$ (molar basis).

Find:

1. Moles of waste stream W out if $F_1 = 3$ moles/time input.
2. Mole % composition of recycle stream.
3. Over-all and once-through conversions of H_2SO_4.

SOLUTION

Basis: 3 moles/time of $C_2H_5OH = F_1$.
Then: $Na_2Cr_2O_7$ in $= 3\ (2/3)\ (1.1) = 2.2$ moles/time
H_2SO_4 in $= 3\ (8/3)\ (1.2) = 9.6$ moles/time
Since C_2H_5OH is the limiting reactant, let it be species A.
C_2H_5OH balance (define as F_A)
Overall conversion $= 0.9 = (F_{Ao} - F_A)/F_{Ao} = (3 - F_A)/3$
$F_A = 3 - 2.7 = 0.3$ moles/time C_2H_5OH out in W.
Once-through conversion $= 0.85 = (F_{Ao} - F_A)/(F_{Ao} + R_A) = (3 - 0.3)/(3 + R_A)$ $R_A = [2.7 - (3)(0.85)]/ 0.85 = [2.7 - 2.55]/0.85 = 0.176$ moles A/time
Since the term $(F_{Ao} + R_A)\ X_A$ is repeated in the material balance calculations, it is often convenient to evaluate it for future use, as
$(F_{Ao} + R_A)\ X_A = (3 + 0.176)(0.85) = 2.7$
H_2SO_4 balance (define as F_s)
$F_s = F_{so} - (F_{Ao} + R_A)\ X_A\ (s/a) = 9.6 - 2.7\ (8/3)$
$= 2.4$ moles/time H_2SO_4 out in W.

The methodology for handling steady-state recycle calculations presented here is not meant to be a panacea nor a replacement for thinking. However, beginning students often need (and welcome) a clear, consistent approach to solving these kinds of problems.

$Na_2Cr_2O_7$ balance (define as F_c)

$F_c = F_{Co} - (F_{Ao} + R_A)\ X_A\ (c/a) = 2.2 - 2.7\ (2/3)$
$= 0.4$ moles/time $Na_2CR_2O_7$ out in W.

CH_3COOH balance (define as F_D).

$F_D = F_{Do} + (F_{Ao} + R_A)\ X_A\ (d/a) = 0 + 2.7\ (3/3)$
$+ 2.7$ moles/time CH_3COOH out in P.

$Cr_2(SO_4)_3$ balance (define as F_E).

$F_E = F_{Eo} + (F_{Ao} + R_A)\ X_A\ (e/a) = 0 + 2.7\ (2/3)$
$= 1.8$ moles/time $Cr_2(SO_4)_3$ out in W.

Na_2SO_4 balance (define as F_F).

$F_F = F_{Fo} + (F_{Ao} + R_A)\ X_A\ (f/a) = 0 + 2.7\ (2/3)$
$= 1.8$ moles/time Na_2SO_4 out in W.

H_2O balance (define as F_w).

$F_w = F_{wo} + (F_{Ao} + R_A)\ X_A\ (w/a) = 0 + 2.7\ (11/3)$
$= 9.9$ moles/time H_2O out in W.

Recycle stream analysis

$R/F_1 = 1 \rightarrow R = F_1 = 3$ moles/time
$R_A + R_s = R \rightarrow R_s = 3 - 0.176 = 2.824$ moles/time H_2SO_4 in R.

We can now find:

1. Moles of waste stream W out.
   $W = F_A + F_s + F_E + F_F + F_w$
   $W = 0.3 + 2.4 + 0.4 + 1.8 + 1.8 + 9.9 = 16.6$ moles/time of W.
2. Mole % composition of recycle stream.
   % $C_2H_5OH = (0.176/3)\ 100 = 5.9$ mole %
   % $H_2SO_4 = 100 - 5.9 = 94.1$ mole%
3. Over-all conversion of $H_2SO_4 = [(F_{So} - F_S)/F_{So}] = (9.6 - 2.4)/9.6 = 0.75$ or 75%
   Once-through conversion of $H_2SO_4 = [(F_{So} - F_S)/(F_{So} + R_S)] = (9.6 - 2.4)/[9.6 + (3 - 0.176)] = 0.58$ or 58%

A total over-all material balance shows that

$$\left(\frac{\text{moles out}}{\text{time}} - \frac{\text{moles in}}{\text{time}}\right) \begin{aligned} &= (W + P) - (F_1 + F_2) \\ &= 16.6 + 2.7 - 3\ (2.2 + 9.6) = 4.5 \end{aligned}$$

Comparing this with the term $[F_{Ao} + R_A)\ X_A\ \Delta n]/a = [(3 + 0.176)(0.85)]\ [(3 + 2 + 2 + 11) - (3 + 2 + 8)]/a = 4.5$
which emphasizes its equality to the change in moles for the over-all process. Also, weight compositions or flow rates are readily obtainable by using the molecular weights of the various species.

CONCLUDING REMARKS

The methodology for handling steady-state recycle calculations presented here is not meant to be a panacea nor a replacement for thinking. However, beginning students often need (and welcome) a clear, consistent approach to solving these kinds of problems. Based on my teaching experience in this area, I have found this approach to be direct and appealing to the students. It incorporates the chemical stoichiometry and the fundamental definition of the once-through degree of conversion of limiting reactant which are repeating elements in the material balance calculations. □

ChE news

KELLY LECTURER NAMED

Dr. Warren E. Stewart of the University of Wisconsin at Madison, has been named the Kelly Lecturer for 1979 by Purdue University. Stewart has been an outstanding contributor to ChE literature and his contributions in the area of approximate methods have had a profound impact on many diverse areas of chemical engineering. He has published, lectured and consulted extensively on transport phenomena, reactor modelling and numerical methods.

DONALD L. KATZ AWARD

The 1979 recipient of the Donald L. Katz Lectureship Award, presented annually by the University of Michigan, is Dr. Robert S. Schechter of the University of Texas at Austin. Dr. Schechter has served in a number of administrative capacities during his career and has authored or co-authored more than 100 technical publications and three books in the areas of applied surface science and irreversible thermodynamics.

ChE conferences

ADVANCED SEMINAR ON DYNAMICS AND MODELLING OF REACTIVE SYSTEMS

- The Mathematics Research Center at the University of Wisconsin-Madison will hold an Advanced Seminar on Dynamics and Modelling of Reactive Systems, October 22-24, 1979. Lecturers will include N. R. Amundson, R. Aris, D. G. Aronson, G. F. Carrier, M. Feinberg, E. D. Gilles, P. S. Gough, L. N. Howard, J. B. Keller, D. Luss, J. Rinzel, R. A. Schmitz, J. H. Seinfeld and F. A. Williams. A detailed program will be available in August. Further information may be obtained from Mrs. Gladys Moran, Mathematics Research Center, Univ. of Wisconsin, 610 Walnut Street, Madison, Wisconsin 53706.

M.I.T.

- July 23 - August 1: **"New Developments in Modeling, Simulation and Optimization of Chemical Processes,"** at Massachusetts Institute of Technology. For further information, contact: Director, Summer Session, M.I.T., Room E19-356, Cambridge, MA 02139.

MICHIGAN

- 1979 Engineering Summer Conferences at the University of Michigan include:

- June 25-29: **"Applied Numerical Methods"**
- July 9-13: **"Physiological Systems for Engineers"**
- July 9-10: **"Solar Energy Measurements and Instrumentation"**

For further information, contact: Continuing Engineering Education, 300 Chrysler Center, North Campus, University of Michigan, Ann Arbor, MI 48109.