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A COMPUTER SOLUTION OF THE FIRST ORDER IRREVERSIBLE CHEMICAL REACTION TO MAXIMIZE THE OVERALL YIELD PRODUCT

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This paper shows that for any first order irreversible chemical reaction, we can determine the reaction time (t_0 hours) required to maximize the overall yield of product per hour for different values of the down time between the reaction cycles (t_c hours) and the reaction rate constant (k hr^{-1}) at a specified temperature (T). Two iterative processes are applied to obtain the reaction time t_0, the modified iterative M.I. and the half-interval search procedure H.I. The first method involves relative little computation-time. The initial values of t_0 for different values of t_c and k are calculated initially for the M.I. method. Also, the initial values for the isolated interval (a, b) are calculated for the H.I. search procedure. The two methods are represented in computer FORTRAN IV program. The Wang Computer (Model No. PC-S2- 2) is used for obtaining the numerical results for the chemical problem. In conclusion, the accuracy of the results is discussed.

Problem Statement

The first-order irreversible chemical reaction A → B has a reaction rate constant k hr^{-1} at a temperature T. A stirred batch reactor is charged with V cu ft of reactant solution of initial concentration a_0 lb moles/cu ft and is operated isothermally at a temperature T for t_0 hours. The reaction products are then removed for product separation, and the reactor vessel is cleaned for subsequent reloading with fresh reactant.

The reactor is operated cyclically; that is, the process of loading fresh reactant, allowing the reaction to proceed, dumping the product, and cleaning the reactor is repeated indefinitely. If the down time between reaction cycle is t_0 hours, it is shown that the reaction time t_0 required to maximize the overall yield of product B per hour is given by the solution of the transcendental equation:

$$t_0 - [\ln (t_0k + t_ck + 1)]/k = 0 \quad (1)$$

Now this equation is required to be solved using the following data:

TABLE 1

V (cu ft)	10	10	10	10
a_0 (lb moles/cu ft)	0.1	0.1	0.1	0.1
k (hr^{-1})	2.5	2.5	1.0	1.0
t_c (hr)	0.5	1.0	1.0	2.0

Mathematical Discussion

From equation (1), we have

$$e^{kt_0} = kt_0 + kt_c + 1, \qquad \text{where } t_c k + 1 > 0,\ t_0 > 0.$$

Let

$$y_1 = e^{kt_0}$$

and

$$y_2 = kt_0 + kt_c + 1$$

i.e.

$$[y_2/(kt_c + 1)] + [t_0/-(t_c + 1/k)] = 1$$

The graphical representation shows that there exists one and only one positive solution of equation (1).

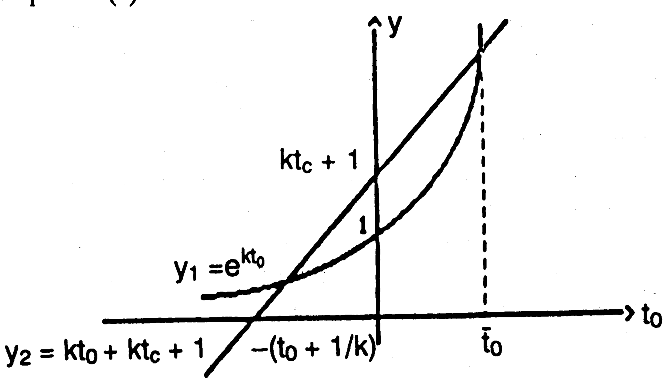

Fig. 1

Modified Iterative Method

Let

$$f(t_0) = e^{kt_0} - kt_0 - kt_c - 1;$$

then

$$f'(t_0) = k(e^{kt_0} - 1)$$

and

$$f''(t_0) = k^2 e^{kt_0}$$

Therefore the modified iterative method applied to (1) gives:

$$t_{0,i+1} = t_{0,i} - \{\frac{e^{kt_{0,i}} - kt_{0,i} - kt_c - 1}{k(e^{kt_{0,i}} - 1)},^{5} \qquad i = 0(1)\ldots$$

where k, t_c are parameters (Table1) and $t_0 > 0$.

The method converges when

$$|(e^{kt_0} - kt_0 - kt_c - 1)(k^2 e^{kt_0})| < k^2 (e^{kt_0} - 1)^2$$

i.e. when

$$|e^{kt_0} - kt_0 - kt_c - 1| < (e^{kt_0} - 1)^2 / e^{kt_0}, ^6 \quad \text{where } e^{kt_0} > 0.$$

The initial values for t_0 for the different values of t_c and k are calculated in the following table:

TABLE 2

t_0	k	$t_{0,0}$
0.5	2.5	0.5
1.0	2.5	0.5
1.0	1.0	1.5
2.0	1.0	1.5

In the following, the M.I. method is represented in a computer FORTRAN IV program[7]. The Wang Computer (Model No. PC-S2-2) is used for obtaining the numerical results for the chemical problem.

A FORTRAN IV PROGRAM FOR SOLVING THE CHEMICAL PROBLEM USING THE MODIFIED ITERATIVE METHOD

```
C     THIS PROGRAM SOLVES NONLINEAR EQUATIONS USING
C                MODIFIED ITERATIVE METHOD
C
      READ(*,100)TC,AK,XO,EPS1,EPS2
      E=2.718281828
      L=1
      H=TC*AK+1
      X=X0
      I=0
      WRITE(*,700)
   10 1=1+1
      Y=E**(X*AK)
      F=Y-X*AK-H
      DF=AK*Y-AK
      DDF=AK*AK*Y
      ADF=ABS(DF)
      IF(ADF-EPSI)20,20,30
   20 IF(L-1)80,75,80
   30 DELTA=F/DF
      CONV=F*DDF/DF**2
```

```
      ACONV=ABS(CONV)
      IF(ACONV-1.)40,70,70
 40   WRITE(*,200)I,X,F,DF,DELTA,CONV
      IF(L-1)90,50,90
 50   X=X-DELTA
      ADELTA=ADS(DELTA)
      IF(ADELTA-EPS2)60,60,65
 60   L=-1
 65   GO TO 10
 70   IF(L-1)80,95,80
 75   WRITE(*,300)
      STOP
 80   WRITE(*400)X,F,DF
 90   WRITE(*,500)
      STOP
 95   WRITE(*,600)X,F,DF,DELTA,CONV
      STOP
100   FORMAT(2(F3.1,2X),F6.3,2X,2(E7.1,2X))
200   FORMAT(3X,12,3X,F12.9,3(2X,E10.4),2X,E8.2,'CON')
300   FORMAT(5X,16H CRITICAL POINT)
400   FORMAT(3X,F12.9,2(3X,E10.4))
500   FORMAT(5X,22H THE PROBLEM IS SOLVED)
600   FORMAT(3X, F12.9,3(2X,E10.4),2X,E8.2, 'DIV')
700   FORMAT(3X,1HI,9X,1HX,12X,1HF,11X,2HDF,8X,
      5HDELTA,7X,4HCONV)
      END
```

The Numerical Results

TC	K	$T_{0,0}$	EPS1	EPS2
B > 0.5	2.5	0.5	1.0E–07	1.0E–07

I	X	F	DF	DELTA	CONV
1	.500000000	–.9657E–02	.6226E+01	–.1551E–02	–.54E–02CON
2	.501551200	.2646E–04	.6260E+01	.4228E–05	.15E–04CON
3	.501546900	–.1490E–06	.6260E+01	–.2381E–07	–.83E–07CON
4	.501546900	–.1490E–06	.6260E+01	–.2381E–07	–.83E–07CON

THE PROBLEM IS SOLVED

Stop—Program terminated.

1.0 2.5 0.5 1.0E–07 1.0E–07

I	X	F	DF	DELTA	CONV
1	.500000000	–.1260E+01	.6226E+01	–.2023E+00	–.71E+00CON
2	.702326700	.5324E+00	.1197E+02	.4447E–01	.13E+00CON
3	.657854100	.3448E–01	.1045E+02	.3301E–02	.10E–01CON
4	.654553400	.1760E–03	.1034E+02	.1701E–04	.53E–04CON
5	.654536400	.5066E–06	.1034E+02	.4899E–07	.15E–06CON
6	.654536400	–.7749E–06	.1034E+02	–.7493E–07	–.23E–06CON

THE PROBLEM IS SOLVED
Stop—Program terminated.

1.0, 1.0 1.5 1.E–07 1.0E–07

I	X	F	DF	DELTA	CONV
1	1.500000000	.9817E+00	.3482E+01	.2820E+00	.36E+00CON
2	1.218042000	.1625E+00	.2381E+01	.6827E–01	.97E–01CON
3	1.149772000	.7702E–02	.2157E+01	.3570E–02	.52E–02CON
4	1.146203000	.2015E–04	.2146E+01	.9387E–05	.14E–04CON
5	1.146193000	.0000E+00	.2146E+01	.0000E+00	.00E+00CON
6	1.146193000	.0000E+00	.2146E+01	.0000E+00	.00E+00CON

THE PROBLEM IS SOLVED
Stop—Program terminated.

2.0 1.0 1.5 1.0E–07 1.0E–07

I	X	F	DF	DELTA	CONV
1	1.500000000	–.1831E–01	.3482E+01	–.5259E–02	–.68E–02CON
2	1.505259000	.6223E–04	.3505E+01	.1775E–04	.23E–04CON
3	1.505242000	–.1192E–06	.3505E+01	–.3401E–07	–.44E–07CON
4	1.505242000	–.1192E–06	.3505E+01	–.3401E–07	–.44E–07CON

THE PROBLEM IS SOLVED
Stop—Program terminated.

The Half-interval Search Procedure

To use this method, we should have two points a and b such that $f(a)f(b) < 0$. It is known that the H.I. search procedure is always convergent and x will be a good approximation if $|f(x)| < \varepsilon_1$ and $|b - a| < \varepsilon_2$,[5] where ε_1 and $\varepsilon 2$ are very small positive given numbers. The initial values for the interval (*a*, *b*) are calculated in the following Table:

TABLE 3

tc	*k*	*a*	*b*
0.5	2.5	0.0	1.0
1.0	2.0	0.0	1.0
1.0	1.0	1.0	2.0
2.0	1.0	1.0	2.0

In the following the H.I. search procedure is represented in a computer FORTRAN IV program. The Wang Computer is used for calculating the results of the chemical problem.

A FORTRAN IV PROGRAM FOR SOLVING THE CHEMICAL PROBLEM USING THE HALF-INTERVAL SEARCH PROCEDURE

```
C   A COMPUTER PROGRAM FOR SOLVING NONLINEAR EQUA-
C   TIONS USING THE HALF INTERVAL SEARCH PROCEDURE
C
      READ(*,100)TC,EPS1,EPS2
      E=2.718281828
      H=TC*AK+1
      I=0
    5 READ(*,200)A,
      WRITE(*,700)
      FA=E**(AK*A)-A*AK-H
      FB=E**(AK*B)-B*AK-H
      IF(FA*FB)10,40,90
   10 I=I+1
      X=(A+B)/2.
      F=E**(X*AK)-X*AK-H
      WRITE(*,300)I,X,F,A,B
      IF(FA*F)20,85,30
   20 B=X
      FB=F
      GO TO 35
   30 A=X
      FA=F
   35 AF=ABS(F)
      IF(AF-EPSI)60,60,10
   40 IF(FA)50,70,50
   50 IF(FB)90,80,90
   60 AB=ABS(B-A)
      IF(AB-EPS2)85,85,10
```

```
 70 WRITE(*,400)A,FA
    GO TO 85
 80 WRITE(*,400)B,FB
 85 WRITE(*,500)
    STOP
 90 WRITE(*,600)
    GO TO 5
100 FORMAT(2X,2(F3.1,2X),2(E7.1,2X))
200 FORMAT(2X,2(F6.3,2X))
300 FORMAT(3X,12,3X,F12.9,3X,E10.4,2(3X,F12.9))
400 FORMAT(3X,F12.9,3X,E10.4)
500 FORMAT(5X,22H THE PROBLEM IS SOLVED)
600 FORMAT(5X,12H CHANGE A,B)
700 FORMAT(4X,1HI,9X,1HX,13X,1HF,13X,1HA,13X,1HB/)
    END
```

The Numerical Results

TC	K	EPS1	EPS2
0.5	2.5	1.0E–07	1.0E–07

H 0.0 B 1.0

I	X	F	A	B
1	.500000000	–.9657E–02	.000000000	1.000000000
2	.750000000	.2396E+01	.500000000	1.000000000
3	.625000000	.9582E+00	.500000000	.750000000
4	.562500000	.4244E+00	.500000000	.625000000
5	.531250000	.1958E+00	.500000000	.562500000
6	.515625000	.9032E–01	.500000000	.531250000
7	.507812500	.3965E–01	.500000000	.515625000
8	.503906300	.1483E–01	.500000000	.507812500
9	.501953100	.2544E–02	.500000000	.503906300
10	.500976600	–.3567E–02	.500000000	.501953100
11	.501464800	–.5138E–03	.500976600	.501953100
12	.501709000	.1015E–02	.501464800	.501953100
13	.501586900	.2503E–03	.501464800	.501709000
14	.501525900	–.1318E–03	.501464800	.501586900
15	.501556400	.5913E–04	.501525900	.501586900
16	.501541100	–.3624E–04	.501525900	.501556400
17	.501548800	.1144E–04	.501541100	.501556400
18	.501545000	–.1240E–04	.501541100	.501548800
19	.501546900	–.4768E–06	.501545000	.501548800

20	.501547800	.5484E–05	.501546900	.501548800
21	.501547300	.2384E–05	.501546900	.501547800
22	.501547100	.1073E–05	.501546900	.501547300
23	.501547000	–.5960E–07	.501546900	.501547100
24	.501547000	.7451E–06	.501547000	.501547100
25	.501547000	–.5960E–07	.501547000	.501547000

THE PROBLEM IS SOLVED
Stop—Program terminated.

1.0 2.0 1.0E–7 1.0E–07
0.0 1.0

I	X	F	A	B
1	.500000000	–.1260E+01	.000000000	1.000000000
2	.750000000	.1146E+01	.500000000	1.000000000
3	.625000000	–.2918E+00	.500000000	.750000000
4	.687500000	.3588E+00	.625000000	.750000000
5	.656250000	.1777E–01	.625000000	.687500000
6	.640625000	–.1408E+00	.625000000	.656250000
7	.648437500	–.6247E–01	.640625000	.656250000
8	.652343800	–.2260E–01	.648437500	.656250000
9	.654296900	–.2476E–02	.652343800	.656250000
10	.655273400	.7630E–02	.654296900	.656250000
11	.654785200	.2573E–02	.654296900	.655273400
12	.654541000	.4768E–04	.654296900	.654785200
13	.654418900	–.1215E–02	.654296900	.654541000
14	.654480000	–.5836E–03	.654418900	.654541000
15	.654510500	–.2680E–03	.654480000	.654541000
16	.654525800	–.1101E–03	.654510500	.654541000
17	.654533400	–.3099E–04	.654525800	.654541000
18	.654537200	.8106E–05	.654533400	.654541000
19	.654535300	–.1144E–04	.654533400	.654537200
20	.654536200	–.1431E–05	.654535300	.654537200
21	.654536700	.3099E–05	.654536200	.654537200
22	.654536500	.8345E–06	.654536200	.654536700
23	.654536400	–.7749E–06	.654536200	.654536500
24	.654536400	.5066E–06	.654536400	.654536500
25	.654536400	–.7749E–06	.654536400	.654536400
26	.654536400	–.7749E–06	.654536400	.654536400

1.0 1.0 1.0E–07 1.0E–07
1.0 2.0

I	X	F	A	B
1	1.500000000	.9817E+00	1.000000000	2.000000000
2	1.250000000	.2403E+00	1.000000000	1.500000000
3	1.125000000	–.4478E–01	1.000000000	1.250000000
4	1.187500000	.9137E–01	1.125000000	1.250000000
5	1.156250000	.2174E–01	1.125000000	1.187500000
6	1.140625000	–.1190E–01	1.125000000	1.156250000
7	1.148438000	.4824E–02	1.140625000	1.156250000
8	1.144531000	–.3563E–02	1.140625000	1.148438000
9	1.146484000	.6249E–03	1.144531000	1.148438000
10	1.145508000	–.1470E–02	1.144531000	1.146484000
11	1.145996000	–.4232E–03	1.145508000	1.146484000
12	1.146240000	.1009E–03	1.145996000	1.146484000
13	1.146118000	–.1612E–03	1.145996000	1.146240000
14	1.146179000	–.3028E–04	1.146118000	1.146240000
15	1.146210000	.3529E–04	1.146179000	1.146240000
16	1.146194000	.2623E–05	1.146179000	1.146340000
17	1.146187000	–.1383E–04	1.146179000	1.146194000
18	1.146191000	–.5722E–05	1.146187000	1.146194000
19	1.146193000	–.1431E–05	1.146191000	1.146194000
20	1.146194000	.4768E–06	1.146193000	1.146194000
21	1.146193000	–.4768E–06	1.146193000	1.146194000
22	1.146193000	.0000E+00	1.146193000	1.146194000

THE PROBLEM IS SOLVED
Stop - Program terminated.

2.0 1.0 1.0e–07 1.0e–07
1.0 2.0

I	X	F	A	B
1	1.500000000	–.1831E–01	1.000000000	2.000000000
2	1.750000000	.1005E+01	1.500000000	2.000000000
3	1.625000000	.4534E+00	1.500000000	1.750000000
4	1.562500000	.2082E+00	1.500000000	1.625000000
5	1.531250000	.9270E–01	1.500000000	1.562500000
6	1.515625000	.3664E–01	1.500000000	1.531250000
7	1.507813000	.9027E–02	1.500000000	1.515625000

8	1.503906000	-.4676E-02	1.500000000	1.507813000
9	1.505859000	.2166E-02	1.503906000	1.507813000
10	1.504883000	-.1257E-02	1.503906000	1.505859000
11	1.505371000	.4539E-03	1.504883000	1.505859000
12	1.505127000	-.4015E-03	1.504883000	1.505371000
13	1.505249000	.2623E-04	1.505127000	1.505371000
14	1.505188000	-.1879E-03	1.505127000	1.505249000
15	1.505219000	-.8059E-04	1.505188000	1.505249000
16	1.505234000	-.2718E-04	1.505219000	1.505249000
17	1.505241000	-.4768E-06	1.505234000	1.505249000
18	1.505245000	.1287E-04	1.505241000	1.505249000
19	1.505243000	.6199E-05	1.505241000	1.505245000
20	1.505242000	.2861E-05	1.505241000	1.505243000
21	1.505242000	.9537E-06	1.505241000	1.505242000
22	1.505242000	.2384E-06	1.505241000	1.505242000
23	1.505242000	-.1192E-06	1.505241000	1.505242000
24	1.505242000	.2384E-06	1.505242000	1.505242000
25	1.505242000	.2384E-06	1.505242000	1.505242000

Conclusion

Let the reaction rate constant be k hr^{-1} at a temperature T, the down time between reaction cycles be t_c hours, and the reaction time required to maximize the overall yield of product per hour be t_0 hours.

For the different values of t_c and k, the numerical results give the following informations.

(i) For $t_c = 0.5^{hour}$ and $k = 2.5^{hr-1}$ we find that $t_0 = 0.501546900^{hour}$ after 3 iterations by M.I. method and after 18 iterations by the H.I. search procedure. Then, the time of the calculations in the second method is about 6 times of the first method[3,4].

(ii) For $t_c = 1.0^{hour}$ and $k = 2.0^{hr-1}$ we find that $t_0 = 0.65436400^{hour}$ after 5 iterations by M.I. method and after 22 iterations by the H.I. search procedure. Then, the time of the calculations in the second method is more than four times of the first method.

(iii) For $t_c = 1.0^{hour}$ and $k = 1.0^{hr-1}$ we find that $t_0 = 1.146193000^{hour}$ after 5 iterations by M.I. method and after 18 iterations by the H.I. search procedure. Then, the time of the calculations in the second method is more than three times of the first method.

(iv) For $t_c = 2.0^{hour}$ and $k = 1.0^{hr-1}$ we find that $t_0 = 1.505242000^{hour}$ after 3 iterations by M.I. method and after 19 iterations by the H.I. search procedure. Then, the time of the calculations in the second method is more than 6 times of the first method.

This paper shows that for any first order irreversible chemical reaction we can determine the reaction time t_0 required to maximize the overall yield of product per hour for different values of t_c and k.

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