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REAKTOR *SEMIBATCH*

(Unsteady Stirred Tank Reactors; Semi-Batch = Semi-Kontinyu)

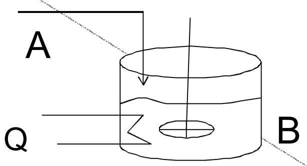
I Gusti S. Budiaman, Gunarto, Endang Sulistyawati
Siti Diyar Kholisoh

PERANCANGAN REAKTOR (1210323)
SEMESTER GENAP TAHUN AKADEMIK 2016-2017
JURUSAN TEKNIK KIMIA – FTI – UPN "VETERAN" YOGYAKARTA

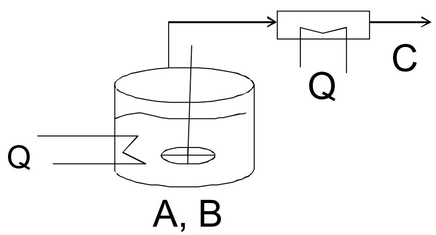
Tipe Reaktor *Semibatch*

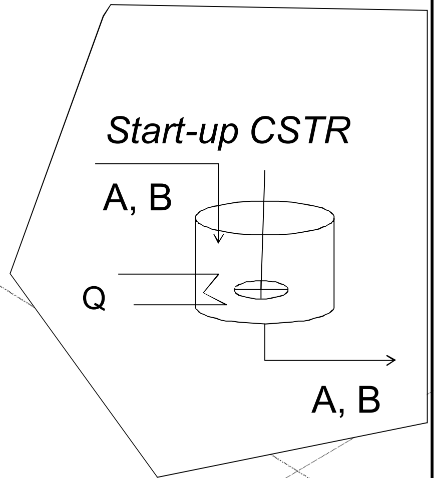
- **Reaktor *semibatch* tipe -1**
  - Digunakan untuk reaksi-reaksi sangat eksotermis.
  - Salah satu umpan dimasukkan secara perlahan selama reaksi berlangsung.
  - Konsentrasi A>> → terjadi reaksi samping
- **Reaktor *semibatch* tipe -2**
  - Umpan dimasukkan secara bersamaan.
  - Salah satu produk diuapkan supaya reaksi tetap bergeser ke kanan.
  - Laju reaksi besar → konversi besar

Reaktor *semibatch* tipe -1

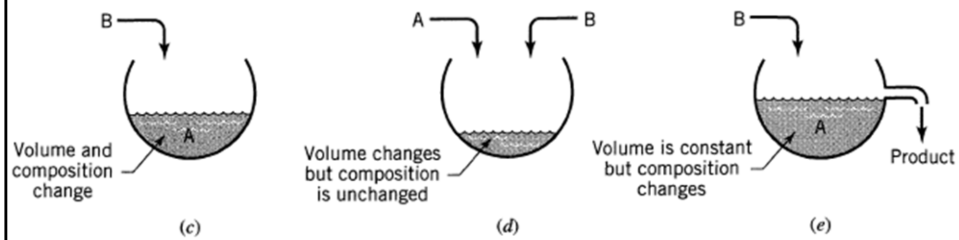


Reaktor *semibatch* tipe -2





Beberapa model pengoperasian reaktor *semibatch:*



(Levenspiel, 1999, page 84)

Tools Penyelesaian Masalah Perancangan:

1. Neraca massa
   - *total (overall) mass balance*
   - *component mole balance*
2. Neraca energi (entalpi)
3. Neraca momentum *(optional)*
4. Persamaan laju reaksi (kinetika)
5. Stoikiometri
6. Persamaan[2] pendukung
7. *Combining* dan penyelesaian matematika

"Semibatch = semi kontinyu"

Review Penyelesaian Matematika:

1. Penyelesaian persamaan diferensial biasa linier (orde 1), **secara analitik:**

$$\frac{dy}{dx} + P(x).y = Q(x)$$

dengan ***initial value (IV):*** $x = x_0$; $y = y_0$

$$y\ e^{\int P(x)\,dx} = \int Q(x)\,.\,e^{\int P(x)\,dx}\,dx + C$$

Review Penyelesaian Matematika:

2. Penyelesaian persamaan diferensial biasa linier (orde 1), **secara numerik:**

$$\frac{dy}{dx} = f(x, y)$$

dengan ***initial value (IV):*** $x = x_0$; $y = y_0$

$$y_{i+1} = y_i + h\,.\left.\frac{dy}{dx}\right|_{x_i, y_i}$$

[Misal: **metode Euler**, *dengan step size h (= Δx)]*

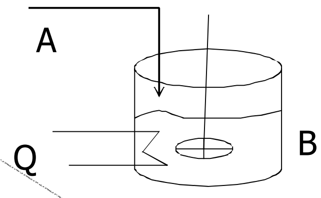
Ilustrasi: Reaktor *Semibatch* Tipe -1

- Contoh reaksi:
  - Amonolisis
  - Khlorinasi
  - Hidrolisis
- Misal, reaksi fasa cair:

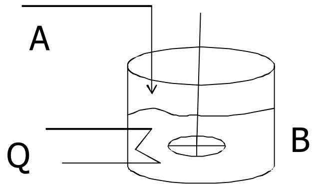
A + B → C

pada kondisi isotermal.

Reaktan B dimasukkan secara sekaligus pada saat awal (t = 0). Reaktan A dialirkan secara kontinyu dengan debit q_0.



Lanjutan:



- Laju reaksi dianggap **berorde-satu-semu terhadap A**.
- Jabarkanlah persamaan yang menyatakan konsentrasi A (C_A) di dalam reaktor sebagai fungsi waktu (t).
- Ulangi untuk C_B dan C_C.

Neraca mol A:

$$F_{A0} - 0 + r_A V = \frac{d\,n_A}{dt} \qquad (1)$$

Dalam bentuk konsentrasi:

$$q_0\,C_{A0} + r_A V = \frac{dC_A V}{dt} = C_A\frac{dV}{dt} + V\frac{dC_A}{dt} \qquad (2)$$

Selama reaksi berlangsung: ***volume V berubah terhadap waktu***.

Neraca massa total:

$$R_{in} - R_{out} + R_{gen} = R_{acc}$$

$$\rho_0\,q_0 - 0 + 0 = \frac{d(\rho V)}{dt} \qquad (3)$$

Apabila densitas larutan konstan, berlaku:

$$\frac{dV}{dt} = q_0 \rightarrow \int_{V_0}^{V} dV = \int_0^t q_0\,dt \rightarrow \boxed{V = V_0 + q_0 t} \qquad (4)$$

Persamaan (4) dibagi q_0:

$$\frac{V}{q_0} = \frac{V_0}{q_0} + t \rightarrow \tau = \tau_0 + t \qquad (5)$$

Substitusi (4) ke (2):

$$q_0 C_{A0} + r_A V = C_A q_0 + V\frac{dC_A}{dt}$$

$$q_0(C_{A0} - C_A) + r_A V = V\frac{dC_A}{dt} \qquad (6)$$

Chain rule:

$$\frac{dC_A}{dt} = \frac{dC_A}{d\tau}\frac{d\tau}{dt} = \frac{dC_A}{d\tau}(1) = \frac{dC_A}{d\tau} \qquad (*)$$

Substitusi (*) ke (6) dan kemudian dibagi q_0:

$$(C_{A0} - C_A) + r_A\tau = \tau\frac{dC_A}{d\tau} \qquad (7)$$

Jika: <u>reaksi elementer</u>, <u>umpan A ditambahkan secara perlahan</u>, dan <u>C_B awal sangat besar (>>>)</u>:

→ reaksi dianggap berorder 1 terhadap A

$$-r_A = k'C_A C_B = k'C_A C_{B0} = k\,C_A \qquad (8)$$

$$C_{A0} - C_A + \tau k C_A = \tau\frac{dC_A}{d\tau}$$

$$\boxed{\frac{dC_A}{d\tau} + \left(\frac{1+\tau k}{\tau}\right)C_A = \frac{C_{A0}}{\tau}} \qquad (9)$$

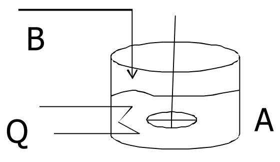
<u>Initial value</u>: $\tau = \tau_0$ jika: $C_A = C_{Ai}$ (≡ konsentrasi A awal di dalam reaktor)

Dapat diselesaikan secara analitik atau numerik.

Kasus lain:

Jika reaksi bukan berorder nol atau bukan berorder 1, dan jika operasi non-isotermal, maka sebaiknya penyelesaian model/persamaan matematika dilakukan dengan menggunakan **metode numerik**, untuk *menentukan konversi atau konsentrasi sebagai fungsi waktu.*

Contoh:



Mula-mula dalam reaktor hanya berisi A, lalu B diumpankan perlahan secara kontinyu. Reaksi berorder 1 terhadap A dan berorder 1 terhadap B:

Reaksi: **A + B → C + D**

$$-r_A = k\, C_A C_B \qquad (10)$$

Mol A dalam reaktor (pada t):

[mol A dlm reaktor pd t] = [mol A mula-mula] – [mol A bereaksi]

$$\boxed{n_A = n_{A0} - n_{A0}\, X_A} \qquad (11)$$

Mol B dalam reaktor (pada t), dengan cara yang sama:

$$n_B = n_{Bi} + \int_0^t F_{B0}\, dt - n_{A0}\, X_A \qquad (12)$$

Jika F_{B0} tetap: $\boxed{n_B = n_{Bi} + F_{B0}\, t - n_{A0}\, X_A}$ (13)

Dari neraca mol A:

$$r_A V = \frac{dn_A}{dt} \quad \text{atau}: \ -r_A V = n_{A0} \frac{dX_A}{dt} \qquad (14)$$

dan, volume fluida (pada t): $V = V_0 + q_0\, t$ (15)

Selanjutnya, persamaan (14) dapat diselesaikan secara numerik, misal dengan metode Euler:

$$\frac{dX_A}{dt} = \frac{-r_A V}{n_{A0}}$$

maka: $\boxed{X_{A,i+1} = X_{A,i} + \frac{(-r_A V)_i}{n_{A0}} \Delta t}$

Dalam hal ini, nilai C_A dan C_B:

$$C_A = \frac{n_A}{V}$$

$$C_B = \frac{n_B}{V}$$

Contoh 4-10 (Fogler, 1992):

Produksi metil bromida melalui reaksi elementer fasa cair:

$$\mathbf{CNBr + CH_3NH_2 \rightarrow CH_3Br + NCNH_2}$$

dilangsungkan dalam reaktor *semibatch*. Larutan metil amina (B) dengan konsentrasi 0,025 mol/dm^3 diumpankan dengan laju 0,05 dm^3/s ke dalam reaktor yang berisi larutan bromin sianida (A). Mula-mula: reaktor berisi 5 dm^3 larutan A dengan konsentrasi 0,05 mol/dm^3. Tetapan laju reaksi pada kondisi ini: k = 2,2 dm^3/s.mol.

Tentukan konversi A, konsentrasi CH_3Br, dan laju reaksi sebagai fungsi waktu.

Penyelesaian:

- *Mole balance:* $n_{A0}\dfrac{dX_A}{dt}=(-r_A)V$

  atau: $\dfrac{dX_A}{dt}=\dfrac{(-r_A)V}{n_{A0}}$

- *Rate law:* $-r_A = k\,C_A\,C_B$

- Stoikiometri: $C_A=\dfrac{n_A}{V}$ $C_B=\dfrac{n_B}{V}$ $C_C=\dfrac{n_C}{V}$

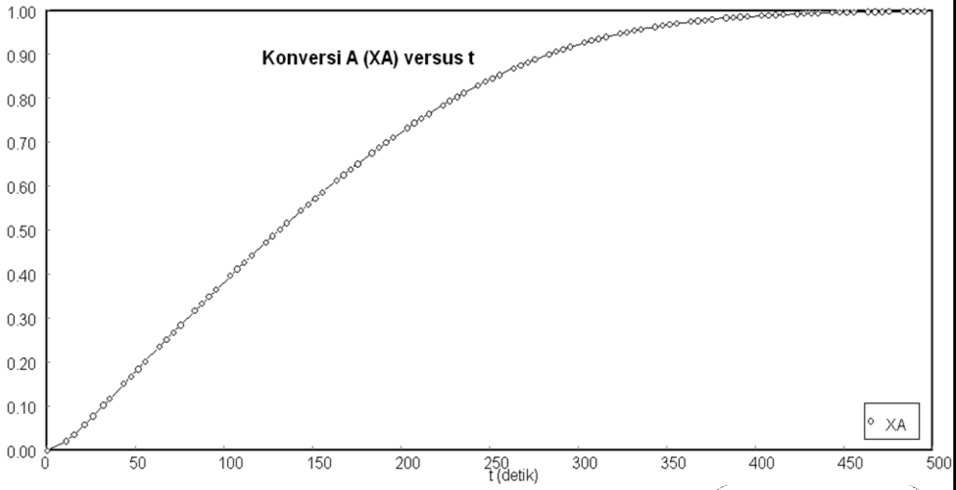
  dengan: $n_A = n_{A0}(1-X_A)$

  $n_B = n_{Bi} + F_{B0}\,t - n_{A0}X_A$

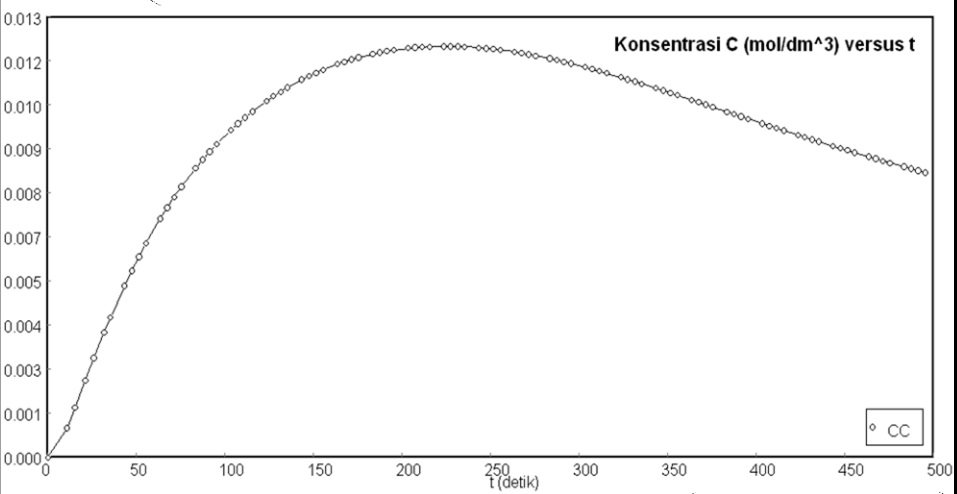
  $n_C = n_{A0}X_A$

  $V = V_0 + q_0\,t$

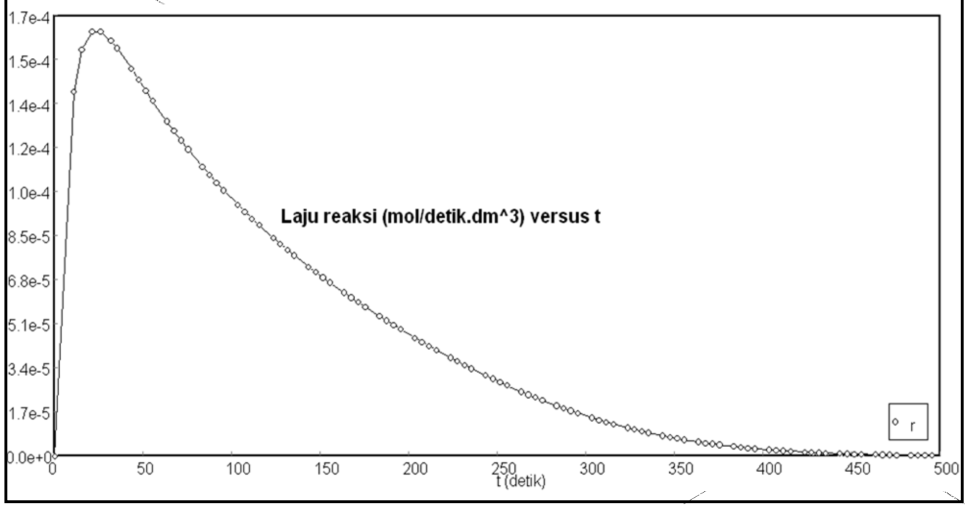
Profil X_A versus t:



Profil C_C versus t:



Profil $-r_A$ versus t:



Contoh 4-14 (Smith, 1981):

Contoh Kasus: Start-Up RATB

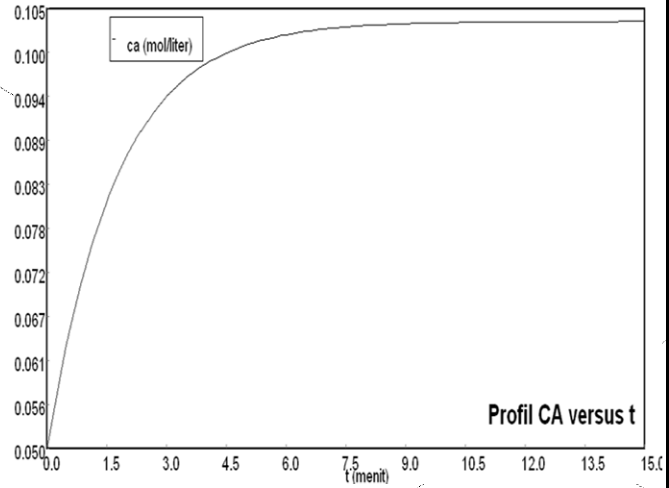
Acetic anhydride (A) dihidrolisis pada 40°C menurut reaksi: **A → produk**; dalam sistem reaktor *semibatch*. Mula-mula reaktor tangki berpengaduk berisi 10 liter larutan A dengan konsentrasi 0,5 x 10^{-4} mol/cm^3. Setelah tercapai kondisi reaksi, larutan umpan dengan konsentrasi A sebesar 3 x 10^{-4} mol/cm^3 dialirkan dengan laju 2 liter/menit. Produk juga dialirkan keluar reaktor dengan laju volumetrik yang sama. Densitas campuran reaksi dianggap konstan. Reaksi dianggap berorder 1 terhadap A, dengan k (pada 40°C) sebesar 0,380 $menit^{-1}$. *Tentukan konsentrasi A yang keluar dari reaktor sebagai fungsi waktu!*

Alur Penyelesaian:

- Gambaran masalah: secara skematik
- Tuliskan semua data yang diketahui
- Neraca massa *overall* (pada periode *start-up*, sebelum mencapai *steady-state)*
- *Mole balance* (dalam hal ini: ditinjau terhadap A)
- Persamaan laju reaksi *(rate law)*
- *Combining* → persamaan diferensial biasa tingkat 1, dengan nilai awal: $C_A = C_{Ai}$ pada t = 0.
- Penyelesaian matematika (misal, dari: t = 0, t = 1 menit, t = 2 menit, dst.. t = 10 menit, **hingga mencapai *steady state*)**

Hasil/Jawaban:

t (menit)	C_A x 10^5 (mol/cm^3)
0	5,00
1	7,35
2	8,67
3	9,40
5	10,05
∝	10,34



Contoh 14-3:
(Missen, 1999)

Tinjaulah proses *startup* dari sebuah RATB untuk reaksi fasa cair: **A → produk**. Mula-mula reaktor diisi dengan umpan ketika *steady flow of feed* (q) dimulai. Tentukan waktu (t) yang diperlukan untuk mencapai 99% dari konversi A (X_A) pada kondisi *steady*-nya.

Data: V = 8000 L; q = 2 L s^{-1}; C_{A0} = 1,5 mol L^{-1}; k_A = 1,5 x $l0^{-4}$ s^{-1}.

Beberapa Soal Latihan tentang Reaktor *Semibatch:*

1. Problem P4-25$_B$
2. Problem P4-26$_B$
3. Problem P4-27$_B$

[Fogler, 1992]

1. Problem 4-29
2. Problem 4-30

[Smith, 1981]

1. Problem 14-1
2. Problem 14-2
3. Problem 14-3

[Missen, 1999]

Latihan Soal

Reactant A is fed (at t = 0) at a constant rate of 5 L.s^{-1} to an empty 7000-L CSTR until the CSTR is full. Then the outlet valve is opened. If the rate law for the reaction: **A → products** is: **$(-r_A) = k_A\, C_A$**, where: **$k_A = 8 \times 10^{-4}\ s^{-1}$**, and if the inlet and outlet rates remain constant at 5 L.s^{-1}, calculate C_A:

(a) at t = 15 min, and
(b) at t = 40 min.

Assume that the temperature and density of the reaction system are constant, and that C_{A0} = 2 mol.L^{-1}.

Problem 4-29 (Smith, 1981)

Repeat Example 4-14 with the modification that the effluent from the first reactor is fed to a second reactor. The second reactor originally contains 10 liters of an anhydride solution of concentration 0,5 x 10^{-4} mol/cm^3. Product is withdrawn from reactor 2 at a constant rate of 2 liters/min. Temperature in both are 40^{o}C, and all other conditions are the same as in Example 4-14.

a) Determine the concentration of anhydride in the solution leaving the second reactor from zero time until steady-state conditions are reached.
b) Suppose that reactor 2 was originally empty and that its capacity is 10 liters. After it is filled, product is withdrawn at the rate of 2 liters/min. What would be the concentration of the first anhydride solution leaving the second reactor?

Problem P4-27$_B$ (Fogler, 1992, 2nd Ed, Page 180)

The liquid-phase reaction: **2 A + B → C + D** is carried out in a *semibatch reactor.* The reactor volume is 1.2 m^3. The reactor initially contains 5 mol of B at a concentration of 0.015 kmol/m^3. A at an aqueous concentration of 0.03 kmol/m^3 is fed to the reactor at a rate of 4 dm^3/min. The reaction is first order in A and half order in B with a specific reaction rate of k = 6 (m^3/kmol)$^{1/2}$/min. The activation energy is 35 kJ /mol. The feed rate to the reactor is discontinued when the reactor contains 0.53 m^3 of fluid.

(a) Plot the conversion, volume, and concentration as a function of time.

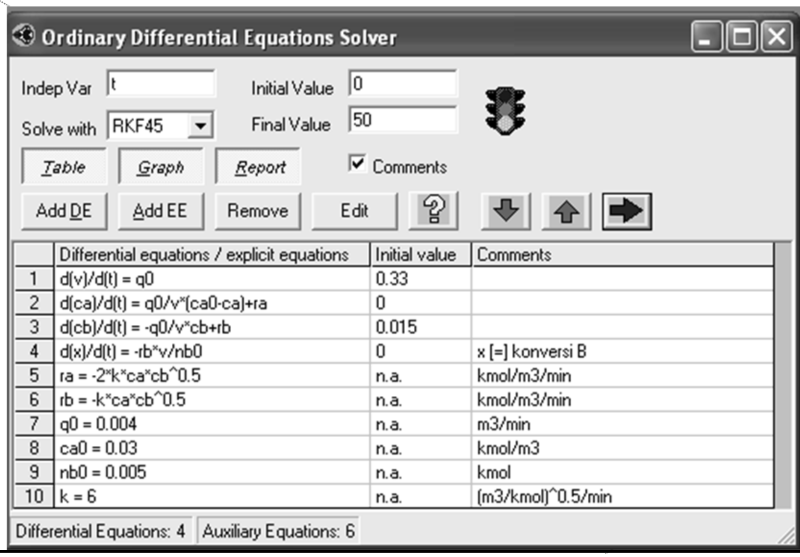
Calculate the time necessary to achieve:

(b) 97% conversion of A.

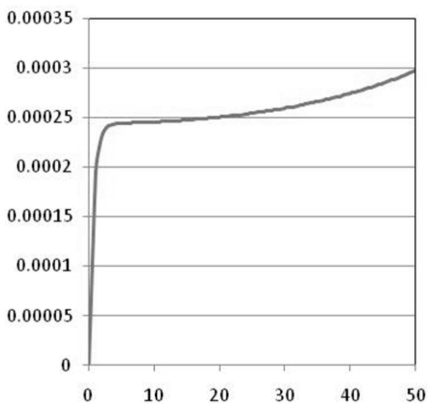
(c) 59% conversion of B. → *Ans: 50,48 min*

(d) The reaction temperature is to be increased from 25°C to 70°C and the reaction is to be carried out isothermally. At this temperature the reaction is reversible with an equilibrium constant of 10 $(m^3/kmol)^{1/2}$. Plot the conversion of A and B and the equilibrium conversion of A as a function of time.

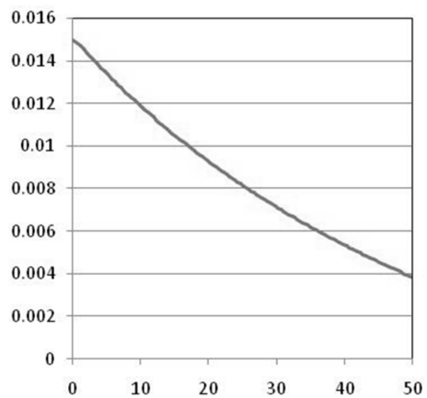
Solution by using: Polymath 5.1



	Differential equations / explicit equations	Initial value	Comments
1	d(v)/d(t) = q0	0.33	
2	d(ca)/d(t) = q0/v*(ca0-ca)+ra	0	
3	d(cb)/d(t) = -q0/v*cb+rb	0.015	
4	d(x)/d(t) = -rb*v/nb0	0	x [=] konversi B
5	ra = -2*k*ca*cb^0.5	n.a.	kmol/m3/min
6	rb = -k*ca*cb^0.5	n.a.	kmol/m3/min
7	q0 = 0.004	n.a.	m3/min
8	ca0 = 0.03	n.a.	kmol/m3
9	nb0 = 0.005	n.a.	kmol
10	k = 6	n.a.	(m3/kmol)^0.5/min

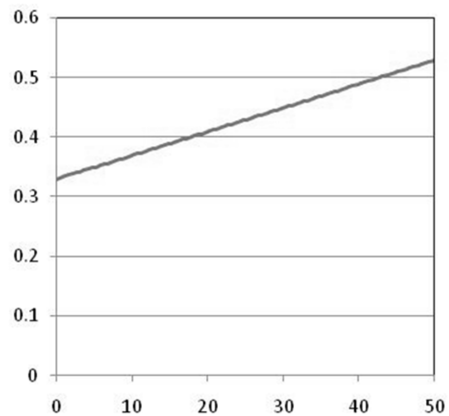


Profil C_A versus t

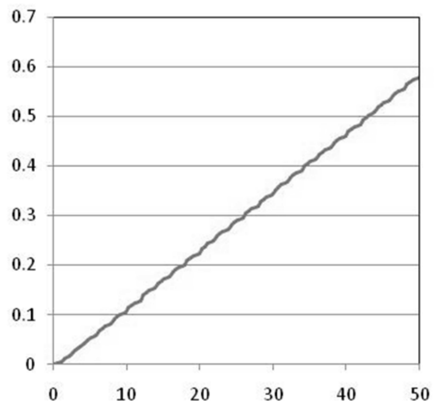


Profil C_B versus t

Keterangan: t [=] menit, C_A, C_B [=] $kmol/m^3$



Profil V versus t



Profil X_B versus t

Keterangan: t [=] menit, V [=] m^3

Differential Equations Solution #4

POLYMATH Results

11-01-2011, Rev5.1.230

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	50	50
v	0.33	0.33	0.53	0.53
ca	0	0	2.98E-04	2.98E-04
cb	0.015	0.0038282	0.015	0.0038282
x	0	0	0.5842075	0.5842075
k	6	6	6	6
ra	0	-3.437E-04	0	-2.212E-04
q0	0.004	0.004	0.004	0.004
ca0	0.03	0.03	0.03	0.03
nb0	0.005	0.005	0.005	0.005
rb	0	-1.719E-04	0	-1.106E-04

Terima kasih atas perhatiannya.

Selamat belajar!