UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2015/2016 Academic Session

June 2016

EKC 338 – Reactor Design and Analysis
[Rekabentuk Dan Analisis Reaktor]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains ELEVEN printed pages before you begin the examination.

[Sila pastikan bahawa kertas peperiksaan ini mengandungi SEBELAS muka surat yang bercetak sebelum anda memulakan peperiksaan ini.]

Instruction: Answer **ALL** questions.

*[**Arahan:** Jawab **SEMUA** soalan.]*

In the event of any discrepancies, the English version shall be used.

[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai].

...2/-

Answer ALL questions.

1. [a] The hydrogenation reaction of i-octene (A) by Co-Mo/MCM-41 catalyst to produce i-octane (C) is carried out in a differential reactor operated at 200 °C. Hydrogen (B) and i-octene are fed in a stoichiometric proportion at a total rate of 2.5 mol/min at 200 °C and 1.5 bar. The rate law is

$$-r_A = \frac{0.1113\, P_A\, P_B}{(1 + 0.475P_A + 0.322P_B + 0.414P_C)^2}$$

[i] What does the exponent on the denominator of the rate law imply?

[2 marks]

[ii] Explain the presence of P_A, P_B and P_C in the denominator of the rate law?

[2 marks]

[iii] Neglecting the pressure drop in the reactor, calculate the amount of catalyst needed to achieve 80% conversion of i-octene in a continuous flow stirred tank reactor (CSTR).

[12 marks]

[b] What are the advantages and disadvantages of a fixed bed reactor? Sketch a multi-tubular fixed bed reactor.

[4 marks]

[c] What is the difference between incipient wetness (dry) and wet impregnation methods in preparing supported catalysts? Draw a schematic of steps in the preparation of supported catalysts by impregnation to incipient wetness.

[5 marks]

2. [a] In a study of formaldehyde oxidation ($H_2CO + O_2 \rightarrow CO_2 + H_2O$) over Ag catalysts, the following reaction mechanism steps was proposed.

$$O_{2(g)} + 2S \rightarrow 2O.S$$

$$H_2CO_{(g)} + 2O.S \leftrightarrow HCO_2.S + OH.S$$

$$HCO_2.S + O.S \rightarrow CO_2 + OH.S + S$$

$$2OH.S \rightarrow H_2O_{(g)} + O.S + S$$

[i] Derive a rate expression based on this mechanism assuming the surface reaction is the rate-limiting step and the OH.S concentration is very small.

[10 marks]

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Jawab <u>SEMUA</u> soalan.

1. [a] *Tindak balas penghidrogenan i-oktena (A) oleh mangkin Co-Mo/MCM-41 untuk menghasilkan i-oktana telah dijalankan dalam sebuah reaktor pembezaan yang beroperasi pada 200 °C. Hidrogen (B) dan i-oktena disuapkan dengan kadaran stoikiometri pada jumlah kadar sebanyak 2.5 mol/min pada 200 °C dan 1.5 bar. Hukum kadar tersebut adalah*

$$-r_A = \frac{0.1113\, P_A\, P_B}{(1 + 0.475P_A + 0.322P_B + 0.414P_C)^2}$$

[i] *Apakah yang tersirat pada eksponen bagi bahagian pembawah dalam hukum kadar?*

[2 markah]

[ii] *Terangkan mengenai kewujudan* P_A, P_B *dan* P_C *pada pembawah dalam hukum kadar?*

[2 markah]

[iii] *Dengan mengabaikan kejatuhan tekanan di dalam reaktor, kirakan jumlah mangkin yang diperlukan untuk mencapai 80% penukaran i-oktena dalam reaktor tangki teraduk berterusan (CSTR).*

[12 markah]

[b] *Apakah kelebihan dan kekurangan sebuah reaktor lapisan tetap? Lakarkan sebuah reaktor lapisan berbilang tiub.*

[4 markah]

[c] *Apakah perbezaan antara kaedah kebasahan awal (kering) dan pengisitepuan basah dalam menyediakan mangkin tersokong? Lukiskan langkah skematik di dalam penyediaan mangkin tersokong melalui pengisitepuan hingga kebasahan awal.*

[5 markah]

2. [a] *Dalam satu kajian pengoksidaaan formaldehid* ($H_2CO + O_2 \rightarrow CO_2 + H_2O$) *di atas mangkin* Ag, *langkah mekanisma tindak balas yang berikut telah dicadangkan.*

$$O_{2(g)} + 2S \rightarrow 2O.S$$

$$H_2CO_{(g)} + 2O.S \leftrightarrow HCO_2.S + OH.S$$

$$HCO_2.S + O.S \rightarrow CO_2 + OH.S + S$$

$$2OH.S \rightarrow H_2O_{(g)} + O.S + S$$

[i] *Terbitkan satu ungkapan kadar berasaskan mekanisma tersebut dengan menganggap permukaan tindak balas adalah langkah penghad dan kepekatan OH.S adalah sangat kecil.*

[10 markah]

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[ii] Can the derived rate law be further simplified to give either of the following two power rate law expressions? If so, what assumptions are involved in each case?

The power rate laws are
$r = k\,P_{O_2}$ (over Ag powder)
$r = kP_{O_2}^{0.3}\,P_{H_2CO}^{0.3}$ (over supported Ag catalyst)

[2 marks]

[b] The primary goal of scale-up of tubular reactor is to maintain acceptable product quality. What are three conceptually different ways of increasing the capacity of a tubular reactor?

[3 marks]

[c] Safety precautions in chemical plants are very important to avoid a serious accidents particularly with exothermic reactions. Nitroanline is produced from ammonia and o-nitrochlorobenzene and normally carried out isothermally in a jacketed batch-reactor at 175 °C and about 500 psi. The reactor has a safety relief valve which disk would rupture when the pressure exceeded approximately 700 psi. The temperature-time trajectory was recorded from 9:55 pm till 12:18 am as shown in Figure Q.2.[c].

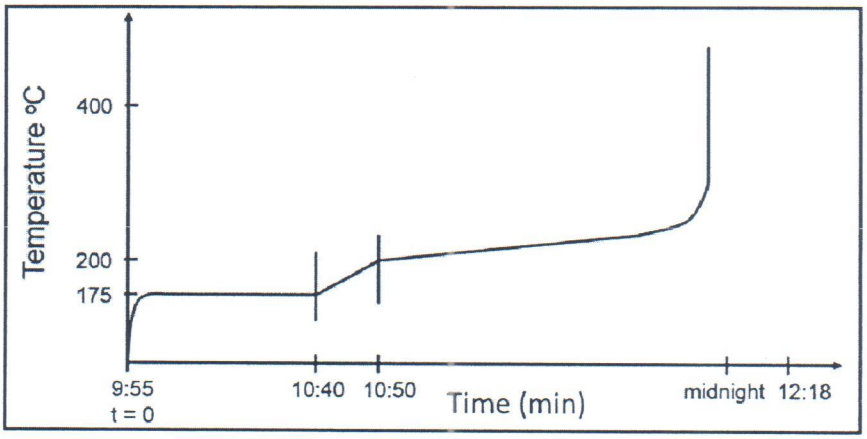


Figure Q.2.[c] Temperature-time trajectory

[i] Describe the reactor's temperature profile from time 9:55pm till 12:00 midnight indicating the possible problems occurred during the operation.

[ii] At what time the reactor may be exploded?

[iii] What are the possible conditions that have been present for the explosion to occur?

[6 marks]

[d] The preparation of supported catalysts by the co-precipitation of metal ions with the support ions usually produces an intimate mixing of catalysts and support. Give an example of preparing a catalyst by this technique.

[4 marks]

...5/-

[ii] *Bolehkah hukum kadar terbitan diringkaskan lebih lanjut untuk menjadi salah satu dari dua ungkapan hukum kadar kuasa yang berikut? Jika ya, apakah anggapan-anggapan yang diambil untuk setiap kes?*

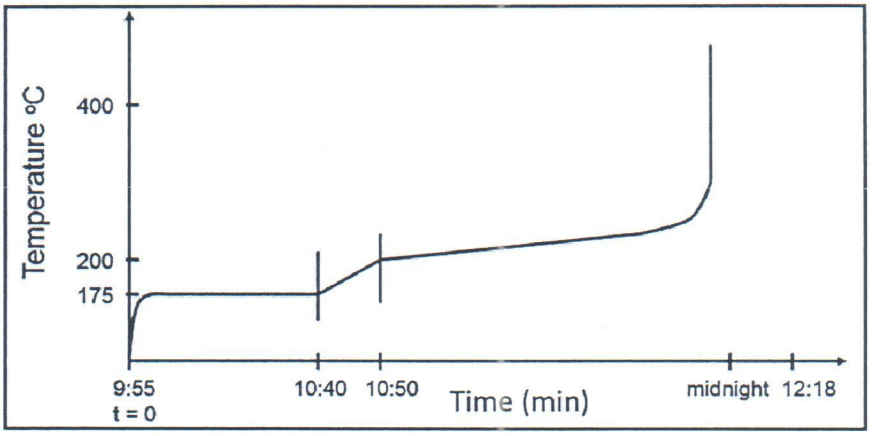
Hukum kadar kuasa tersebut adalah
$r = k\,P_{O_2}$ *(di atas serbuk* Ag*)*
$r = kP_{O_2}^{0.3}\,P_{H_2CO}^{0.3}$ *(di atas mangkin tersokong* Ag*)*

[2 markah]

[b] *Tujuan utama menaik-skala reaktor tiub adalah untuk mengekalkan kualiti produk yang boleh diterima secara konsepnya. Apakah tiga cara berbeza untuk meningkatkan kapasiti reaktor tiub?*

[3 markah]

[c] *Langkah keselamatan dalam loji kimia adalah sangat penting untuk mengelakkan kemalangan yang serius terutamanya yang melibatkan tindakbalas eksotermik. Nitroanilin dihasilkan menggunakan amonia dan o-nitroklorobenzena, biasanya dilakukan secara sesuhu dalam reaktor kelompok berjaket pada 175 °C dan 500 psi. Reaktor tersebut mempunyai injap pelepas keselamatan di mana cakera akan pecah apabila tekanan melebihi 700 psi. Trajektori suhu-masa direkodkan dari jam 9:55 pm sehingga 12:18 am seperti yang ditunjukkan dalam Rajah S.2.[c]*



Rajah S.2.[c] Trajektori suhu-masa

[i] *Terangkan profil suhu reaktor dari masa 9:55 pm sehingga 12:00 tengah malam dengan menunjukkan masalah yang mungkin berlaku ketika operasi.*

[ii] *Bilakah reaktor mungkin meletup?*

[iii] *Apakah keadaan yang mungkin wujud yang menyebabkan letupan berlaku?*

[6 markah]

[d] *Penyediaan mangkin tersokong melalui pemendakan-bersama ion-ion logam dengan ion-ion sokongan biasanya menghasilkan satu pencampuran sempurna antara mangkin dan sokongan. Berikan contoh penyediaan mangkin yang menggunakan kaedah ini.* *[4 markah]*

...6/-

3. [a] Define the following terminologies that are commonly used in nitrogen adsorption surface analysis.

[i] Physisorption

[ii] Adsorption isotherm

[iii] Monolayer coverage

[iv] Multilayer coverage

[v] Hysteresis loop

[5 marks]

[b] The thermogravimetric analysis (TGA) and temperature-programmed desorption of ammonia (NH_3-TPD) profiles of 0.1 g of Beta zeolite sample are as shown in Figure Q.3.[b]. Calculate the amount of weak and strong acid sites in mmol NH_3/g_{cat}.

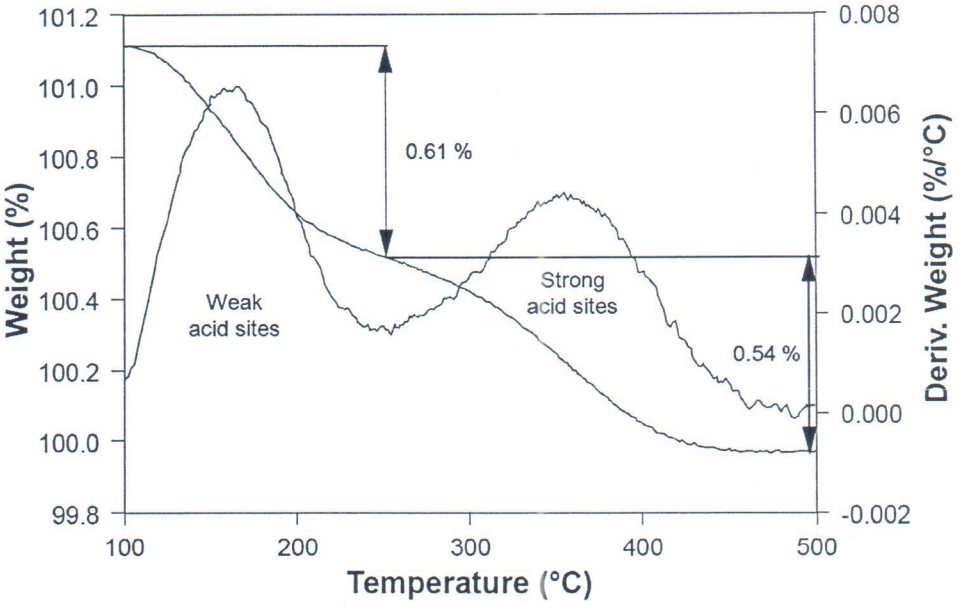


Figure Q.3.[b]

[6 marks]

[c] An instantaneous reaction occurs on the external surface of a non-porous spherical catalyst pellet 1.20 cm in diameter. It is suspended in a large body of dilute liquid reactant A. When the free-system liquid velocity is increased, corresponding increase in the rate of surface reaction is detected which suggests an external mass transfer phenomenon. Calculate the free-system liquid velocity to be used to achieve a reaction rate per unit catalyst surface area of 0.0046 mol/(m^2.s).

3. [a] *Takrifkan istilah-istilah berikut yang biasanya digunakan dalam analisis permukaan berasaskan penjerapan nitrogen.*

[i] Jerapan fizik

[ii] Sesuhu penjerapan

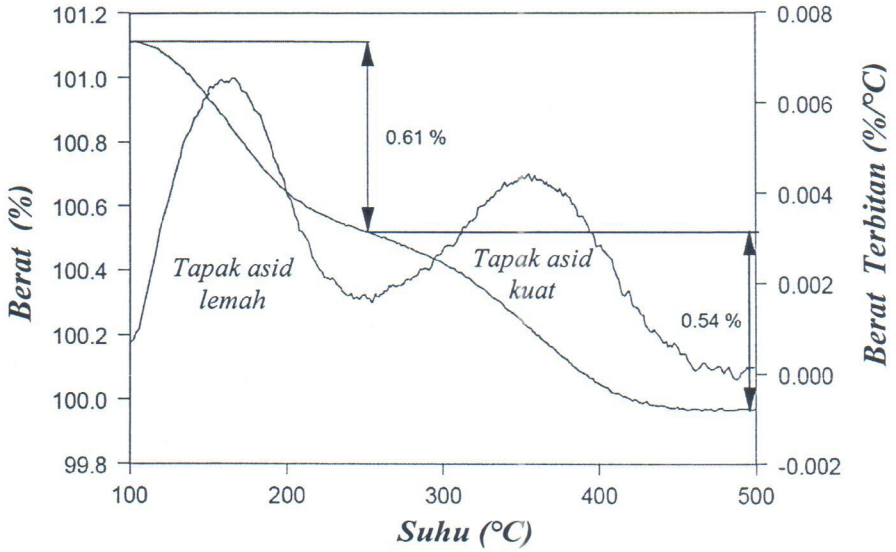
[ii] Liputan ekalapisan

[iv] Liputan berbilang lapis

[v] Gelung histeresis

[5 markah]

[b] *Profil bagi analisis termogravimetri (TGA) dan penjerapan amonia berprogramkan suhu (NH_3-TPD) bagi 0.1 g sampel zeolit Beta diberikan dalam Rajah S.3.[b]. Kirakan amaun tapak asid lemah dan tapak asid kuat dalam unit mmol NH_3/g_{cat}.*



Rajah S.3.[b].

[6 markah]

[c] *Suatu tindakbalas ketika berlaku pada permukaan luar pelet mangkin sfera tak-berliang berdiameter 1.20 sm yang diampaikan dalam suatu bahan tindak balas cecair A. Apabila halaju cecair sistem bebas ditingkatkan, peningkatan yang sepadan dalam kadar tindak balas permukaan dikesan dan ini menunjukkan fenomena pemindahan luar jisim. Kirakan halaju cecair sistem bebas yang perlu digunakan untuk mencapai kadar tindakbalas permukaan per unit luas permukaan mangkin sebanyak 0.0046 mol/(m^2.s).*

Given:

The bulk concentration of the reactant is 1.05 M, kinematic viscosity is 0.62 centistoke (1 centistoke = 10^{-6} m^2/s) and the liquid diffusivity of A is 1.22×10^{-10} m^2/s.

Useful equations;

$$\text{Sh} = \frac{k_c d_p}{D_{AB}},\ \text{Re} = \frac{\rho d_p U}{\mu},\ \text{Sc} = \frac{\nu}{D_{AB}},\ \text{Sh} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3}$$

[6 marks]

[d] Consider a liquid state isomerisation reaction A→ B taking place on the external surface on a non-porous spherical catalyst. The reaction is found to follow a Langmuir-Hinshelwood single-site mechanism and the rate of reaction on the surface can be expressed as

$$-r''_A = \frac{k_c k_r C_A}{k_r + k_c}$$

where $-r''_A$ is the rate of reaction per unit surface area of catalyst, k_c is the mass transfer coefficient, k_r is the reaction rate constant and C_A is the bulk concentration of the reactant A in the reaction system.

Considering two extreme cases in which the reaction system is either strongly mass transfer controlling or kinetic controlling, two corresponding profiles of $-r''_A$ versus free-system liquid velocity (U) are as shown in Figure Q.3.[d];

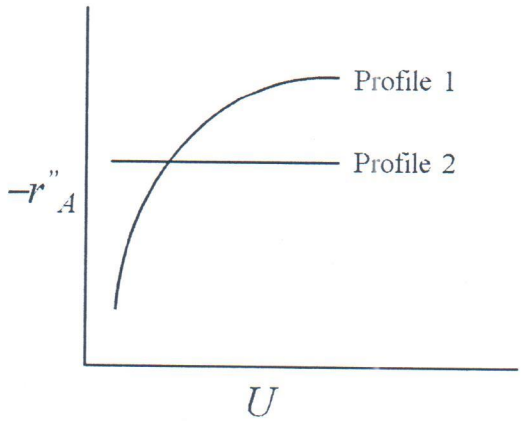


Figure Q.3.[d]

[i] With the help of necessary mathematical derivation, assign each of the two extreme cases to the suitable $-r''_A$ versus U profile.

[ii] In the case of the reaction with profile 2, suggest two measures that can be taken to increase the rate of reaction.

[8 marks]

...9/-

Diberi:

Kepekatan pukal bahan tindakbalas tersebut ialah 1.05 M, kelikatan kinematik ialah 0.62 sentistoke (1 sentistoke = 10^{-6} m^2/s) dan kemeresapan cecair A *ialah 1.22 $\times 10^{-10}$ m^2/s.*

Persamaan-persamaan yang berguna;

$$\mathrm{Sh} = \frac{k_c d_p}{D_{AB}},\ \mathrm{Re} = \frac{\rho d_p U}{\mu},\ \mathrm{Sc} = \frac{\nu}{\mathrm{D_{AB}}},\ \mathrm{Sh} = 2 + 0.6\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}$$

[6 markah]

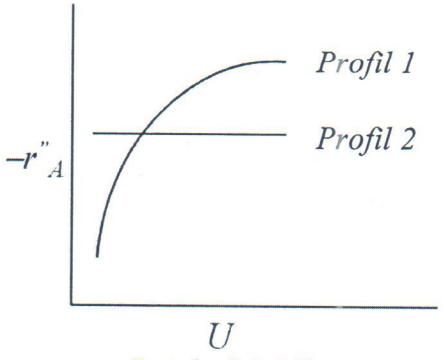
[d] *Pertimbangkan tindakbalas isomerisasi fasa cecair* A→ B *yang berlaku pada permukaan luar suatu mangkin sfera tak-berliang. Tindakbalas tersebut didapati mengikuti mekanisme tapak-tunggal Langmuir-Hinshelwood dan kadar tindakbalas pada permukaan diungkapkan sebagai;*

$$-r''_A = \frac{k_c k_r C_A}{k_r + k_c}$$

di mana,

$-r''_A$ *ialah kadar tindakbalas per unit luas permukaan mangkin,* k_c *ialah pekali pemindahan jisim,* k_r *ialah pemalar kadar tindakbalas,* C_A *ialah kepekatan pukal bahan tindakbalas* A *dalam sistem tindakbalas tersebut.*

Pertimbangkan dua kes lampau di mana tindakbalas tersebut dikawal oleh pemindahan jisim atau kinetik, dua profil bagi $-r''_A$ *melawan halaju cecair sistem bebas* (U) *ditunjukkan dalam Rajah. S.3.[d];*



Rajah. S.3.[d]

[i] *Dengan bantuan terbitan matematik yang sesuai, padankan setiap satu kes lampau tersebut dengan profil* $-r''_A$ *melawan* U *yang sesuai.*

[ii] *Dalam kes tindakbalas dengan profil 2, cadangkan dua langkah yang boleh diambil untuk meningkatkan kadar tindak balas.*

[8 markah]

4. A slurry reactor is used for the hydrogenation of glucose to sorbitol according to the chemical reaction given below

$$\underset{(A)}{H_2\,(g} \longrightarrow \underset{(B)}{l) + C_6H_{12}O_6\,(l)} \longrightarrow C_6H_{14}O_6\,(l)$$

The catalyst employed is a porous Rayney nickel, for which the intrinsic rate of reactions is given by

$$r_B = 2.75\times10^{-6}\, C_A C_B \qquad \text{(mol/kg.s)}$$

Data for the process are given below;

Effective diffusivity of ***A*** in catalyst (D_{eA}):	2×10^{-9} m/s
Catalyst loading in liquid phase (g_L):	500 kg/m^3
Reactor volume (V_R):	2.0 m^3
a_v:	2500 m^2/m^3
ε_g:	0.5
Henry's Law constant of compound ***A*** (H_A):	2.75×10^5 Pa.m^3/mol
Operating pressure:	200 bar
Liquid-side mass transfer coefficient (k_L):	4×10^{-4} m/s
Feed concentration of compound ***B***:	2000 mol/m^3

The following may also be assumed; the flow of gas and liquid in the reactor is well-mixed, negligible gas-film and catalyst external-film mass transfer resistances, pure feed of hydrogen and glucose into the reactor and the reaction proceeds relatively slow with $\gamma < 2.0$.

[a] Write down the material balances describing the process.

[4 marks]

[b] Assuming excess ***B*** in the liquid phase, and spherical catalyst pellet of 5 μm radius, show that the catalyst effectiveness factor is approximately 1.0 for this case.

[7 marks]

[c] Given that a gas phase hydrogen consumption rate of 50 mol/s, calculate the molar flux of hydrogen from the gas to the liquid phase, and the liquid phase hydrogen concentration.

[7 marks]

[d] Calculate the liquid phase concentration and the volumetric flow rate of glucose and its corresponding conversion. Given that the concentration of dissolved hydrogen gas during the reaction is 17.36 mol/m^3.

[7 marks]

4. *Sebuah reaktor buburan digunakan untuk proses penghidrogenan glukosa kepada sorbitol berdasarkan tindak balas kimia di bawah:*

$$\underset{\textbf{(A)}}{H_2\,(g} \longrightarrow \underset{\textbf{(B)}}{l) + C_6H_{12}O_6\,(l)} \longrightarrow C_6H_{14}O_6\,(l)$$

Pemangkin yang digunakan ialah nikel Rayney berliang yang mana kadar berliang tindak balas hakiki diberikan oleh;

$$r_B = 2.75\times10^{-6}\, C_A C_B \qquad (mol/kg.s)$$

Data bagi proses tersebut diberikan seperti berikut;

Resapan berkesan bagi komponen **A** *dalam pemangkin* (D_{eA})*:*	2×10^{-9} *m/s*
Beban pemangkin pada fasa cecair (g_L)*:*	$500\ kg/m^3$
Isipadu reaktor (V_R)*:*	$2.0\ m^3$
a_v:	$2500\ m^2/m^3$
ε_g:	0.5
Pekali Hukum Henry bagi sebatian **A** (H_A)*:*	$2.75\times10^5\ Pa.m^3/mol$
Tekanan operasi:	200 *bar*
Pekali pemindahan jisim sebelah cecair (k_L)*:*	4×10^{-4} *m/s*
Kepekatan suapan bagi sebatian **B***:*	$2000\ mol/m^3$

Anggapan-anggapan berikut boleh digunakan; aliran gas dan cecair dalam reaktor diaduk dengan sekata; filem gas dan filem luaran rintangan pemindahan jisim pemangkin boleh diabaikan, suapan gas hidrogen dan glukosa tulen ke dalam reaktor dan tindak balas berjalan secara lambat dengan $\gamma < 2.0$.

[a] Tuliskan imbangan jisim bagi menerangkan proses ini.

[4 markah]

[b] Dengan menganggap lebihan **B** *pada fasa cecair dan pelet pemangkin sfera dengan jejari 5 μm, tunjukkan bahawa faktor pemangkin berkesan adalah lebih kurang 1.0 bagi kes ini.*

[7 markah]

[c] Diberikan bahawa kadar penggunaan hidrogen pada fasa gas adalah 50 mol/s, kirakan fluks kemolaran bagi hidrogen dari fasa gas kepada fasa cecair dan kepekatan hidrogen pada fasa cecair.

[7 markah]

[d] Kirakan kepekatan fasa cecair dan halaju aliran isipadu glukosa dan penukarannya yang sepadan. Diberi bahawa kepekatan gas hidrogen terlarut semasa tindak balas berlaku adalah 17.36 mol/m^3.

[7 markah]