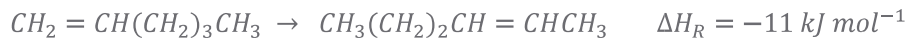


1. BACKGROUND

Negative environmental consequences of fossil fuels and concerns about petroleum supplies have spurred the search for second-generation biofuels. To be a viable alternative, these biofuels must have environmental benefits, be economically competitive, and have the same (or even better) quality as the fuels they are to replace. For example, hydrocarbon olefins available from pyrolysis of waste wood can be catalytically isomerized to yield olefins having more desirable physical or chemical properties or more similar characteristics to current motor fuels. Olefin isomerization may be used to supply high-octane motor fuel for which the lowerboiling olefins are especially useful, or to supply branched-chain hydrocarbons for subsequent hydrogenation to yield high-octane paraffins for sustainable aviation fuels (SAF).

The purpose of this investigation is to test a newly developed catalyst for the isomerization of light olefins in a bubbling fluidised bed reactor operated at 500 °C and atmospheric pressure. The fluid fed to the reactor is a gaseous mixture containing 20 vol% of 1-hexene (C₆H₁₂) in inert nitrogen (N₂, 80 vol%). In the reactor, 1-hexene converts into 2-hexene according to the reaction:



The chosen catalyst particles are spherical, with particle density 2700 kg m⁻³ and in the size range of 350-1000 µm, as indicated in the particle size distribution in Table Q.1. The solid fraction of the bed at rest (no flow of gas) is equal to 0.55.

Table Q.1: Particle Size Distribution (of a 120 g sample)

Size range (µm)	Mass (g)
350-400	1
400-450	2.5
450-500	4.1
500-550	5.1
550-600	5.3
600-650	8.5
650-700	15.1
700-750	25.6
750-800	20.5
800-850	17.6
850-900	6.1
900-950	5.4
950-1000	3.2

2. REACTOR CHARACTERISTICS

- a) Determine the Sauter mean diameter of the catalysts particles and classify them according to Geldart classification.

[3]

- b) During operation, the reactor is operated at 4 times the minimum fluidization velocity. Demonstrate that, at this velocity, the reactor behaves like a bubbling fluidized bed, and estimate the fraction of catalyst particles that are carried upwards with the product gas leaving the reactor.

[7]

3. REACTOR OPERATION

- c) Using the two-phase theory, we can model the isomerization reactor as shown in Figure Q.3. The meaning of the symbols adopted and the values of some of them are reported in Table Q.3. Explain using entirely your own words what the two-phase theory states and discuss the assumptions on which the two-phase theory of Toomey & Johnstone is based.

[3]

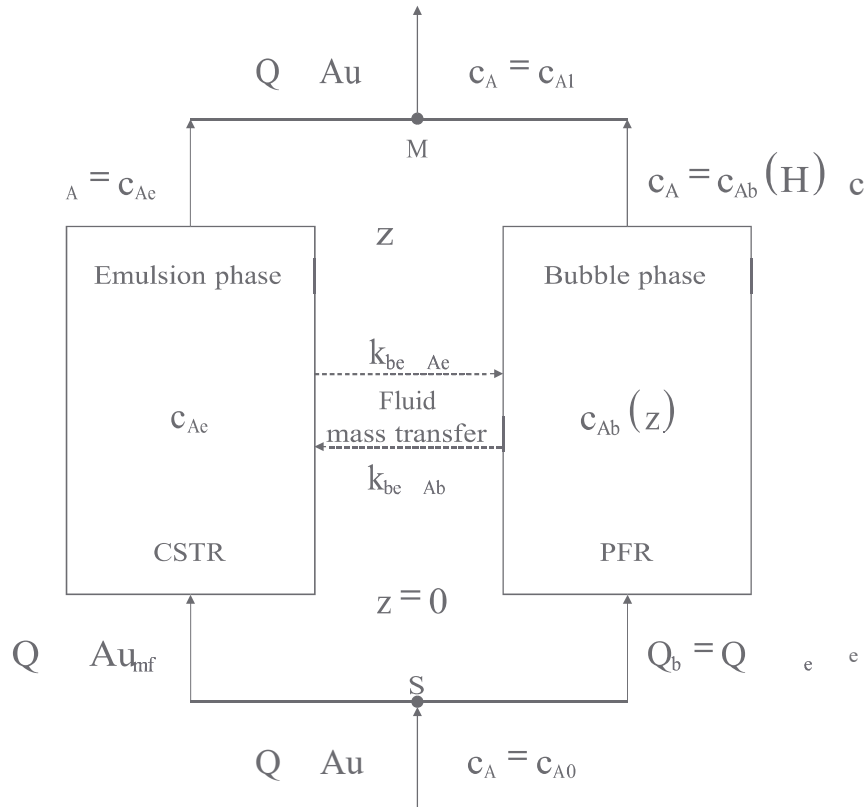


Figure Q.3: Schematic block diagram of the bubbling fluidized bed combustor.

- d) Draw the concentration profiles of 1-hexene in the radial direction within the catalyst particle for: i) a very active catalyst and ii) a nearly inactive catalyst. Comment on the shape of the concentration profiles.

[4]

- e) When very active catalysts are used, the catalyst pellets are often prepared by depositing the expansive catalytic material in a thin layer on the outside of the pellet surface. Explain the reason for this.

[3]

- f) The number of moles of 1-hexene per unit time can be calculated $W_c = 4\pi r_c^2 k_e^s c_{Ae}$ that convert in one catalyst particle using the relationship: , where the subscript A refers to the reactant, 1-hexene. Prove that:

$$k_e^s = \left[\frac{1}{k_c^s} + \frac{3}{r_c \sigma k_s \eta_A} \right]^{-1}$$

Report all the steps in your derivation.

[4]

g) Calculate the external mass transfer resistance related to the flow of 1-hexene from the bulk of the emulsion phase to the outer surface of the particles.

[4]

h) Assuming that the internal mass transfer resistance is negligible compared to the external one, calculate the value of c_{Ae} , i.e. of the concentration of 1-hexene in the emulsion phase of the fluidized bed.

[10]

i) Calculate the value of c_{A1} , i.e. of the concentration of 1-hexene at the outlet of the fluidized bed reactor.

[2]

4. DESIGN & OPERATIONAL CHANGES

j) Due to the mild exothermicity of the reaction, a heat exchange system would be required to maintain isothermal conditions during prolonged operation. Estimate the heat transfer coefficient h on a vertical exchanger surface immersed in the reactor during normal operation.

[5]

k) A number of electrically heated tubes of constant temperature 150 °C are available to be used as heat exchanging surface. Each tube has 10mm external diameter and 2m length. Estimate the number of tubes that would be needed to operate the isomerization reactor at constant temperature of 500 °C.

[10]

l) Repeat calculations for questions g), h), i), j), and k) using 4 different superficial velocities of your choice, at which the reactor would still operate at bubbling regime.

Discuss the above results and explain what the effect of gas superficial velocity is on the operation of the isomerization reactor, both from a hydrodynamic and chemical reaction perspectives.

Finally, state if you would run the reactor at a specific velocity, and explain why you would do so.

[35]

USEFUL FORMULAS

Bubble frequency
$$n_w = \left(0.52 \left(\frac{d_b}{D} \right)^{1.48} + 0.05 u_b^{-4.4} d_b \right)^{-1}$$

Bubble size at height z
$$d_{b(z)} = \frac{0.54}{g^{0.2}} (u_o - u_{mf})^{0.4} (z + 4N_{or}^{-0.5})^{0.8}$$

Table Q.3: Notation and numerical values.

A	area of the cross-section of the cylindrical reactor	m^2
D	diameter of the cross-section of the cylindrical reactor	0.5 m
c_A	molar density of 1-hexene in the mixture	mol m^{-3}
c_{A0}	molar density of 1-hexene at the reactor inlet	mol m^{-3}
c_{A1}	molar density of 1-hexene at the reactor outlet	mol m^{-3}
c_{Ae}	molar density of 1-hexene in the bulk of the emulsion phase	mol m^{-3}
c_{Ab}	molar density of 1-hexene in the bubble phase	mol m^{-3}
D_A	molecular diffusivity of 1-hexene in the gaseous mixture	$3.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$
H	expanded bed height	1.5 m (at $4 u_{mf}$)
k_{be}	mass transfer coefficient per unit bubble volume between emulsion and bubble phases	s^{-1}
k_e^c	external mass transfer coefficient	m s^{-1}
k_e^s	effective reaction kinetic constant that refers to the catalyst particle outer surface	m s^{-1}
Q	volume flow rate of fluid entering the reactor	$\text{m}^3 \text{ s}^{-1}$
Q_b	volume flow rate of fluid through the bubble phase	$\text{m}^3 \text{ s}^{-1}$
Q_e	volume flow rate of fluid through the emulsion phase	$\text{m}^3 \text{ s}^{-1}$
r_c	radius of the catalyst particle	m
u	superficial fluid velocity	m s^{-1}
u_{mf}	minimum fluidization velocity	m s^{-1}
W_c	number of moles of 1-hexene converting in one catalyst particle per unit time	mol s^{-1}
z	axial coordinate along the reactor	m
ε_{mf}	volume fraction of fluid at minimum fluidization	-
η_A	effectiveness factor of the catalyst particle	-
μ	fluid viscosity	$5.0 \times 10^{-5} \text{ Pa s}$
ρ	fluid density	kg m^{-3}
ρ_c	catalyst particle density	2700 kg m^{-3}
σk_s	pore catalyst surface per particle unit volume (σ) multiplied by the intrinsic kinetic constant (k_s) of the 1-hexene reaction	s^{-1}
ΔH_R	Heat of reaction	kJ mol^{-1}
h	Bed-to-Surface heat transfer coefficient	$\text{W m}^{-2} \text{ K}^{-1}$
N_{or}	Number of orifices in distributor plate	20
d_b	Mean bubble diameter	m
u_b	Mean bubble velocity	m s^{-1}
n_w	Bubble frequency	s^{-1}
C_{ps}	Catalyst specific heat capacity	$828 \text{ J kg}^{-1} \text{ K}^{-1}$
k_s	Catalyst thermal conductivity	$1.20 \text{ W m}^{-1} \text{ K}^{-1}$
C_{pg}	Gas mixture specific heat capacity	$1050 \text{ J kg}^{-1} \text{ K}^{-1}$
k_g	Gas mixture thermal conductivity	$0.07 \text{ W m}^{-1} \text{ K}^{-1}$

PART 2 – Design of Industrial Crystallization

List and explain the main factors that determine the crystal size distribution (CSD) from a continuous well-mixed crystallizer.

Show, with the aid of an information-flow diagram, how a change in one of such factors affects the others.

Finally, propose the main design and operation principles for two-different crystallisers containing aqueous solutions of potassium nitrate (KNO_3) and sodium chloride (NaCl), respectively.

Clearly describe the differences in the two cases, and justify your choices.

[10]