Design of a Fixed-Bed Reactor for Dehydration of Butanediol to Butadiene and Methyl Ethyl Ketone

A PROJECT REPORT
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BONAFIDE CERTIFICATE

Certified that this Design Project IV report titled "**Design of a Fixed-Bed Reactor for Dehydration of 2,3-Butanediol to 1,3-Butadiene and Methyl Ethyl Ketone**" is the bonafide work of "" who carried out the project work under my supervision. Certified further that to the best of my knowledge the work reported here does not form part of any other project / research work on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

SIGNATURE

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INTERNAL EXAMINER **EXTERNAL EXAMINER**

The Design Project Viva-Voce Examination is held on ___________________

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ABSTRACT

The dehydration of 2,3-Butanediol (2,3-BDO) to 1,3-Butadiene (1,3-BD) and Methyl Ethyl Ketone (MEK) over an amorphous calcium phosphate catalyst in a fixed-bed reactor. The rate equation of a Fixed bed reactor for Dehydration of Butanediol to Butadiene and Methyl Ethyl Ketone is determined. The external surface area of the catalyst particle required for the Dehydration of Butanediol to Butadiene and Methyl Ethyl Ketone is evaluated.

INTRODUCTION

2,3-Butanediol has been considered as a potential intermediate for the production of hydrocarbons including Butadiene and methyl ethyl ketone because 2,3-Butanediol can be produced through bio-fermentation using various biomasses, synthetic gases (syngas) from coal gasification, and industrial gas waste as feedstock.

Research on the dehydration of 2,3-Butanediol to 1,3-Butadiene and methyl ethyl ketone using various catalysts has been conducted by several research group.The catalysts are bentonite clay, metal and earth oxides, zeolites , a perfluorinated resin with sulfonic acid groups, heteropolyacids, calcium phosphates, Cs/SiO2, sodium phosphates and so on.

Recently, reaction kinetics and a deactivation model of the dehydration of 2,3-Butanediol to 1,3- Butadiene and methyl ethyl ketone over a-CP catalyst were proposed.In addition, a process design for the recovery of 1,3- Butadiene and methyl ethyl ketone from Butanediol-dehydration products, which were obtained from lab-scale experiments, was proposed as a conceptual design for the industrial scale.

REVIEW OF LITERATURE

2,3-BDO has been considered as a potential intermediate for the production of hydrocarbons including 1,3-BD and MEK because 2,3-BDO can be produced through bio-fermentation using various biomasses, synthetic gases (syngas) from coal gasification, and industrial gas waste as feedstock observed by Daniell et al. (2012), Kopke et al. (2011) and Zheng et al. (2015).

Research on the dehydration of 2,3-BDO to 1,3-BD and MEK using various catalysts hasbeen conducted by several research group since the 1940s. The catalysts are bentonite clay,metal and earth oxides, zeolites, a perfluorinated resin with sulfonic acid group,heteropolyacids, calcium phosphates, Cs/SiO2, sodium phosphates investigated byKim et al. (2014),Nikitina et al. (2016) and Song et al. (2017).

Recently, reaction kinetics and a deactivation model of the dehydration of 2,3-BDO to 1,3-BD and MEK over a-CP catalyst were proposed. In addition, a process design for the recovery of 1,3-BD and MEK from BDO-dehydration products, which were obtained from lab-scale experiments, was proposed as a conceptual design for the industrial scale validated by Song et al. (2017).

A solid acid catalyst consisted of sulfonic groups covalently bound to an inorganic matrice was developed to dehydrate 2,3-butanediol into methyl ethyl ketone. The strategy of maintaining constant degree of dehydration was employed to lengthen the lifetime of catalyst proposed by Robert et al. (1987).

The catalytic activity of Al- and Zr-containing BEA zeolites and an alumina-based catalyst in 2,3-butanediol dehydration has been investigated. It has been shown that the presence of Bronsted or Lewis sites leads to the selective formation of MEK . Various acid systems (metal oxides, heteropoly acids, zeolites, etc.) can serve as a dehydration catalysts. Under milder conditions, the main product of 2,3-butanediol dehydration is MEK observed byTorok et al. (1996), Lee et al. (2000), Duan et al. (2015).

The purpose of this work is, therefore, to determine the rate of reaction and the external surface area of the catalyst particle forthe dehydration of 2,3-Butanediol to 1,3- Butadiene and methyl ethyl ketone over a Calcium phospate catalyst, using a fixed-bed reactor.

OBJECTIVE

- To determine the rate equation of a Fixed bed reactor for Dehydration of Butanediol to Butadiene and Methyl Ethyl Ketone .

- To analyse the external surface area of the catalyst particlefor the Dehydration of Butanediol to Butadiene and Methyl Ethyl Ketone .

METHODOLOGY

Figure 1 illustrates a schematic drawing of the reaction system used for the dehydration of 2,3-BDO. 2,3-BDO including 1.45% water was fed to the reactor by an HPLC pump (P1) to a ceramic fiber heater (CFH1) and N_2 as a carrier gas was fed through a line heater (LE1) to raise it to the reaction temperature by a mass flow meter (MFM). 2,3-BDO reached the reaction temperature by passing through three ceramic fiber heaters (CFH1-3).The heated mixture of 2,3-BDO and N_2 was fed to one of two reactors (R1&R2) through a line mixer and the temperature of the reactors was maintained by electric heaters around R1 and R2. The product of the reactor was cooled by a cooler (HE1).

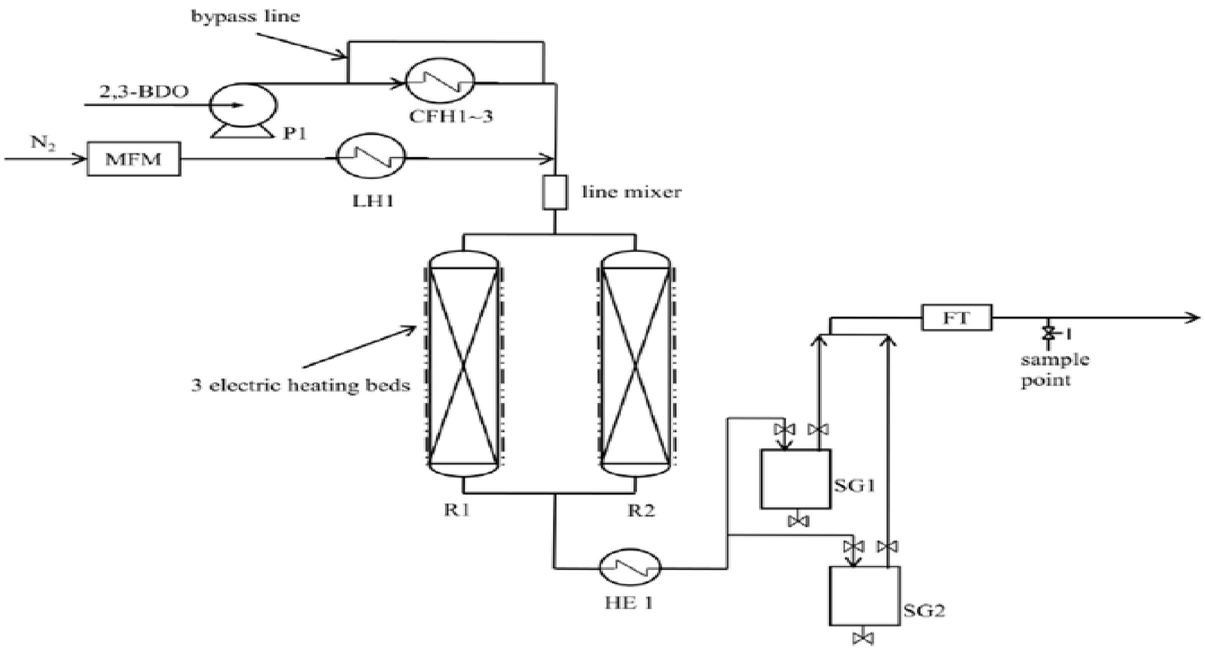

Figure 1: Schematic of the reaction system for the dehydration of 2,3-BDO.(Song et al. 2018)

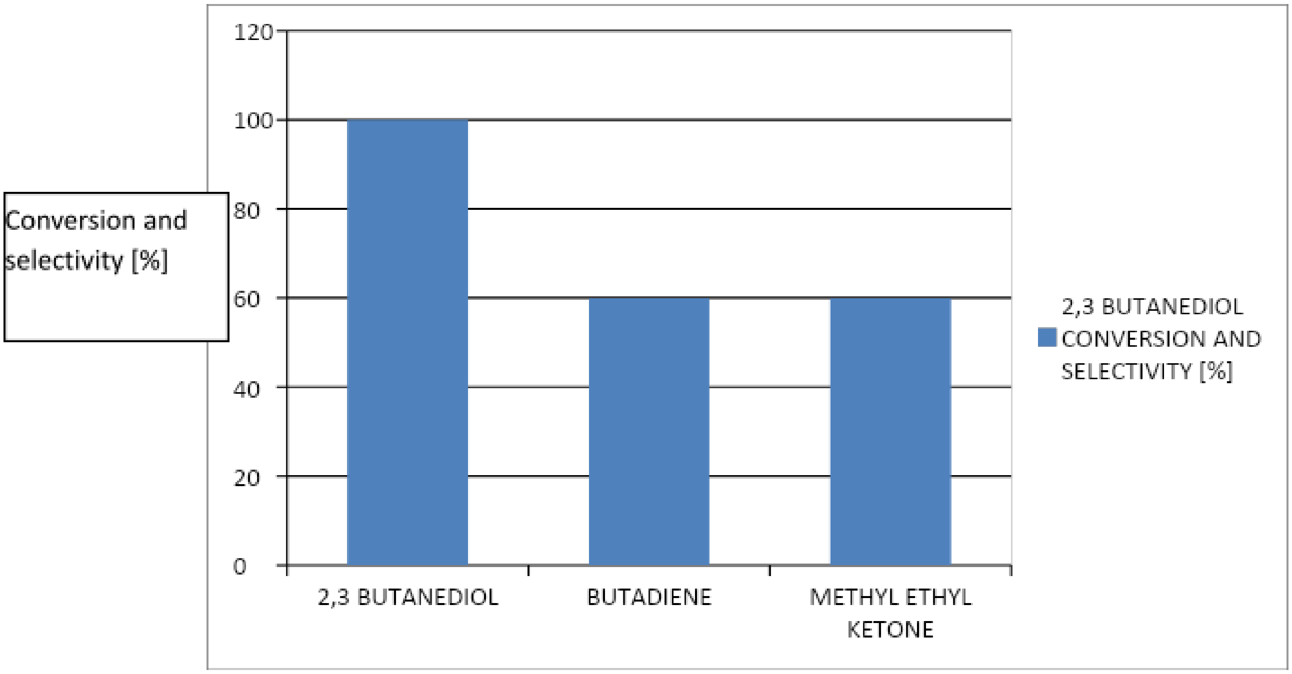

Figure 2: Conversion and Selectivity of Butanediol and Methyl Ethyl Ketone.(Song et al. 2018)

RESULTS

The reaction kinetics of the dehydration of 2,3 Butanediol to 1,3-Butadiene and Methyl Ethyl Ketone using a Calcium Phosphate as a catalyst, were used for the reactor model.

$$C_4H_{10}O_2\, r1 \rightarrow C_4H_8O + H_2O, \Delta H_{r1} =- 21,675 \frac{J}{mol}$$

$$C_4H_8O\, r2 \rightarrow C_4H_6 + H_2O, \Delta H_{r2} = 129,579 \frac{J}{mol}$$

$$C_4H_{10}O_2\, r3 \rightarrow C_4H_8O + H_2O, \Delta H_{r3} = 1,482 \frac{J}{mol}$$

$$C_4H_{10}O_2\, r4 \rightarrow C_4H_8O + H_2O, \Delta H_{r4} = 24,682 \frac{J}{mol}$$

The reaction rates based on the power law are

$$r_i = K_i C_{react,i}^{ni}$$

$$C_j = \frac{P_j}{RT}$$

$$K_i = \left[K_{T_{ref,i}} \times exp\left(\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)\right]$$

where (i) is the number of reaction, r is the reaction rate, react is the reactant, C is the mole concentration, n is the reaction order, j is the number of species, P is the pressure, R is the ideal gas law constant, T is the temperature in bulk gas phase, k is the reaction rate constant, k_{Tref} is the transformed adsorption pre-exponential factor, E is the activation energy and T_{ref} is the reference temperature.

Data taken from Song et al. (2018)

Gas constant, R=8.314$\frac{m^3 atm}{molK}$

Temperature, T=603.15K

$Referencetemperature, T_{ref} = 298.15K$

$Rateconstant,\ K_{T_{ref,1}} = 7.45 \times 10^{-4}$**$S^{-1}$**

$Activationenergy,\ E_1 = 2.33 \times 10^5$ **J/mol**

Mass flow rate, V=80g/h

Density, ρ_p=460Kg/m^3

Diameter of the catalyst particle, d_p=2.855×10^{-3}m

$$C_j = \frac{P_j}{RT} = \frac{1}{8.314\times10^{-5}\times603.15} = 19.94\frac{mol}{m^3}$$

$$K_i = \left[K_{T_{ref,i}}\times exp\left(\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)\right]$$

K_1=[7.45×10^{-4}]exp$\left[\frac{-2.33\times10^5}{8.314}\left(\frac{1}{603.15} - \frac{1}{298.15}\right)\right]$

K_1=7.45×10^{-4} exp[4.39×10^{20}]

K_1=3.27×$10^{17}$$S^{-1}$

$$r_i = K_i C_{react,i}^{ni}$$

r_1=3.27×10^{17}(19.94)

Rate of the reaction,r_1=6.52×10^{18}mol/m^3 s

$$S_g = \frac{6}{\rho_p d_p}$$

$$S_g = \frac{6}{460\times2.855\times10^{-3}}$$

Surface area per gram of particle, S_g=4.57$\frac{m^2}{Kg}$

DISCUSSIONS

The graph shows the conversion and selectivity of the major products .Graph also represents good performance of the model for the prediction of 2,3-BDO conversion and selectivity of the target products, 1,3-BD and MEK, at the outlet of the catalyst bed.From the theoretical data for pilot-scale reactor, the rate of reaction and the external surface area of the catalyst particlefor industrial scale reactor is evaluated.The rate of the reaction is calculated as **$r_1=6.52\times10^{18}$mol/m^3 s** and **Surface area per gram of particle, $S_g=4.57\frac{m}{Kg}^2$.**

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