MODELING OF REACTIVE DISTILATION FOR ACETIC ACID ESTERIFICATION

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DECLARATION

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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The above candidate has carried out research for the Master's thesis under my supervision.

Signature of the supervisor: Date

DEDICATION

I dedicate this thesis and to my mother who has brought me thus far on her shoulders and to my husband supporting in every way in my life.

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ABSTRACT

Reactive distillation is the combination of unit operations reactor and distillation column into one unit. Reactive distillation offers higher conversions, reacting away azeotropes , heat integration, product selectivity and significant capital saving. Reactive distillation is industrially applied for many reactions. Equilibrium and non-equilibrium models are commonly used for modeling of reactive distillation. The equations used for modeling are called MESH equations. M-material E-equilibrium S-summation H-enthalpy. The model equations were developed for a reactive distillation unit consisting of a batch reactor and one stage distillation unit. The model was applied in an ethanol and acetic acid esterification reaction considering homogeneous and heterogeneous reaction kinetics. Nineteen modelling equations were developed with 22 variables and three variables being specified. The differential equations were converted into algebraic equations by applying forward Euler method. Bubble point program is used to find equilibrium vapour composition and temperature. The initial composition of the reactor and the condenser as 45% acetic acid 45% ethanol,1% water. The holdups are assumed as 5000moles and 100moles respectively. Simulations for solving of algebraic equations and bubble point temperature calculation were developed in matlab environment. Simulation results were observed for different 0.825 to 0.99L0/V1 ratios. Dynamics of reactor and condenser compositions and ethyl acetate purity in the accumulated distillate were simulated for different L0/V1 ratios. Maximum ethyl acetate percentage in the accumulated distillate increases with increase in L0/V1 ratio. The dynamics of reactor temperature and conversion of acetic acid show high conversions of acetic acid in higher reflux ratios. Further the reactor heat load and batch time also increase with increase in L0over V1 ratio. Average production rate reduces with increasing L0/V1 ratio. The simulation was also done for heterogeneous reaction kinetics using Langmiur-Hinshelwood kinetic model. The variation of condenser composition, ethyl acetate percentage in the accumulated distillate, dynamics of reactor temperature and conversion of acetic acid were studied with time. Modelled results show that increase in theL0/V1 ratio increase the reactor batch time, although no variation in the average production rate is observed.

Key words: Reactive distillation, modelling, Simulation, Esterification , ethyl acetate

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LIST OF ABBREVIATIONS

Abbreviation	Description
DAE	differential-algebraic equations
EQ	equilibrium
MeOH	methanol
EAc	ethyl acetate
AcOH	acetic acid
MS	Maxwell Stefan
MTBE	methyl tert-butyl ether
NEQ	non-equilibrium
RD	reactive distillation
TAME	tertiary amyl ether

NOTATIONS

A	molar holdup(mol)
D	distillate flow rate(mol/s)
V	vapor flow rate (mol/s)
v	volume of liquid
L_0	Liquid flow rate (mol/s)
r	rate of reaction($mol/m^3.s$)
x_i	mol fraction of i^{th} component in the liquid phase
y_i	mol fraction of i^{th} component in the vapor phase

Q_0	heat duty on condenser-reflux drum(J/s)
Q_1	heat duty on reboiler(J/s)
ΔH_r	heat of reaction (J/mol)
H_v	Vapor enthalpy (J/mol)
H_L	Liquid enthalpy (J/mol)
P	pressure(N/m^2)
N_i	moles of i^{th} component formed
c	Number of components
P^{sat}_i	Saturation temperature of component i(N/m^2)
i	component number
C_i	concentration of i^{th} component
a	interfacial area, m^2
c	number of components, dimensionless
$\mathcal{D}_{i,k}$	Maxwell-Stefan diffusivity, $m^2\ s^{-1}$
E	energy flux, Wm^{-2}
$\mathbb{E}$	Energy transfer rate, $J\ s^{-1}$
FV	vapor feed stream, $mo\ l\ s^{-1}$
FL	liquid feed stream, $mo\ l\ s^{-1}$
f	component feed stream, $mo\ l\ s^{-1}$
h	heat transfer coefficient, $Wm^{-2}\ K^{-1}$
H	molar enthalpy, $J\ mol^{-1}$

k_1	pseudo-first-order reaction rate constant, s^{-1}
K	vapor liquid equilibrium constant, dimensionless
L	liquid flow rate, mo l s^{-1}
Ni	molar flux of species i, mol m^{-2} s^{-1}
ℕ	Mass transfer rate, mo l s^{-1}
Q	heat duty, J s^{-1}
r	number of reactions, dimensionless
rj	ratio of side stream flow to inter stage flow on stage j, dimensionless
Rm,j	reaction rate, mol m^{-3} s^{-1}
R	gas constant, J mo l^{-1} K^{-1}
t	time, s
T	temperature, K
U	molar hold-up, mol
V	vapor flow rate, mo l s^{-1}
x	mole fraction in the liquid- phase, dimensionless
y	mole fraction in the vapor-phase, dimensionless

GREEK LETTERS

ε	reaction volume, m^3
κ	mass transfer coefficient, m s^{-1}
μ	chemical potential, J mol^{-1}
η	distance along diffusion path, dimensionless

SUBSCRIPTS

i	component index
I	referring to interface
j	stage index
k	alternative component index
m	reaction index

SUPERSCRIPTS

F	referring to feed stream
L	referring to liquid-phase
V	referring to vapor- phase