CFD MODELING OF A BUBBLE COLUMN REACTOR FOR THE PRODUCTION OF LINEAR ALPHA OLEFINS

By
Adil Ali Mohammed Alhussein

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
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Title of Thesis : CFD MODELING OF A BUBBLE COLUMN REACTOR FOR THE PRODUCTION OF LINEAR ALPHA OLEFINS

Key Words: Linear α-olefins, petrochemical synthesis, kinetic model, Computational Fluid Dynamics, oligomerization

Summary :

Linear α-olefins (LAOs) have found wide applications in various areas of petrochemical synthesis including the co-monomer for linear low density polyethylene (LLDPE) and the generation of plasticizers, detergents, surfactants, and lubricants. The purpose of this thesis is to develop a kinetic model and Computational Fluid Dynamics (CFD) model for bubble column reactor for the oligomerization of ethylene to LAOs. The development of such model helps in the study of the behavior of industrial LAOs reactors, as well as in the optimization of their operation. The connection between the reaction kinetics and fluid dynamics can add a real depth and provide a great understanding to industrial LAOs reactor. In addition, the kinetic model has been used in the simulation of falling film column to understanding the specifics of the absorption/reaction process for this reaction.

Three main studies have been performed. The first is the development of a kinetic model of the oligomerization of ethylene to LAOs for zirconium/aluminum and nickel/zinc catalyst systems. The second is the simulation of the oligomerization reaction of ethylene in industrial bubble column reactor for isothermal and non-isothermal operation. Finally, the third is the simulation of the oligomerization reaction of ethylene in a falling film column.In the first study, the kinetic model has been developed based on a four-step mechanism: site activation, initiation and propagation, chain transfer and site deactivation. The values of the kinetic parameters have been obtained for the developed kinetic models for two catalyst systems: zirconium/aluminum- and nickel/zinc-based catalysts systems. The performance of the model with the estimated parameters has been tested against the experimental data. The proposed kinetic model can predict the product distribution for the zirconium/aluminum catalyst system with suitable accuracy. In addition, the model can predict the product distribution for the nickel/zinc catalyst system with good accuracy for all products.

The second study is the development of a Computational Fluid Dynamics (CFD) model for industrial bubble column reactor for both isothermal and non-isothermal operation, using COMSOL Multiphysics software. The concentration profiles of the LAOs products butene and hexane have been simulated. In addition, the volume fraction of the gas phase along the height in 2D for both isothermal and non-isothermal operation and the temperature profile for non-isothermal operation have been investigated. The results show that the concentration profile for the non-isothermal operation is higher than isothermal operation. In addition, the volume fraction of gas phase decrease, while the volume fraction of liquid phase increase in both cases. Moreover, the effect of height, diameter, temperature, and liquid flow rate on the LAOs products have been investigated. In the third study, the COMSOL Mutiphysics software has been used to simulate the mass transfer with chemical reaction in the falling film absorption process. The results show that the concentration profile of the absorption of the products through falling thickness at different time. The effects of liquid film thickness, catalyst concentration, catalyst /co-catalyst ratio, and temperature have been studied. From the results, an increase in temperature lead to an increase in the C4-C10 oligomer concentrations and a decrease in heavy LAOs products. An increase in catalyst concentration leads to an increase in the concentration of C4, C6 and C8, while for the heavy product of C12-C20, the concentration decreases up to a limiting value. The increase in co-catalyst /catalyst ratio lead to an increase in the concentration of C4 and C6, while for the heavy products of C12-C20, the concentration decreases up to a limiting value. Finally, as the liquid film thickness increases, the concentration of C4 increases.

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I dedicate this thesis to all my friends around the world.

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Nomenclature

A	Pre-exponential factor
c	concentration of the species, mol/m^3
c^*	concentration of ethylene at equilibrium, mole/liter
C_{CAT}	catalyst concentration, mol/liter
C_{CAT}^k	active catalyst concentration, mol/liter
$C_{CAT^k.M}$	complex active catalyst/ethylene concentration, mol/liter
C_{decy}	moles of deactivated catalysts , mol
C_M	concentration of ethylene monomer, mole/liter
C_M^k	concentration of active ethylene monomer, mole/liter
$C_{M^k.TEA}$	concentration of complex active ethylene monomer/co- catalyst, mole/liter
C_{P_0}	concentration of active site, mole/liter
C_{P_i}	concentration of living polymers, mole/liter
$C_{P_i^k}$	concentration of active living polymers, mole/liter
$C_{P_i^k.TEA}$	concentration of complex active living polymers/ co-catalyst, mole/liter
C_{TEA}	co-catalyst concentration, mole/liter
C_{TEA}^k	active co-catalyst concentration, mole/liter
$C_{TEA^k.CAT}$	complex active co-catalyst/ catalyst concentration, mole/liter
$C_{TEA_1^k.CAT}$	complex active co-catalyst/ catalyst concentration- catalyst, mole/liter
C_μ	model constant
$C_{\varepsilon 1}$	model constant
$C_{\varepsilon 2}$	model constant

D	diffusion coefficient, m^2/s
De	moles of dead polymer, mol
D	moles of dead oligomer, mol
E	activation energy, cal/mol
F	volume force, N/m^3
g	gravity (m/s^2)
h	Film thickness, mm
k_1	rate constant of active site
k_2	rate constant of chain initiation
k_3	rate constant of chain propagation
k_4	rate constant of chain transfer
k_5	rate constant of deactivation
k_{+1}	rate constant of attachment of the catalyst in the site activation
k_{-1}	rate constant of detachment of the catalyst in the site activation
k_{+2}	rate constant of attachment of the monomer in the site activation
k_{-2}	rate constant of detachment of the monomer in the site activation
k_{+4}	rate constant of attachment in the chain propagation reaction
k_{-4}	rate constant of detachment in the chain propagation reaction
k_{+5}	rate constant of attachment in the chain transfer reaction
k_{-5}	rate constant of detachment in the chain transfer reaction
$k_c^{'}$	rate constant of the first reaction of co-catalyst in the site activation
$k_c^{''}$	rate constant of the second reaction of co-catalyst in the site activation
K_A	equilibrium constant of the catalyst in the site activation
K_B	equilibrium constant of the monomer in the site activation

K_C	equilibrium constant of the co-catalyst in the site activation
K_D	equilibrium constant in the chain propagation reaction
K_E	equilibrium constant in the chain transfer reaction
M	ethylene monomer
M^k	active ethylene monomer
mgl	mass transfer rate from gas to liquid (kg/(m^3·s))
P	concentration of living polymers, mole/liter
p	pressure, Pa
P_i	Living oligomers
P_i^k	Active living oligomers
P_0	Active site
R	gas constant, mol/cal K
ri	reaction rate for species, mol/(m^3·s)
T	temperature, K
Tr	reference temperature, K
u	velocity, m/s
v	volume, liter

Greek Letters

α	alpha position
σ_k	model constant
σ_ε	model constant
ε	dissipation rate of turbulent energy, (m/s^3)
ρ	Density, kg/m^3
ϕ	phase volume fraction, dimensionless
μ_l	dynamic viscosity of the liquid, Pa. s

μ_T	turbulent viscosity, Pa. s

Subscripts

c	calculated mole fractions of product
e	experimental mole fractions of product
CAT	catalyst
CAT^k	active catalyst
TEA	co-catalyst
TEA^k	active co-catalyst
l	quantities related to the liquid phase
g	quantities related to the gas phase