



# **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  
Chemical Engineering

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**Title of Thesis :** CFD MODELING OF A BUBBLE COLUMN REACTOR FOR THE PRODUCTION OF LINEAR ALPHA OLEFINS

**Key Words:** Linear  $\alpha$ -olefins, petrochemical synthesis, kinetic model, Computational Fluid Dynamics, oligomerization

### Summary :

Linear  $\alpha$ -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 Multiphysics 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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## Nomenclature

$A$	Pre-exponential factor
$c$	concentration of the species, mol/m <sup>3</sup>
$c^*$	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
$C_\mu$	model constant
$C_{\varepsilon 1}$	model constant
$C_{\varepsilon 2}$	model constant

D	diffusion coefficient, m <sup>2</sup> /s
De	moles of dead polymer, mol
D	moles of dead oligomer, mol
E	activation energy, cal/mol
F	volume force, N/m <sup>3</sup>
g	gravity ( m/s <sup>2</sup> )
h	Film thickness, mm
k <sub>1</sub>	rate constant of active site
k <sub>2</sub>	rate constant of chain initiation
k <sub>3</sub>	rate constant of chain propagation
k <sub>4</sub>	rate constant of chain transfer
k <sub>5</sub>	rate constant of deactivation
k <sub>+1</sub>	rate constant of attachment of the catalyst in the site activation
k <sub>-1</sub>	rate constant of detachment of the catalyst in the site activation
k <sub>+2</sub>	rate constant of attachment of the monomer in the site activation
k <sub>-2</sub>	rate constant of detachment of the monomer in the site activation
k <sub>+4</sub>	rate constant of attachment in the chain propagation reaction
k <sub>-4</sub>	rate constant of detachment in the chain propagation reaction
k <sub>+5</sub>	rate constant of attachment in the chain transfer reaction
k <sub>-5</sub>	rate constant of detachment in the chain transfer reaction
k' <sub>c</sub>	rate constant of the first reaction of co-catalyst in the site activation
k'' <sub>c</sub>	rate constant of the second reaction of co-catalyst in the site activation
K <sub>A</sub>	equilibrium constant of the catalyst in the site activation
K <sub>B</sub>	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
$mg_l$	mass transfer rate from gas to liquid ( $\text{kg}/(\text{m}^3 \cdot \text{s})$ )
$P$	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
$r_i$	reaction rate for species, $\text{mol}/(\text{m}^3 \cdot \text{s})$
$T$	temperature, K
$T_r$	reference temperature, K
$u$	velocity, m/s
$v$	volume, liter

## Greek Letters

$\alpha$	alpha position
$\sigma_k$	model constant
$\sigma_\varepsilon$	model constant
$\varepsilon$	dissipation rate of turbulent energy, $(\text{m}^2/\text{s}^3)$
$\rho$	Density, $\text{kg}/\text{m}^3$
$\phi$	phase volume fraction, dimensionless
$\mu_l$	dynamic viscosity of the liquid, Pa. s

$\mu_T$                       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