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Dynamic process behavior and model validation of reactive dividing wall columns

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ABSTRACT

Reactive dividing wall columns (RDWC) are a highly integrated column type. The coupling of a reactive distillation and a dividing wall column leads to complex interactions between vapor-liquid mass transfer, chemical kinetics and component split around the dividing wall. In simulation studies such interactions have been shown to lead to complex dynamics and the occurrence of multiple steady states. However, experimental investigations are still missing to verify the theoretical findings. In this work the first comprehensive experimental study of the dynamic behavior of RDWCs is presented. The reference system of enzymatic catalyzed butyl acetate transesterification with hexanol has been employed to investigate the start-up and open loop behavior under different operating conditions. Two different start-up strategies are tested and compared. The experiments demonstrate the reliable and secure start-up and stable operation of a RDWC. Additionally, a developed rigorous dynamic RDWC model is presented that considers the dynamic influence on the vapor distribution in the dividing wall section. A detailed model validation is carried out using the obtained experimental data. The comparison of simulation results and experimental values show good agreement over a wide range of operating conditions.

1. Introduction

The reactive dividing wall column (RDWC) is a highly integrated apparatus that combines the industrially employed integrated column types reactive distillation (RD) and dividing wall column (DWC). The resulting RDWC performs a chemical reaction and a product separation into up to 4 pure fractions in one column shell (Kaibel, 1987) and thus combines the advantages of the RD (Taylor and Krishna, 2000; Sundmacher and Kienle, 2003; Schmidt-Traub and Górak, 2006) and DWC (Glinos and Malone, 1988; Dejanović et al., 2010): Higher conversion, reduced energy consumption and lower investment costs. The RDWC is best employed if a reaction and separation in more than two product fractions is required. These can be reactions with more than two products or systems with an inert component in the feed stream. For two-reactant/two-product systems with excess of one reactant, a RDWC can replace a sequence of an RD with a conventional column. Theoretical studies have shown that the application of a RDWC significantly reduces the energy consumption of a process compared to a RD sequence (Schröder et al., 2016; Schröder and Fieg, 2016). Promising such great cost savings, an increased research interest can be observed since 2000. The feasibility of steady-state operation has first been shown experimentally for the methyl acetate hydrolysis (Sander et al., 2007; Ryll, 2009; Müller, 2010). The second investigated reaction system is the transesterification of butyl acetate with hexanol (Egger and Fieg, 2017; Ehlers et al., 2017). Different steady-state simulation models for the RDWC have been developed and experimentally validated (Mueller and Kenig, 2007; Ryll, 2009; Müller, 2010; Egger and Fieg, 2017; Ehlers et al., 2017). However, to our knowledge, no RDWC has so far been constructed and operated on an industrial scale. This leads to the question: why has an apparatus that promises such large benefits not been built yet? One of the major reasons is surely the still limited experience with the dynamic process behavior. A few dynamic simulation models for RDWCs are presented in the literature that are based on two-column decomposition approaches (An et al., 2015; Dai et al., 2015; Li et al., 2016). However, these models do not take into account changes in the vapor distribution in the dividing wall section that is important for an exact prediction. Additionally, to our best knowledge no experimental investigations of dynamic RDWC behavior have been published so far. Therefore no data are available for the crucial step of model validation. This obviously explains the absence of validated dynamic models in the literature.

The resulting missing operational expertise and lacking confidence in available models are strongly limiting the further

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Notation

A	area, m^2
a_i	activity of component i in the liquid phase
B	bottom stream mass flow, kg/h
CP_1	constant in pressure drop correlation, $Pa^{0.5}/m$
CP_2	constant in pressure drop correlation
CP_3	constant in pressure drop correlation, h/m
c_p	heat capacity, J/K
D	distillate stream mass flow, kg/h
E_A	activation energy, J/mol
F_f	F-factor ($= v_G\sqrt{\rho}$), $Pa^{0.5}$
F	feed stream mass flow, kg/h
H	molar enthalpy, J/mol
h	height, m
K	molar phase equilibrium constant (vapor/liquid)
k	mass-specific reaction rate constant at temperature T, mol/s/kg
k_0	mass-specific reaction rate constant, mol/s/kg
kp,liq	liquid outflow coefficient for each stage, kg/h/m
k_{wall}	heat transfer coefficient for heat loss to the surroundings, $W/m^2/K$
L	molar liquid stream, mol/s
m_{cat}	mass of dry Novozym 435 on a stage, kg
$\dot{m}$	mass flow, kg/h
m_{col}	mass of column internals and wall section, kg
N	amount of moles, mol
N_{stages}	number of stages
Q_{accu}	heat accumulated by the column internals and steel, W
Q_{loss}	heat loss to the surroundings, W
Q_{reb}	reboiler heat duty, kW
R	reflux stream mass flow, kg/h
R_c	universal gas constant (=8.31466), J/mol/K
r	reaction rate depending on catalyst mass, mol/s/kg
S	side stream mass flow, kg/h
T	temperature, K
$T_{ambient}$	temperature of the surroundings, K
T_0	reference temperature for reaction kinetics, K
t	time, s
V	molar vapor stream, mol/s
VS	vapor split (fraction of total vapor stream that goes to the prefractionator)
v_G	gas velocity, m/s
w_L	liquid load, $m^3/m^2/s$
x_i	molar fraction of component i in the liquid phase
y_i	molar fraction of component i in the vapor phase

Greek letters

Δp	pressure difference, Pa
Δp_{MC}	pressure difference of the divided section (main column side), Pa
Δp_{PF}	pressure difference of the divided section (prefractionator side), Pa
Δz	axial length, m
ρ	gas density, Pa

Subscripts

cat	catalyst
col	column
ext	external
h	index
i	component index
in	stage inlet stream
j	reaction index
L	liquid phase
lo	lower
MC	main column
out	stage outlet stream
PF	prefractionator
PH	pseudo homogeneous
stage	value for an equilibrium stage
t	time
up	upper
V	vapor phase
wall	RDWC wall section

Abbreviations

ACM	Aspen Custom Modeler
BuAc	*n*-butyl acetate
BuOH	1-butanol
Cal B	*Candida antarctica* lipase B
CD	collector/distributor
DWC	dividing wall column
E	experiment
eRDWC	enzymatic catalyzed reactive dividing wall column
HETP	height equivalent to a theoretical plate/stage
HeAc	*n*-hexyl acetate
HeOH	1-hexanol
MC	main column
PF	prefractionator
PURE25	pure component databank of Aspen Properties
RD	reactive distillation
RDWC	reactive dividing wall column
UNIQUAC	activity coefficient model by Abrams and Prausnitz
VLE	vapor-liquid-equilibrium

development and research as well as the industrial implementation of reactive dividing wall columns for three reasons. First, experimental data are required by all researchers wanting to verify their RDWC models. Second, for industrial application an efficient control system is required to ensure an efficient RDWC operation and to guarantee stable reactant conversion and product purities. Therefore, a validated dynamic process model is essential for the design of control systems. Finally, a secure start-up strategy has to be developed that unerringly reaches the desired steady-state. A validated dynamic simulation tool helps to minimize the uncertainty introduced by the occurrence of multiple steady-states for the RDWC, as already shown for reactive distillation (Mohl et al., 1999) and very recently for RDWCs (Harbou et al., 2017).

This paper has the objective to address all three of the issues described above by an integrated approach of comprehensive dynamic modeling and systematic experimental investigations. A dynamic model of the RDWC that takes into account dynamic changes in the vapor distribution is presented. A reference system, the enzymatic catalyzed transesterification of hexanol and butyl acetate, is employed in a DN 65 pilot plant to investigate the RDWC start-up and open loop behavior. Two different start-up strategies are tested and compared. Finally, the developed model is validated using the acquired experimental data.

2. Model description

Reliable dynamic simulation models are increasingly important in the chemical industry, especially for complex processes. The ongoing advancement of process automation requires valid

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