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Pilot-scale experimental validation of unsaturated polyesters synthesis by reactive distillation

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HIGHLIGHTS

- Reactive distillation (RD) process for synthesis of unsaturated polyesters.
- Pilot scale experimental validation of the newly proposed RD process.
- Two configurations investigated 1. RD column alone, 2. RD column with pre-reactor.
- Extended rate-based model used for rigorous simulations of the pilot plant.
- Product specification are comparable with the polyester made at industrial scale.

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ABSTRACT

Reactive distillation (RD) is an integrated operation combining both reaction and separation, thus improving the productivity and selectivity, reducing the energy usage, eliminating the need for solvents and leading to intensified highly-efficient systems. In previous work, we performed the conceptual design and modeling of a reactive distillation process for synthesis of unsaturated polyesters. The simulation results of our previous work clearly demonstrated that reactive distillation is a promising alternative for the polyesters synthesis.

This paper presents our pilot scale experimental validation work on the proposed RD process for polyester synthesis. Two configurations are investigated: (1) a RD column alone and (2) a RD column coupled with a pre-reactor. For the first configuration, we demonstrated that mostly monoesters are formed in the RD column, due to the short residence time at pilot scale. Since the combination of a RD column with pre-reactor allows sufficient residence time also at pilot scale, we demonstrated that polyesters are formed in the RD column. The extended rate-based model developed previously was used to simulate the pilot plant RD column. The model adequately predicts and describes the experimental data obtained from the pilot plant. Moreover, the product specification of the polyester produced in the continuous RD column was compared with the polyester product manufactured at industrial scale. Remarkably, it was found that the product specifications of the polyester produced in the RD column is comparable to that of the polyester produced in industry.

1. Introduction

Most chemical processes involve reaction and separation operations that are typically carried out in different sections of the plant and use different equipment types (e.g. reactors and distillation columns) operated under a wide variety of conditions. Recycle streams between these units are often used to improve conversion and selectivity, to minimize the production of undesired by-products, to reduce the energy requirements, and to improve the process controllability [15]. Recent economic and environmental considerations have encouraged industry to focus on technologies based on process intensification. Reactive distillation (RD) is such an integrated operation that combines reaction and separation into a single unit allowing the simultaneous production and removal of products, thus improving selectivity and productivity, reducing the energy use and the need for solvents while also leading to high-efficiency systems with *green engineering* attributes [16,19,21,27,29].

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Notation

a	interfacial area (m^2)
AV	acid value (mg/g)
C	concentration of component (mol/kg)
D_{ax}	axial dispersion coefficient (m^2/s)
E^L, E^V	liquid and vapor energy holdup (J)
H^L	liquid molar enthalpy (J/mol)
H^V	vapor molar enthalpy (J/mol)
$\overline{H}^L$	partial molar enthalpy of liquid (J/mol)
$\overline{H}^V$	partial molar enthalpy of vapor (J/mol)
h^L	heat transfer coefficients of liquid (w/m^2 k)
h^V	heat transfer coefficients of vapor (w/m^2 k)
h	height of a stage (m)
k_l	mass transfer coefficients of liquid (mol/m^2-s)
k_g	mass transfer coefficients of vapor (mol/m^2-s)
L	liquid mass flow rate (kg/s)
$\dot{L}$	liquid molar flow rate (mol/s)
M	liquid holdup (kg)
m	order of reaction (–) ($m = [1 - (1 - 2^{1-q})X]^{1/(1-q)}$)
MW	molecular weight (kg/kmol)
N	normality of titer (mol/l)
N^L	liquid side mass transfer rate (mol/s)
N^V	vapor side mass transfer rate (mol/s)
$\dot{N}_i$	mass transfer flux ($mol/m^2/s$)
n	number of moles of component (mol)
P	pressure (bar)
q	adjustable exponent (–) ($q = 7$)
R	rate of reaction (mol/kg-s)
S	side stream molar flow rate (mol/s)
t	time (s)
T_j	temperature on stage j (K)
V	vapor flow rate (mol/s)
$\dot{V}$	volume of titer (l)
v	liquid velocity (m/s)
W	weight of sample (kg)
x	liquid mole fraction (mol/mol)
X	conversion (–)
y	vapor mole fraction of (mol/mol)

Greek letters

ε_j	reaction volume on stage j (kmol)
$\gamma_{I,j}$	activity coefficient of component i on stage j (–)
$\nu_{I,m}$	stoichiometry coefficient of component i in reaction m (–)
τ	residence time of the liquid in the column (h)

Subscripts

F	feed stage
i	component indices
j	stage indices
R	reflux

Superscripts

$*$	equilibrium
L	liquid phase
V	vapor phase
sat	saturated

Abbreviations

COOH	acid end group
FA	fumaric acid
MA	maleic acid
MAD	maleic anhydride
OH	hydroxyl group
POLY	polyester
$POLY_{1D}$	maleate formed polyester
$POLY_{2D}$	fumarate formed polyester
$POLY_s$	saturated polyester
PG	propylene glycol
SACID	saturated acid

Some of these benefits are obtained by using reaction to improve separation (e.g. overcoming azeotropes, avoiding or eliminating difficult separations) while others are achieved by using separation to improve reactions (e.g. overcoming reaction equilibrium limitations, improving selectivity) – the maximum effect being achieved when both aspects are important (Malone and Doherty, 2000) [7]. However, the application of RD is somewhat limited by constraints, such as: common operating range for distillation and reaction, proper boiling point sequence, providing proper residence time characteristics and more difficult control.

Remarkably, RD has found many industrial applications during the past decades [7–9,18,25,30]. In particular, (trans-)esterification and etherification are some of the most used equilibrium reactions (Malone and Doherty, 2000) [2,11,19,22,27]. Nowadays, the application with the largest number of installations is methyl tertiary butyl ether (MTBE) that is used in gasoline blending [15]. Other esters such as ethyl tertiary butyl ether (ETBE), tert-amyl methyl ether (TAME) or fatty acid methyl esters (FAME), are also produced now by RD [7,8,12].

In previous work we made a review of the available modeling approaches for RD, and applied the findings to the polyester synthesis – the main focus being on extending the dynamic rate-based model [1] to take into account the liquid back mixing [22,23]. The simulation results of previous work demonstrated that reactive distillation is a promising alternative for polyesters synthesis [19,21]. The production time was reduced by 85% and the required volume to produce polyester at industrial scale (typically 100 kton/year) was reduced by 74%. Moreover, the RD model predicted the polymer attribute, isomerization and saturation composition of the polymer to be in the range of industrial production data for the polyester process. Although the ideal reaction temperature of the polyester process is between 210 °C and 220 °C – to avoid the degradation of reactants and products [17] – the reaction temperature of the reactive distillation was varied between 185 °C and 270 °C. It was assumed that there is significantly less risk of destructing the unsaturated acid in the RD process due to the short residence time requirement and the free acid (or anhydride) only being present in the top three stages of the RD column, where the reaction temperature remains between 185 °C and 210 °C as shown previously [19].

Following the modeling work, it is very important to prove experimentally that polyesters can be indeed produced in a RD column, and that the assumption given for operating the RD column at temperatures over 220 °C is reasonable. This paper discusses the experimental work carried out at pilot scale, in a reactive distillation column. The polyester produced in the pilot plant is compared with the polyester produced in industry. Moreover, the experimental results are compared with the simulation results to check the validity of the previously developed model, and the product specifications of the polyester produced in the RD column are compared to that of polyester produced in the traditional industrial batch-reactor setup. To our knowledge, the synthesis of unsaturated polyesters by reactive distillation was never attempted before at pilot-scale – let alone at large scale – so our