Separation and Purification Technology 158 (2016) 193–203

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Methyl lactate synthesis using batch reactive distillation: Operational challenges and strategy for enhanced performance

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ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form 16 November 2015
Accepted 13 December 2015
Available online 15 December 2015

Keywords:
Dynamic modelling
Optimization
Methyl lactate
Conventional reactive distillation
Semi-batch reactive distillation
Esterification

ABSTRACT

Batch reactive distillation is well known for improved conversion and separation of desired reaction products. However, for a number of reactions, the distillation can separate the reactants depending on their boiling points of them and thus not only reduces the benefit of the reactive distillation but also offers operational challenges for keeping the reactants together. Methyl lactate (ML) synthesis via the esterification of lactic acid (LA) with methanol in a reactive distillation falls into this category and perhaps that is why this process has not been explored in the past. The boiling points of the reactants (LA, methanol) are about 490 K and 337 K while those of the products (ML, water) are 417 K and 373 K respectively. Clearly in a conventional reactive distillation (batch or continuous) methanol will be separated from the LA and will reduce the conversion of LA to ML significantly.

Here, first the limitations of the use of conventional batch distillation column (CBD) for the synthesis of ML is investigated in detail and a semi-batch reactive distillation (SBD) configuration is studied in detail where LA is the limiting reactant and methanol is continuously fed in excess in the reboiler allowing the reactants to be together for a longer period. However, this poses an operational challenge that the column has to be carefully controlled to avoid overflow of the reboiler at any time of the operation. In this work, the performance of SBD for the synthesis of ML is evaluated using model based optimization in which operational constraints are embedded. The results clearly demonstrate the viability of the system for the synthesis of ML.

1. Introduction

Since lactic acid (LA) can be manufactured easily by fermentation or by chemical synthesis from many carbohydrates, the conversion of LA into its esters is worth studying [9]. Methyl lactate (ML) is a clear and colorless liquid having a characteristic odor (cool mint). ML is a useful product as chiral pharmaceuticals and agrochemicals, green solvent, cleaning agent, plasticizer agent, or intermediate and its two functional groups can be utilized to prepare numerous derivatives. In general, it constitutes a powerful component which has good possibilities of application at industrial levels, food industries, personal-care and cosmetic (makeup, shampoos, hair dyes and colors, etc.) applications [32,10,1].

The global market for lactate ester products were 2505 kilotons in year 2013 and are expected to be around 3569.6 kilotons by year 2020. Lactate esters accounted for 30% of total market volume in 2013 and emerged as the leading product segment. Increasing demands for lactate esters are expected to have a positive influence on the market growth [12]. There are several reaction schemes which can be used to produce ML and some of these are listed in Table 1.

The esterification process of LA (impure) with many alcohols to yield lactate ester is not new. For example, studies on esterification reaction of LA with ethanol to form ethyl lactate (EL) were investigated by Zhang et al. [36] and Delgado et al. [6]. Adams and Seider [2] proposed a semi-batch reactive distillation (SBD) process for the production of EL from ethanol and LA. Yadav et al. [35] and Toor et al. [31] studied the esterification of LA with isopropanol to synthesize isopropyl lactate. A number of researchers also discussed the reaction of LA with n-butanol to produce n-butyl lactate [3,5,18].

In the past, purification of impure LA has been considered in reactive distillation (batch or continuous) as a two-step process: esterification of impure LA into ML followed by hydrolysis of methyl lactate into pure lactic acid [15,16,17]. However, the main focus of their study was the production of lactic acid and not the methyl lactate (see Fig. 1). Also interestingly, although some of these work mentioned the requirement of removal of large amount of water in the esterification step (due to dilute LA feed and subsequent production of water) before the separation of ML for the

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http://dx.doi.org/10.1016/j.seppur.2015.12.023
1383-5866/

Nomenclature

B_{ij}, B_{ji}	binary interaction parameters for UNIQUAC equation
CVP	control vector parameterisation
D	distillate product (kmol)
DAE	differential algebraic equations
F	methanol feed rate (kmol/h)
H_L, H_V	liquid, vapor enthalpy (kJ/kmol)
K	vapor–liquid equilibrium constant
ke	pre-exponential factor for the esterification reaction
L	liquid rate in the column (kmol/h)
M_{wti}	molecular weight of each component
M_a, M_C	accumulator and condenser holdup respectively (kmol)
M, M_N	stage and re-boiler holdup respectively (kmol)
m_{cat}	the catalyst weight (kg of catalyst)
N	number of stages
NCI	number of control intervals
OP1	optimization
P	pressure (bar)
P^{sat}	vapor pressure of pure component i
Q_C, Q_r	condenser or reboiler duty (kJ/h)
Q_T	total Energy Consumption (m kJ)
R_1, R_2	reflux ratio in time interval 1, and 2
R, R_{Max}	reflux ratio and maximum reflux ratio
r_{ML}	reaction rate of Methyl Lactate (kmol (kg of catalyst)$^{-1}$ min^{-1})
SQP	successive quadratic programming algorithm
T	temperature (K)
T_{r1}, T_{r2}	reference temperatures (K)
t, t_f	batch time, final batch time (h)
t_1, t_2	length of interval 1, and 2 and (h)
V	vapor flow rate in the column (kmol/h)
x	liquid composition (mole fraction)
x_a	accumulated distillate composition (mole fraction)
x_D	instant distillate composition (mole fraction)
y	vapor composition (mole fraction)

Greek letters (superscripts and subscripts)

ε	small positive numbering the order of 10^{-3}
i	component number
j	stage number
λ_i	latent heat of vaporization (kJ/kmol) of component
λ_r	latent heat of vaporization (kJ/kmol) of the reboiler mixture
λ_{bi}	latent heat (kJ/kmol) of component at normal boiling point
γ_i	activity coefficient of component i
Δn	change in moles due to chemical reaction

Abbreviations

AgCL	silver chloride
AgL	silver lactate
AM	acetamide
AmL	ammonium lactate
CH_3CL	methyl chloride
DHA	dihydroxyacetone
ET	ethyl lactate
GLA	glyceraldehyde
HC	hemiacetal

hydrolysis step, no one appreciated the difficulty of keeping methanol and the LA together in the reboiler to enhance the conversion of LA to ML. To overcome the water removal problem, Thotla and Mahajani [30] proposed a reactive distillation configuration with water side draw using both continuous and semi-batch columns, for the esterification step to enhance the conversion of LA. However, they also did not appreciate the difficulty of keeping methanol and the LA together in the system which could further enhance the conversion of LA.

With the above backdrop, it is attempted to focus again at the esterification step in detail with the objective of enhanced production and recovery of ML rather than focusing on the purification of LA which has already received quite a bit of attention in recent years [8,22]. Here, first, the limitations of CBD column are explored for the synthesis of ML. Then the enhancement of the conversion of LA into ML is looked at by continuously feeding methanol into a SBD column and dealt with the operational challenge due to this mode of operation. The ultimate aim was to obtain the best operational strategy of SBD for the synthesis of ML. Note, like others the recovery of water is not attempted or suggested before the recovery of ML. Rather, the proposed strategy will produce ML and water simultaneously in the reboiler and in the distillate. To achieve the above the model based techniques are adopted. A detailed dynamic model based on mass and energy balances is considered and incorporated into the optimization framework within gPROMS [11] software. The performance of SBD is evaluated in terms of minimum batch time and energy consumption for the production of ML. In order to avoid overloading of the reboiler due to additional methanol feeding, an operation constraint is added into the optimization framework. The dynamic optimization problem was transformed to a nonlinear programming problem and solved by using Control Vector Parameterization (CPV) technique using efficient sequential quadratic programming (SQP) method within gPROMS (further details about this technique can be found in [21]. Reflux ratio and methanol feed rate are considered as the control variables of the system and piecewise-constant control strategy is used in the optimization study.

Table 1
Several proposed reaction schemes for methyl lactate production.

Reaction scheme	Reference
$LA + MEOH \Longleftrightarrow ML + H_2O$	[27]
$EL + MEOH \Longleftrightarrow ML + ETOH$	[24]
$AmL + MEOH \Rightarrow ML + AM$	[9]
$AgL + CH_3CL \Rightarrow ML + AgCL$	[24]
GLA or DHA $\Rightarrow$ HC $=>$ ML	[34]

2. Operation modes and energy consumption

Mujtaba [21] reported different modes to operate batch distillation column: (A) Constant vapor boil-up rate mode, (B) Constant reboiler duty mode and (c) Constant condenser vapor load rate mode. For each mode, Mujtaba et al. [22] suggested the following equations to calculate the total energy consumption in the column:

$$\text{Mode A}: Q_T = V\int_0^{t_f} \lambda_r dt \tag{1}$$

$$\text{Mode B}: Q_T = Q_r \times t_f \tag{2}$$

$$\text{Mode C}: Q_T = \int_0^{t_f} Q_r dt \tag{3}$$