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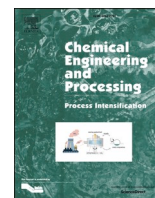
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Analysing separation and reaction stage performance in a reactive cyclic distillation process[☆]

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ABSTRACT

In this paper the production of MTBE from isobutene and methanol via reactive cyclic distillation is studied with a mass and energy balance stage model. This study shows the first application of a reactive cyclic distillation stage model, where reaction equilibrium is assumed. A cyclic distillation process with a column design equivalent to a conventional column for MTBE reactive distillation has been simulated. The cyclic operated column gives high conversions of reactants, high product throughput and low energy requirements. By investigating the reactive stage behaviour it was found that the periodic operation can give an overall higher degree of separation and production of MTBE compared to the conventional column design. This is due to higher degree of separation in the cyclic operation, which favours the desired reaction. With no back-mixing of the liquid holdups the overall mass transfer and conversion in a reactive cyclic distillation process is increased compared to that of a conventional reactive separation scheme. Thereby, an improved cyclic operated column design with reduced number of stages was realised.

1. Introduction

Reactive distillation is a well established intensified process. This process intensification combines both reaction and separation in a single column. This makes it possible to reduce the investment and energy cost [1]. Different industrial applications of reactive distillation exists, such as the production of methyl acetate, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and fatty acid methyl esters (FAME) [2]. One well-known example of the benefits of reactive distillation is the Eastman process for the production of methyl acetate, in which a conventional setup with multiple reactors and separation columns can be replaced by a single reactive distillation column and a couple of subsequent separation columns for removal of impurities [2,3]. The production of MTBE is another well-known implementation of reactive distillation, which has been studied extensively in literature using both chemical equilibrium and rate kinetics reactions due to its fast reaction kinetics [4–11].

Different process intensifying technologies for reactive distillation

have been suggested, such as reactive divided wall columns, reactive cyclic distillation, reactive heat integrated distillation columns, reactive high gravity distillation, membrane assisted reactive distillation, microwave assisted reactive distillation and ultrasound assisted reactive distillation [12]. All of these different technologies provide intensification benefits regarding energy savings and/or capital savings. Some of the technologies are more mature than others with the reactive divided wall column being one of the more readily applicable process intensification [12]. One interesting process intensification technology for reactive distillation is the reactive cyclic distillation, which is currently only studied in few previous publications [12–14].

Cyclic distillation is a process intensification first introduced in the early 1960's [15]. In a cyclic distillation process the phase flows are separated in two; a vapour flow period (VFP), where the liquid is stationary on each stage and vapour travels up through the column, and a liquid flow period (LFP), where the liquid holdups are moved one stage down the column each. During the VFP mass and energy transfer occurs between the liquid and vapour phases, while it is assumed no such phase transfer occurs during the LFP. Earlier studies showed that operating a

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Nomenclature			
a	activity coefficient	t_{LFP}	duration of LFP (s)
B	bottoms (mol/cycle)	t_{VFP}	duration of VFP (s)
BR	boilup ratio	T	temperature (K)
C_p	specific heat capacity (J/(K mol))	T_{ref}	reference temperature (K)
D	distillate (mol/cycle)	V	vapour flow rate (mol/s)
h	liquid enthalpy (J)	x	liquid composition (mol/mol)
H	vapour enthalpy (J/mol)	y	vapour composition (mol/mol)
ΔH_{vap}°	standard heat of vaporisation (J/mol)	Greek	
ΔH^{react}	heat of reaction (J/mol)	ϵ	change in moles to reach chemical equilibrium
K_{eq}	chemical equilibrium constant	γ	activity coefficient
R_i	production rate of component i (mol/s)	ν	stoichiometric coefficient
r	reaction rate (mol/(s kg))	Subscripts	
L	reflux (mol/cycle)	i or j	component ID
M	molar holdup (mol)	n	stage number
m^{cat}	catalyst load (kg)	r	reaction ID
N	number of cycles	Superscripts	
NC	number of components	F	feed
NR	number of reactive stages	eq	chemical equilibrium reaction
NT	number of trays	kin	rate kinetic reaction
P	stage pressure (Pa)	L	liquid phase
p^{sat}	saturation pressure (Pa)	(LFP)	end of LFP
Q	energy (J/s)	SD	side draw
S	side draw (mol/cycle)	V	vapour phase
t	time (s)	(VFP)	end of VFP
		0	initial condition

distillation process with periodic cycling of the phase movements could lead to higher capacity, better degree of separation, reduced number of stages or reduced energy requirements dependent on the process, column and stage design [15–17]. An early study showed that there were issues with non-ideal liquid draining of the trays during the LFP [18]. In 2011 a new tray type was designed [19], which allows for cyclic distillation processes to be realised in full scale industrial columns with simultaneously drained trays.

Current applications of reactive separations utilise that the separation enhance the desired reaction path. Since periodic operation of a column lead to more efficient separations [14,17] the integration of cyclic and reactive distillation is a promising highly intensifying process alternative to conventional reactive distillation. The additional design variables in a cyclic distillation process, i.e. the duration of the two flow periods (VFP and LFP), allows for the time that liquid holdup spends on a stage to be optimised in relation to the reaction. This provides flexibility in terms of catalyst loading and the residence time on the stages. Cyclic operation of reactive separation has been investigated by [12–14]. Kiss [13] outlined some benefits of various reactive distillation processes including a reactive cyclic distillation, which he referred to as catalytic cyclic distillation due to the use of heterogeneous catalyst. Pătruț et al. [14] presented a dynamic mass balance model for reactive cyclic distillation that accounts for the combination of reactive and cyclic distillation for the production of dimethyl ether (DME). Their extensive study on DME investigates the reactive cyclic distillation performance and the possibility of multiple periodic states.

A mass and energy balance stage model for non-reactive cyclic distillation has been presented by Rasmussen et al. [20]. This dynamic stage model includes an energy balance to describe the time dependent vapour flow on each stage and further allows multiple feed locations and incorporating the heat of reaction. These features are important in reactive distillation processes, where reactants commonly are introduced at two or more locations in the column. Currently, there are a number of publications available on non-reactive cyclic distillation and stripping [17,19–24], however, there are only a few on the reactive cyclic distillation. The example of DME by Pătruț et al. with a single feed

location is the only case investigated in reactive cyclic distillation. Table 1 shows the current literature available on reactive (catalytic) cyclic distillation.

The design of a conventional reactive distillation is in itself a difficult task, more so than for the design of a non-reactive distillation, as the simultaneous reaction and separation must be accounted for. Some

Table 1
Current literature available on reactive cyclic distillation.

Authors/Year	Contribution	Conclusions
Kiss [13] / 2019	Overview of various reactions and novel alternatives to conventional reactive distillation processes.	The DME synthesis is a suitable choice for catalytic cyclic distillation, with benefits such as high column throughput, low energy usage and high separation performance.
Kiss, Jobson and Gao [12] / 2019	Overview of reactive distillation equipment including a catalytic cyclic distillation column.	Catalytic cyclic distillation can facilitate slower reactions as the liquid holdup and catalyst load per stage can be higher than in conventional operation. With the cyclic operation more degrees of freedom are introduced, which can complicate the operation and control of the process. There is a need for development and validation of process models, design approaches and control strategies.
Pătruț et al. [14] / 2014	First rigorous mass balance stage model and design method for catalytic cyclic distillation. The synthesis of DME was chosen as a case study for investigation of the cyclic state behaviour and a proposed design method.	Benefits in catalytic cyclic distillation over conventional reactive distillation include: lower energy requirement and higher operational flexibility. Drawbacks include the possibility of unstable periodic states, meaning the column design should be made carefully.

general methods are available such as graphical methods, heuristic methods and optimisation methods [25–28]. The number of rectifying and stripping stages can for the most parts be found using design methods for non-reactive columns, the number of reactive stages is much more difficult to estimate.

A design method for non-reactive cyclic distillation columns was proposed by Toftegård and Jørgensen [29]. With this method the mass balance for the reboiler is integrated backwards in time through the VFP, from the end of the VFP to the beginning of the VFP, with the desired product output as initial condition. After this a stage above the reboiler is added and integrated backwards together with the reboiler. The initial condition for this stage can be found from the mass balance for the LFP. By adding one stage at a time and integrate the mass balance model backwards through the VFP, the number of stages can be determined. The top stage is found when the top product target concentration is reached. This method was also used by Pătruț et al. [14] to find the number of stripping stages for a reactive cyclic column for dimethyl ether production assuming a rate controlled reaction. Here they assumed the change in liquid composition over the reactive zone is small, and based on the reaction rate they find the total amount of catalyst needed, which is then divided over a suitable number of stages. The number of rectifying stages was found by adding stages above the reactive zone one by one until top product purity target was reached. One drawback with this method is the assumption of almost constant liquid composition over the reactive zone, which might not hold for different reactions.

The novelty of the work presented in this paper is focused on the development of process understanding of combining reactive and cyclic distillation in a single column. It is necessary to develop this process knowledge in order to better understand how reactive cyclic distillation can be utilised as an alternative to conventional reactive distillation. The reactive cyclic distillation column design is a difficult task, with the introduction of two additional design variables, t_{VFP} and t_{LFP} . An analysis of how the different design variables must be done in order to give an overview of the important factors for the designing of a reactive cyclic distillation process. The MTBE production in a reactive distillation column is a well-known process with fast reaction kinetics, which for the solving of the model eliminates some of the complexity, thus a simple process can be analysed to give indications of how reactive cyclic distillation behave.

The purpose of this study is to analyse the implication of periodic operation on the stage behaviour in reactive separations. This will further the understanding of the difference between conventional and cyclic operated reactive distillation performance. For this study a rigorous mass and energy balance model will be applied and the well known case of MTBE will be studied using an equilibrium assumption. The assumption of chemical equilibrium was applied to reduce the process complexity and serve as a limiting test case for fast chemical reactions.

In the following sections, a description of the cyclic stage model for reactive separations is given. Afterwards, the case study of MTBE production is presented. The reactive cyclic distillation model is used to make a cyclic column design equivalent to the conventional reactive column for MTBE. The performance and stage dynamics of the equivalent cyclic column are analysed and compared to the conventional column. Based on this a discussion of important design variables is given in order to give an overview of the challenges in designing a reactive cyclic distillation process. This is followed by a proposal of an improved, but not necessarily optimal, realisation of a reactive cyclic distillation process for MTBE. A discussion of possible future studies concerning reactive cyclic distillation is then given, followed by the conclusion.

2. Models for reactive separation

This section will present the model for reactive cyclic distillation used in this paper. The model for the conventional reactive distillation

process is provided in the appendix A.1. These models are formulated in general terms to fit a wide range of applications in reactive separation.

The following assumptions for the reactive distillation are made in addition to the assumptions for a non-reactive distillation process [30]:

- Reaction only takes place in the liquid phase.
- Reaction only takes place in the reactive zone of the column.
- Reaction can either be described by rate kinetics or chemical equilibrium.

2.1. Reactive cyclic distillation model

The mass and energy balance model used for the reactive cyclic distillation process is given. This model is based on the mass and energy balance stage model by Rasmussen et al. [20] with the same assumptions, expanded to include reactions. It is further assumed that the reaction only occurs during the VFP. This is a reasonable assumption, as the reaction is catalysed by a heterogeneous catalyst placed on the stages. This model can handle multiple feed locations and thus presents a generalised model. The mass and energy balance for tray $n = 1, \dots, NT$ and component $i = 1, \dots, NC$ is shown below both for the VFP and the LFP. This model is a general reactive cyclic distillation model, with rate kinetics or equilibrium reaction and possibility for side draws, S_n . The presented reactive cyclic distillation model is a vapour liquid equilibrium distillation model, similar to then non-reactive MESH equation model by Wang and Henke [30] and the reactive MESH equation model presented by Taylor and Krishna [31], but for cyclic operation. The stages are numbered from top to bottom, with the condenser being stage $n = 1$ and the reboiler stage $n = NT$.

VFP mole balance

$$\frac{dM_{n,i}(t)}{dt} = V_{n+1}(t)y_{n+1,i}(t) - V_n(t)y_{n,i}(t) + V_{n+1}^F(t)y_{n+1,i}^F(t) + R_{n,i}^r(t) \quad (1)$$

With the initial conditions $M_{n,i}(0) = M_{n,i}^0$ and $y_{n,i}(0) = y_{n,i}^0$ for $n = 1, \dots, NT$ and $i = 1, \dots, NC$. A total molar holdup balance can be made by summing up the mole balances for the components, $\frac{dM_n}{dt} = \sum \frac{dM_{n,i}}{dt}$. The reaction rate for stage n and component i is denoted $R_{n,i}^r$.

LFP mole balance

$$M_{n,i}^{(LFP)} = M_{n-1,i}^{(VFP)} + M_{n-1,i}^F - S_n x_{n,i}^{(VFP)} \quad (2)$$

For the stage below the condenser the reflux is equal to the holdup after a LFP, $M_2^{(LFP)} = L$. The superscript (LFP) denotes the end of a LFP and (VFP) the end of a VFP. In a cyclic process the end of a LFP is also the start of the next VFP and vice versa.

VFP energy balance

$$\begin{aligned} \frac{dM_n(t)h_n(t)}{dt} &= V_{n+1}(t)H_{n+1}(t) - V_n(t)H_n(t) + V_{n+1}^F(t)H_{n+1}^F(t) + \Delta H_n^{reac} \\ &\times \sum_{i=1}^{NC} R_{n,i}^r(t) + Q_n(t) \end{aligned} \quad (3)$$

With the initial conditions $T_n(0) = T_n^0$, $M_n(0) = M_n^0$ and $y_{n,i}(0) = y_{n,i}^0$ for $n = 1, \dots, NT$ and $i = 1, \dots, NC$. This energy balance is used to describe the time-dependent vapour flow rate as described by Rasmussen et al. [20]. The reaction takes place in the liquid phase, so this does not have any explicit effect on the vapour flow rate. The heat of reaction, ΔH_n^{reac} , is included in the energy balance as it will have an effect on the liquid temperature as the reaction takes place. It is included here to ensure a high fidelity model, although for many reactive separation applications this contribution is usually small.

LFP energy balance

$$M_n^{(LFP)}h_n^{(LFP)} = M_{n-1}^{(VFP)}h_{n-1}^{(VFP)} + M_{n-1}^F h_{n-1}^F - S_n h_n^{SD} \quad (4)$$

Figure 1 shows a stage n in the reactive cyclic distillation process during the VFP and LFP. As shown the reaction only occurs during the VFP.

The reaction terms are zero for nonreactive stages, i.e. the reboiler, condenser, rectifying and stripping stages. It is further assumed energy is only added to the reboiler and removed from the condenser, $Q_n = 0$ for $n = 2 \dots NT - 1$.

The reboiler and condenser duties are calculated as [20]:

$$Q_C = V_2(H_2 - h_1) \tag{5}$$

$$Q_B = \frac{M_{NT}^0 \cdot BR}{t_{VFP}} (H_{NT} - h_{NT}) \tag{6}$$

Where BR is the boilup ratio and M_{NT}^0 is the initial holdup in the reboiler. The initial reboiler holdup is assumed to be equal to the reboiler holdup after each LFP, and the same for the condenser.

The following general equations describe the vapour liquid equilibrium, enthalpy and liquid holdups on each stage. The vapour liquid equilibrium (VLE) is the summation and equilibrium equations from the MESH equation system [30]. These are algebraic equations that ensures the molar compositions of the vapour and the liquid phases sum up and that the vapour and liquid phases are in equilibrium.

$$0 = 1 - \sum_{i=1}^{NC} y_{n,i} \tag{7}$$

$$0 = 1 - \sum_{i=1}^{NC} x_{n,i} \tag{8}$$

$$0 = y_{n,i} - \frac{x_{n,i} \gamma_{n,i} P_{n,i}^{sat}}{P_n} \tag{9}$$

The vapour and liquid enthalpies of a stage, H_n and h_n respectively, are defined with assumption of temperature independent heat capacities and enthalpies of vaporisation as:

$$H_n = \sum_{i=1}^{NC} y_{n,i} (C_{p,i}^V (T_n - T_{ref})) \tag{10}$$

$$h_n = \sum_{i=1}^{NC} x_{n,i} (C_{p,i}^V (T_n - T_{ref}) - \Delta H_i^{vap}) \tag{11}$$

If the total and component molar liquid holdups of stage n are known, the liquid compositions can be calculated as:

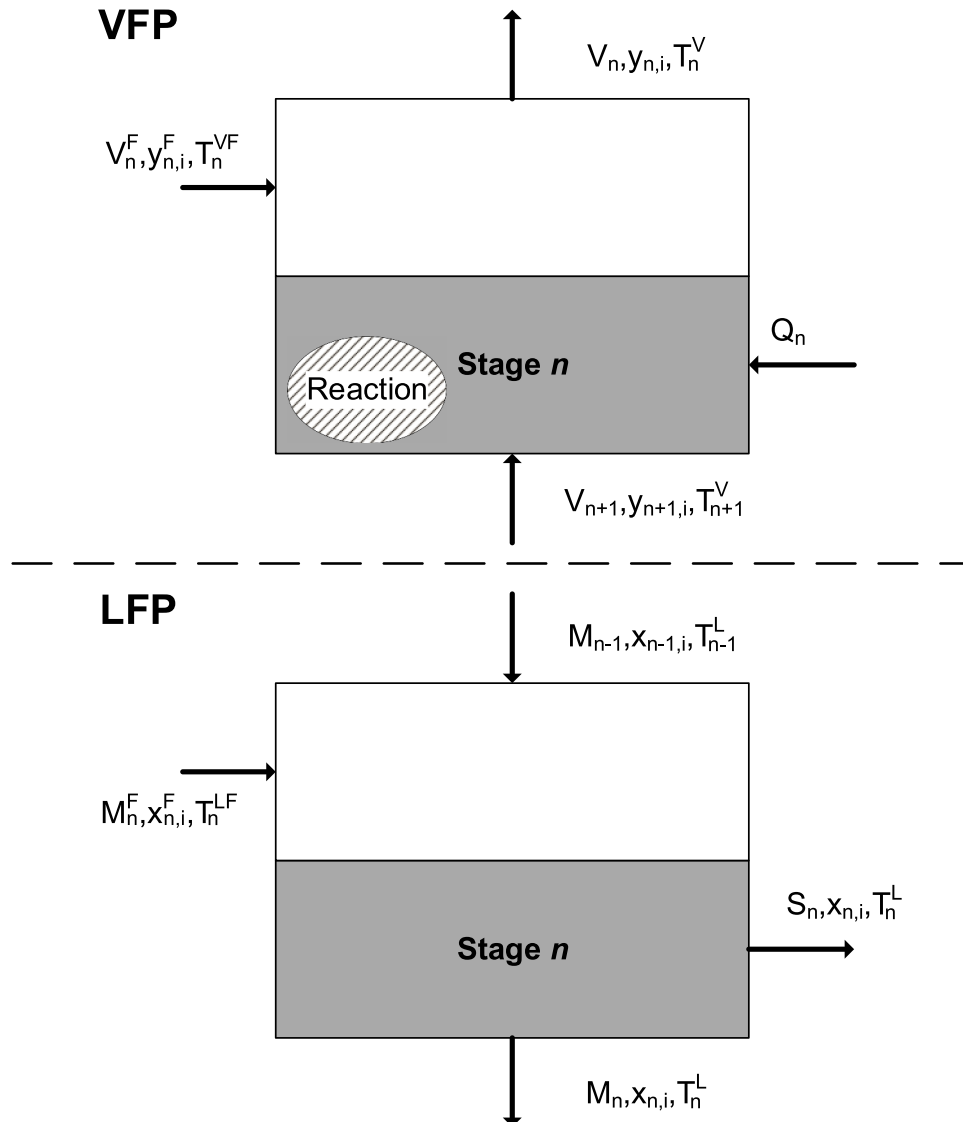


Fig. 1. Stage n in reactive cyclic distillation during the VFP (top) and LFP (bottom).

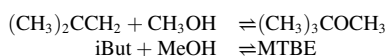
$$x_{n,i} = \frac{M_{n,i}}{M_n} \quad (12)$$

This dynamic model constitutes a differential algebraic equation system (DAE). Such a DAE system is often seen in dynamic distillation processes, where the differential equations describe the mass and energy balances equations and the algebraic equations describe the phase equilibrium. In order to simplify the problem for simulation, the differential equations are solved here as an ordinary differential equation (ODE) system and the algebraic equations are solved at each time step [20,32,33]. A more detailed model and degree of freedom analysis is given by Rasmussen et al. [20], where the mass and energy balance stage model for non-reactive cyclic distillation is described. The model presented here has been solved using MATLAB® with the *ode15s* solver to calculate the dynamic vapour flow periods, where at each time step the algebraic equations are solved. After a VFP the algebraic LFP equations are solved with initial conditions from the dynamic VFP solution. A new cycle is initiated with solving the dynamic VFP equations using the results from the LFP as initial conditions and so on.

3. MTBE reactive distillation

The production of MTBE is a well-known application of a reactive distillation process. The case study presented by Jacobs and Krishna [5] has been used as a base case in multiple publications, mainly focusing on the multiplicity in conversions of isobutene [4,9–11]. The work of Wang et al. [11] presents a reactive distillation process of MTBE assuming chemical equilibrium reaction, and is used as basis for this study. That is, in this paper only a chemical equilibrium reaction is considered. This is done in order to simplify the problem and make it easier to analyse the effect of the combined periodic separation and reaction. Currently, no other studies on reactive cyclic distillation assuming equilibrium reaction or for MTBE are available in literature.

Isobutene (iBut) and methanol (MeOH) can react over an acidic catalyst, e.g. Amberlyst 15, to form MTBE in a fast reversible reaction [34]:



Inert n-butene (nBut) is mixed with isobutene in the vapour feed to help with the reactive separation process [4,5].

The UNIQUAC model is used for the liquid activities and the vapour is assumed to be ideal. Due to the similar interactions between n-butene/isobutene and methanol or MTBE, it is assumed that n-butene and isobutene have the same UNIQUAC interaction parameters [34]. It should be noted that both the butenes and MTBE form azeotropes with methanol.

The activity coefficients of isobutene, methanol and MTBE, are found with the UNIQUAC model, with the binary interaction parameters from Rehfinger and Hoffmann [34], listed in Table 2.

The UNIQUAC thermodynamic model has been used to describe the liquid activities in many previous studies on reactive distillation of MTBE [4,5,9,11,34]. Among the former studies where the UNIQUAC model have been used is the work by Wang et al. [11], which is also the reference for the process design presented in this paper. In order to be able to compare a conventional and cyclic reactive distillation process the UNIQUAC model is thus also used in this work. The reaction rate

Table 2
UNIQUAC interaction parameters a_{ij} from Rehfinger and Hoffmann [34] in J/mol.

i j	Butenes	MTBE	MeOH
Butenes		434.01	5872.24
MTBE	-204.73		3897.10
MeOH	-294.14	-731.95	

expression, which was proposed by Rehfinger and Hoffmann [34], includes the activities of the reactants and product. This means that the choice of thermodynamic model affects both the separation and reaction.

The temperature dependency of the reaction enthalpy is assumed to be negligible over the column operation temperature, thus the heat of reaction is constant: $\Delta H_n^{\text{reac}} = -43.6$ kJ/mol [34]. The above reaction for MTBE production is relatively fast and can be described either by reaction kinetics or chemical equilibrium. As previously described the production or consumption of component i on stage n is defined as $R_{n,i}^{\text{rt}}$, which is positive for production and negative for consumption. The superscript "rt" denotes the reaction type, which can either be a reaction rate expression determined by reaction kinetics, denoted $R_{n,i}^{\text{kin}} = \nu_{n,i,r} r_{n,r} m_n^{\text{cat}}$ with $rt = \text{kin}$, or by a chemical equilibrium term, denoted $R_{n,i}^{\text{eq}} = \nu_{n,i,r} \epsilon_n$ with $rt = \text{eq}$. Only one reaction is considered here, so $\nu_{n,i,r} = \nu_{n,i}$ and $r_{n,r} = r_n$.

The coefficient ϵ_n is the change in the molar holdup or composition needed to reach equilibrium. With the new variable ϵ_n an equation, which describes the chemical equilibrium, for $n = 1, \dots, NT$, is necessary:

$$0 = K_{\text{eq}}(T_n) - \frac{a_{n,\text{MTBE}}}{a_{n,\text{iBut}} a_{n,\text{MeOH}}} = K_{\text{eq}}(T_n) - \frac{\gamma_{n,\text{MTBE}}}{\gamma_{n,\text{iBut}} \gamma_{n,\text{MeOH}}} \frac{x_{n,\text{MTBE}}}{x_{n,\text{iBut}} x_{n,\text{MeOH}}} \quad (13)$$

If this is not satisfied the direction of the reaction can be determined. If $K_{\text{eq}}(T_n) < \frac{a_{n,\text{MTBE}}}{a_{n,\text{iBut}} a_{n,\text{MeOH}}}$ then the activity of MTBE is too high and iBut and MeOH are formed, the stoichiometrics are then: $[\nu_{n,\text{nBut}}, \nu_{n,\text{iBut}}, \nu_{n,\text{MTBE}}, \nu_{n,\text{MeOH}}] = [0, 1, -1, 1]$.

Otherwise, if $K_{\text{eq}}(T_n) > \frac{a_{n,\text{MTBE}}}{a_{n,\text{iBut}} a_{n,\text{MeOH}}}$ then the activity of MTBE is too low and iBut and MeOH are consumed, the stoichiometrics are then: $[\nu_{n,\text{nBut}}, \nu_{n,\text{iBut}}, \nu_{n,\text{MTBE}}, \nu_{n,\text{MeOH}}] = [0, -1, 1, -1]$. At equilibrium, $K_{\text{eq}}(T_n) = \frac{a_{n,\text{MTBE}}}{a_{n,\text{iBut}} a_{n,\text{MeOH}}}$, no changes in the molar holdups occur due to reaction and $[\nu_{n,\text{nBut}}, \nu_{n,\text{iBut}}, \nu_{n,\text{MTBE}}, \nu_{n,\text{MeOH}}] = [0, 0, 0, 0]$. The equation (13) and the variable ϵ_n must be included in the model for an equilibrium reaction, thus adding another algebraic equation and variable that must be solved for at each time step.

Wang et al. [11] investigated the multiplicity in MTBE reactive distillation assuming chemical equilibrium reaction, with an equilibrium constant defined as [11]:

$$\ln K_{\text{eq}} = -16.33 + \frac{6820}{T} \quad (14)$$

With the temperature T in Kelvin. Since the reaction enthalpy is assumed to be constant in this paper, any correlation between the equilibrium constant and heat of reaction is not accounted for.

For a rate kinetics controlled reaction the reaction rate in mol/(s kg catalyst) is given by Rehfinger and Hoffmann [34]. The reaction rate presented by Rehfinger and Hoffmann [34] is a Langmuir-Hinshelwood rate expression, and is used in previous studies on reactive distillation of MTBE [5,9,10]. Hauan et al. [4] and Wang et al. [11] assumed chemical equilibrium reaction with temperature dependent equilibrium constants based on the work by Rehfinger and Hoffmann [34].

In this work it is assumed the reaction is fast and can therefore be described as an equilibrium reaction. This assumption simplifies the process as the reaction equilibrium is considered to be instantaneously reached at each time step. The dynamic behaviour of a rate kinetic reaction is neglected and the process can be solved easily. The results can be analysed in terms of the effects of a simultaneous fast reaction and separation, e.g. with regards to the duration of the VFP, effect of liquid holdup and feed stream locations. When reaction is combined with separation, where light components are removed continuously from the liquid holdup during the VFP, a combined effect of t_{VFP} on reaction and separation can be investigated. As the goal of this work is to develop process understanding of the intensified reactive cyclic distillation technology, this is deemed a sufficient assumption. The presented model

for reactive cyclic distillation in section 2.1 is, however, capable of handling either equilibrium or non-equilibrium reactions.

The assumption of chemical equilibrium was tested by setting up a simple batch reactor simulation using the rate expression from Rehfinger and Hoffmann [34]. The initial conditions for the temperature and liquid compositions were found by taking the average of the values for the reactive zone in the conventional column given by Wang et al. [11] and a catalyst loading from Jacobs and Krishna [5]. Within 1.6 seconds the liquid composition of MTBE was 90 % of the equilibrium value and after approximately 2 seconds the chemical equilibrium was reached. This is deemed sufficiently fast in relation to the VFP of 10 seconds to justify the assumption of chemical equilibrium for the purpose of this study.

4. Comparison of conventional and cyclic reactive distillation of MTBE

In this section the conventional column based on Wang et al. [11] has been reproduced and a reactive cyclic column equivalent to the conventional is made with the models described above. The column design proposed by Wang et al. consists of 17 stages, of which 8 are reactive, and has both a liquid methanol and a vapour butene (nBut/iBut) feed. The overall conversion from column inlet to outlet of iBut was 90 % and the bottom product composition of MTBE was 99.2 mol%. For the equivalent cyclic column design the number of stages, feed specifications, pressure and pressure drop are kept constant. The desired bottom product purity of 99.2 mol% MTBE is kept as a constraint, while the other outputs, such as product flow rates, reactant conversion and top product composition, are not constrained. This is done since the product of interest is the MTBE in the bottom, while the top product is mainly inert n-butene and unreacted methanol and isobutene. This means that for the periodic operated column the product flow rates, reactant conversions and top products can increase or decrease compared to the conventional column as long as the bottom product purity is kept. In order to achieve the bottom product specification in the equivalent cyclic column the reflux and boilup ratios are adjusted.

When going from classical to cyclic operation of a distillation column two new variables are introduced: the duration of the VFP and the LFP, these needs to be specified. Here the cycle time is also used to describe the in- and outputs so that the liquid and vapour feeds are scaled with regards to the duration of the cycles.

$$L^F(cyc) = L^F(conv) \cdot t_{cyc} \quad [\text{mol}/\text{cyc}] \quad (15)$$

$$V^F(cyc) = V^F(conv) \cdot t_{cyc} \quad [\text{mol}/\text{cyc}] \quad (16)$$

Where the duration of the complete cycle is $t_{cyc} = t_{VFP} + t_{LFP}$ in seconds per cycle. With these scaled feeds, the same processing capacity as the conventional column in terms of the volumetric feed rate can be accommodated in the cyclic operation over a cycle time. The liquid feed will be introduced to the column during the LFP and the vapour feed continuously over the VFP.

4.1. Equivalent cyclic column design

A cyclic column equivalent to the conventional is made. When going from a conventional to a cyclic distillation process, as the reactive distillation for MTBE, all the column inputs are kept. That is, the same feed per cycle time, same feed concentrations and temperatures are kept. The column design in terms of rectifying, reactive and stripping stages etc. are also maintained. In order to ensure a high purity product output, here MTBE in the bottom, it is necessary to adjust the boilup and reflux. The MTBE reactive distillation has multiple steady states with both a low and a high state of conversion for isobutene as shown by Jacobs and Krishna [5]. The reflux and boilup should be chosen or adjusted to ensure the desired high state of conversion of isobutene. The column

specifications are shown in Table 3 for both the conventional and the equivalent cyclic column.

The boilup ratio was chosen as a low value that gives the high conversion state. A lower boilup ratio would result in low conversion of the reactants and a higher boilup ratio would lead to the product, MTBE, being sent up through the column as vapour. The choice of reflux must also be chosen carefully, as the reflux flow rate is equal to the liquid holdup on stage 2 after a LFP. The vapour flow over liquid flow ratio, V/L , calculated as averaged vapour flow from reboiler divided by the reflux plus liquid feed over a cycle, shows the internal vapour and liquid dynamics. In the cyclic column there is a higher amount of vapour going through the column, despite shorter time for vapour flow movement. The duration of the VFP and LFP must also be specified, here $t_{VFP} = 10$ s and $t_{LFP} = 5$ s are chosen. The duration of the LFP is assumed to be sufficient enough to allow the liquid to drain completely. In a pilot study by Maleta et al. [35] a draining period of 2 seconds was found to be satisfactory for complete draining. This was, however, a pilot study with a liquid feed of 50-100 L/hr, so in order to account for a higher liquid holdup in the reactive MTBE column the t_{LFP} is set to 5 seconds. As mentioned, the VFP is the period where vapour is sent up through the column while the liquid holdups are kept on each stage. During the VFP there is both mass and heat transfer between the phases and reaction taking place in the liquid phase. The duration of the vapour flow period should therefore be selected with care. Here it is set to $t_{VFP} = 10$ s, as the MTBE reaction is assumed to be described by chemical equilibrium, i.e. it is a fast reaction. The LFP is the period, where the liquid holdups are drained one stage down the column. Since no mass/heat transfer between liquid and vapour phase nor reaction takes place during this period the effect of the duration of the LFP is less noticeable than the duration of the VFP. However, t_{LFP} should be selected so that there is time for each stage to be drained and the liquid feed can be introduced to the column and products can be removed. Furthermore, the duration of the LFP also influences the liquid and vapour feed, see equations (15)-(16).

The temperature and composition profiles for the equivalent cyclic column are shown in Figure 2 compared to the conventional column.

The equivalent cyclic column is not optimally designed as it is also shown on the profiles in Figure 2, where especially the stages 12-14

Table 3
Conventional and equivalent cyclic column design specifications.

Parameter	Conventional column	Cyclic column
No. of trays (NT)	17	17
Rectifying stages	2	2
Reactive stages (NR)	8	8
Stripping stages	5	5
Condenser type	Total	Total
Reboiler type	Partial	Partial
Overhead pressure (P)	1110 kPa	1110 kPa
Column pressure drop (ΔP)	50 kPa	50 kPa
Boilup ratio (BR)		0.223
Reflux ratio (RR)	7	6.022
V/L (mol/cyc)/(mol/cyc)	0.529	0.617
Duration of VFP (t_{VFP})		10 s
Duration of LFP (t_{LFP})		5 s
<i>First feed (liquid)</i>		
Flow rate (L^F)	198 mol/s	2970 mol/cyc
Composition (x_i^F)	Pure MeOH	Pure MeOH
Temperature (T^{LF})	320 K	320 K
Feed to above stage (NF)	10	10
<i>Second feed (vapour)</i>		
Flow rate (V^F)	547 mol/s	8205 mol/cyc
Composition (y_i^F)	36 mol% iBut 64 mol% nBut	36 mol% iBut 64 mol% nBut
Temperature (T^{VF})	350 K	350 K
Feed to above stage (NF)	12	12

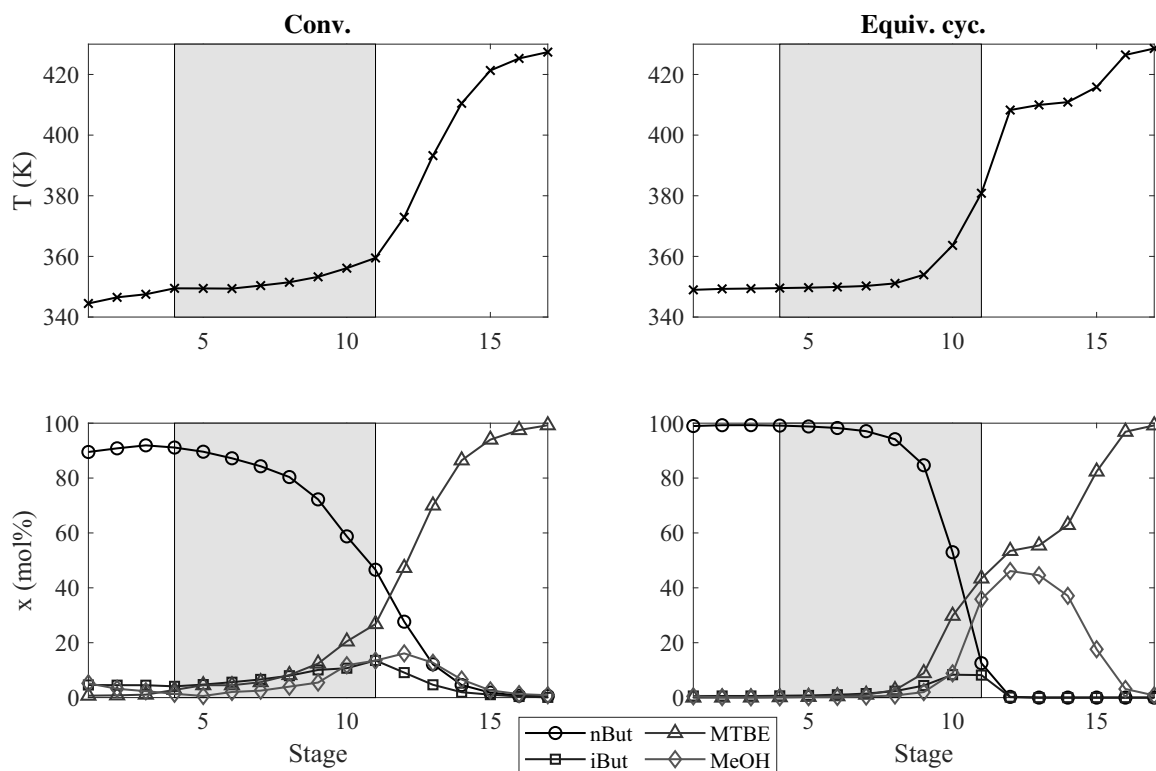


Fig. 2. Column profiles, temperature (top) and liquid composition (bottom), for the MTBE process in a conventional column (left) and the equivalent cyclic column (right) after a VFP.

seems to have low change in temperature and compositions compared to the conventional column. Figure 2 shows that there is a higher n-butene purity in the top product for the cyclic case than for the conventional. The explanation for this is that the cyclic column has a higher conversion of both methanol and isobutene, thus less reactants are lost in the product streams.

The heat of reaction was set to be constant at $\Delta H_n^{react} = -43.6$ kJ/mol, this gives a relatively small contribution to the energy balance in equation (3). For example for stage 11 in the cyclic column at time $t = 0$ the total value of the energy balance was found to be $\frac{dM_{11}^{h_{11}}}{dt}(t=0) = 1.66$ MJ/s. Of this the reaction heat contribution $\Delta H_{11}^{react} \sum R_{11,i}^{eq}(t=0)$ is only 1.41 kJ/s or 0.09 % of the total value of $\frac{dM_{11}^{h_{11}}}{dt}(t=0)$. It seems the effect of the heat of reaction is negligible for the MTBE case; however, the contribution to the internal column flows is rigorously accounted for.

Key results from the conventional and cyclic columns are shown in Table 4.

As shown in Table 4, the cyclic column has a significant lower energy requirement per cycle. Where the conventional column needs a continuous energy supply over the 15 seconds per cycle, the cyclic

Table 4
Summary of reactive distillation cases. The cycle time is 15 seconds, of which 10 seconds is the vapour flow period.

	Conventional Column	Cyclic Column
B (mol/cycle)	2670	2946
D (mol/cycle)	5835	5306
x_{nBut}^D (mol%)	89.5	99.0
x_{MTBE}^B (mol%)	99.2	99.2
χ_{iBut} (%)	90.8	98.9
χ_{MeOH} (%)	89.0	98.4
Q_B (MJ/cycle)	648	619
Q_C (MJ/cycle)	1004	771

column only has energy supplied and removed during the vapour flow period, which is 10 seconds in this case. There is a higher bottom output flow rate and a lower distillate flow rate for the cyclic case compared to the conventional. This is related to the conversions of the reactants, which are also higher for the cyclic case, meaning less reactants are removed from the column than for the conventional case. While the same bottom product purity of MTBE is reached in both cases, the cyclic column has a higher purity of n-butene in the top product.

The equivalent reactive cyclic distillation column is not based on an optimisation criteria, as can be seen in Figure 2, where the stripping stages 12-14 have little difference in composition and temperature after a VFP. The conventional column design, which was taken from Wang et al. [11] and was the basis for designing the equivalent reactive cyclic column in this paper, was previously presented by Jacobs and Krishna [5] and has been used in other papers for the conventional reactive distillation of MTBE [4,9,10].

With a reduction of both the reboiler and condenser energy requirements for the cyclic column, a more environmental friendly process is achieved. A reduction in energy means a lower operational cost. As can be seen in Figure 2 the number of stages in the equivalent cyclic column seems to be too high, as stages 12-14 have very little change in liquid composition and temperature. If some of these, or potential other stages, can be removed and the cyclic column can be made shorter the capital cost could also be reduced. It should be noted that reducing the number of stages in a distillation column usually means higher reflux and thus a higher operational cost.

When going from a conventional distillation process to a cyclic operation two additional design variables are introduced: the duration of the VFP and of the LFP. These variables must be accounted for in a degree of freedom analysis for control purposes. The variable t_{VFP} would be an interesting candidate for a controlled variable as it has a direct effect on the residence time for the liquid holdups.

In the following section the stage performance of the reactive stages will be investigated in more depth.

4.2. Analysis of the separation and reaction behaviour on selected stages

The reactive stages 4, 6, 9 and 11 are investigated in details in order to analyse the difference in operating the reactive distillation in a conventional column and a cyclic column.

Figure 3 shows the number of moles of MTBE per second per total molar holdup formed on stage 4, 6, 9 and 11 in the conventional case and the equivalent cyclic column case over a cycle. The figure also shows the liquid and vapour compositions of the reactants and products isobutene, MTBE and methanol. The conventional operation is in steady state, i.e. there is no change in how much MTBE is formed over time nor is there change in the compositions.

The liquid compositions of methanol and isobutene and the vapour compositions of isobutene and MTBE in stage 11 are almost equal for the conventional case. Note that the reaction rate in the conventional column stage 4 and 6 is not zero, but merely very low compared to the cyclic case. The production of MTBE in stage 9 is $1.83 \cdot 10^{-2}$ moles MTBE per cycle per total molar holdup for the conventional column during the 15 seconds per cycle. For the equivalent cyclic case, during a VFP, it was $2.66 \cdot 10^{-2}$ moles MTBE per cycle per total molar holdup in stage 9, during the 10 seconds of VFP per cycle. So with the equivalent cyclic column a significant increase can be seen in the overall formation of MTBE, which also explains the high conversions of isobutene and methanol in the cyclic column. For stage 4, $1.49 \cdot 10^{-5}$ moles MTBE per cycle per total holdup for the conventional and $1.17 \cdot 10^{-3}$ moles MTBE per cycle per total holdup for the cyclic column are produced. For stage 6 it is $3.89 \cdot 10^{-5}$ moles MTBE per cycle per total holdup produced for the conventional column and $1.55 \cdot 10^{-3}$ for the cyclic column. For these 3 stages, stage 4, 6 and 9, there is a higher production of MTBE per cycle per total holdup in the cyclic column compared to the conventional column. As shown in Figure 3 for stage 11 with the cyclic operation the equilibrium is surpassed and MTBE goes from being produced to being consumed. The conventional case has a production of $6.12 \cdot 10^{-2}$ moles MTBE per cycle per total holdup, while the cyclic case has a production

of $9.73 \cdot 10^{-3}$ moles MTBE per cycle per total holdup in stage 11. So while the top stages in the reactive zone shows an improvement in the production of MTBE for the cyclic case, the reaction in stage 11, goes from producing MTBE to consuming MTBE, thus reducing the overall production per cycle. The overall production of MTBE on stage 11 is still high compared to the production rate in the top reactive stages, such as stage 4 and 6.

In the reactive cyclic column liquid feed enters stage 10 during LFP, mixes with the holdup, and is then drained to stage 11 when a VFP is initiated. The vapour feed is introduced above stage 12, i.e. the first stage this vapour will come into contact with is the stage above, stage 11. For the cyclic operated column on stage 11 at the start of a VFP there is a liquid with high content of methanol and a vapour with a high concentration of isobutene.

In Figure 2 the degree of change in the liquid compositions over the reactive zone of the conventional case is lower than in the cyclic case. This also means the methanol in the liquid leaving the reactive zone of the cyclic column has a higher concentration compared to the conventional case. The cyclic operation have high tray efficiency compared to conventional operation, therefore, this high concentration of methanol can be stripped away before the liquid holdups reaches the reboiler. In the conventional case less methanol in the liquid enters the stripping section, thus less methanol needs to be removed from the liquid before the reboiler. With the reduced tray efficiency, compared to cyclic operation, this lower amount of methanol can still be removed in the conventional case.

For stage 11 in Figure 3 the liquid and vapour compositions are shown to follow the reaction rate for the cyclic column. In the beginning of the cycle methanol and isobutene reacts to form MTBE. Around time $t = 4$ s, when the reaction goes from producing to consuming MTBE, the liquid composition of methanol start to grow, while the composition of MTBE in the liquid slowly approaches a maximum. The isobutene in the liquid is almost constant, due to the constant vapour feed from below. The compositions in the vapour all increase over the cycle, due to the simultaneous reaction and separation as well as the continuous supply of

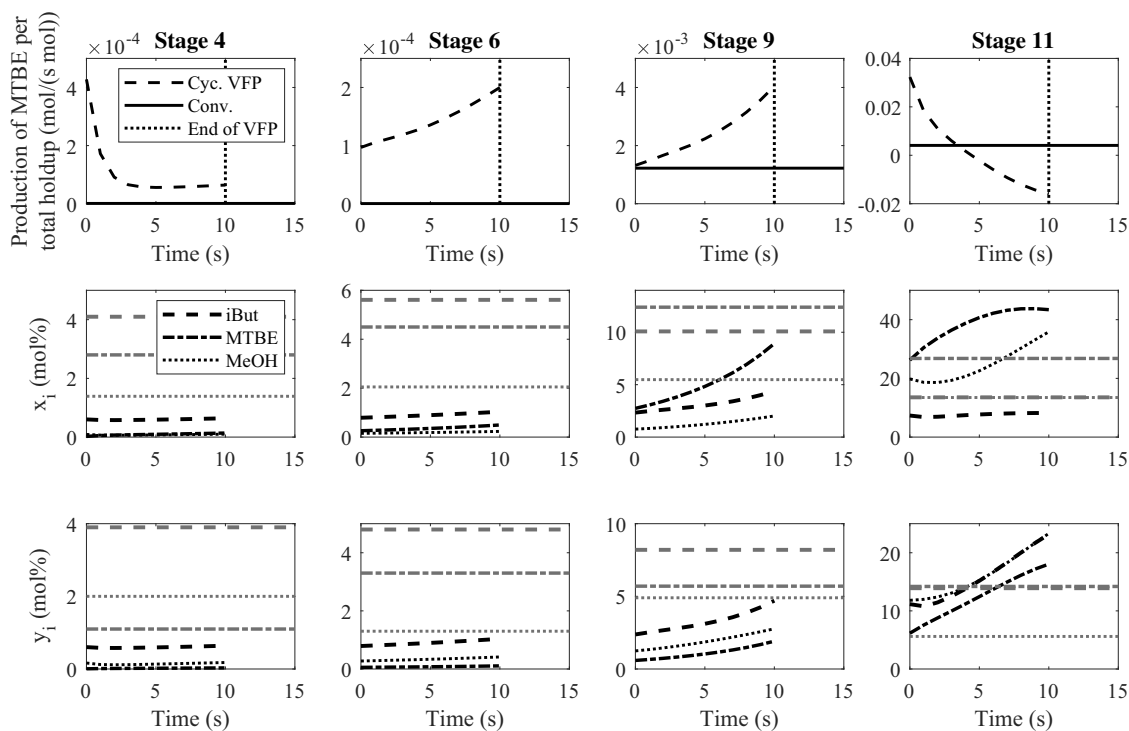


Fig. 3. MTBE produced in stage 4, 6, 9 and 11 for chemical equilibrium cases (top). Dotted line indicates the end of VFP. Middle plots shows the liquid composition, and bottom plots are the vapour composition. For middle and bottom plots, the black lines are for the cyclically operated column and the grey lines are for the conventional column.

vapour from stages below. In stage 4 and 6, there is only a low degree of reaction as is shown in Figure 3, which is also seen in the low change in compositions. In stage 9, there is a higher degree of reaction rate as also visible in the composition profiles.

For further analysis of the contributions from both the reactive part and the separation part of the mass balance, see equation (1), $\frac{dx_{n,i}}{dt}$, are plotted for the stages 4, 6, 9 and 11 in Figure 4 for isobutene, MTBE and methanol. The inert n-butene is not shown. Both the reactive part, the separation part and the combined contributions of $\frac{dx_{n,i}}{dt}$ are plotted. The change in liquid composition over time are found as $\frac{dx_{n,i}}{dt} = \frac{dM_{n,i}}{dt} / \sum \frac{dM_{n,i}}{dt}$, see equation (1).

It should be noted that the reactive part for MTBE in Figure 4 is the same as the reaction rates in the top rows of Figure 3 for the cyclic process. A negative $\frac{dx_{n,i}}{dt}$ means, for the reactive part that the component is being consumed and for the separation part that the component will go to the vapour phase.

Generally, it seems the reactive part of the mass balances are lower than the separation part in stage 4, 6 and 9. For the stages 4, 6 and 9 there are a clear order in the reactive and separation parts, with the reactive parts with the lowest contribution to the mass balance. For MTBE, where the reaction rate is positive in these three stages, the separation part is also positive, giving a large positive combined effect, meaning an increase in the liquid composition of MTBE. For the isobutene and methanol the reaction rates are negative, i.e. the reactants are consumed, the separation parts of these mass balances are positive, giving a combined effect somewhere between the reactive and separation parts.

In stage 11, where the reaction equilibrium being surpassed, significant changes in $\frac{dx_{n,i}}{dt}$ can be seen in Figure 4 as well. Looking at MTBE in stage 11 in Figure 4, the separation part of the mass balance is slowly increasing, i.e. more and more of the MTBE in the vapour phase is going to the liquid phase. When the equilibrium is surpassed and high concentrations of MTBE are present in the liquid holdup, the separation part of MTBE will slowly decrease, indicating less MTBE are moved from the

vapour to the liquid phase due to the amount of MTBE in the liquid. The reaction part goes from positive to negative, corresponding to the reaction going from producing MTBE to consuming it. The methanol composition in stage 11 also follows the observations made in Figure 3. At first there is a consumption of methanol, until it switches to being produced. The combined effects of the separation and reaction for the methanol in the liquid phase results in an initial reduction in the amount of methanol in the liquid phase. After this the amount of methanol in the liquid phase increases as also shown in Figure 3. Isobutene is starting by being consumed, with the methanol, and then is produced. However, the separation part shows that after the reaction equilibrium is reached the isobutene in the liquid goes to the vapour phase, since isobutene is a light component.

Looking at Figure 4, if the combined effects of the reaction and the separation in the mass balance is equal to zero, no change in liquid composition occurs. If it is positive the liquid composition will increase and if negative it will decrease. This follows the liquid compositions shown in Figure 3.

The analysis of the stage behaviour for reactive cyclic distillation of MTBE, shown in Figure 3 and 4, shows that both the reaction and separation plays important parts. This is evident even with the assumption of equilibrium reaction. For the bottom reactive stage 11, see Figure 3 and 4, it is clear that while reaction and separation occurs simultaneously they also have their own significant contribution to the stage behaviour. For example, as the production rate of MTBE decreases the mass transfer of MTBE to the liquid phase increases, but since the consumption rate of MTBE is higher than the mass transfer rate, the overall combined liquid composition is decreasing at the end of the VFP.

As previously mentioned non-reactive cyclic distillation can benefit a distillation process with higher tray efficiencies. This is due to the back-mixing of liquid holdups being eliminated in a cyclic operated process. This benefit in increased separation also benefits the reactive cyclic distillation. The combined separation and reaction in a periodic operated distillation process helps push the reaction to form more and more MTBE over the duration of a cycle, as the mass transfer between vapour and liquid phases occurs simultaneously with the formation of MTBE.

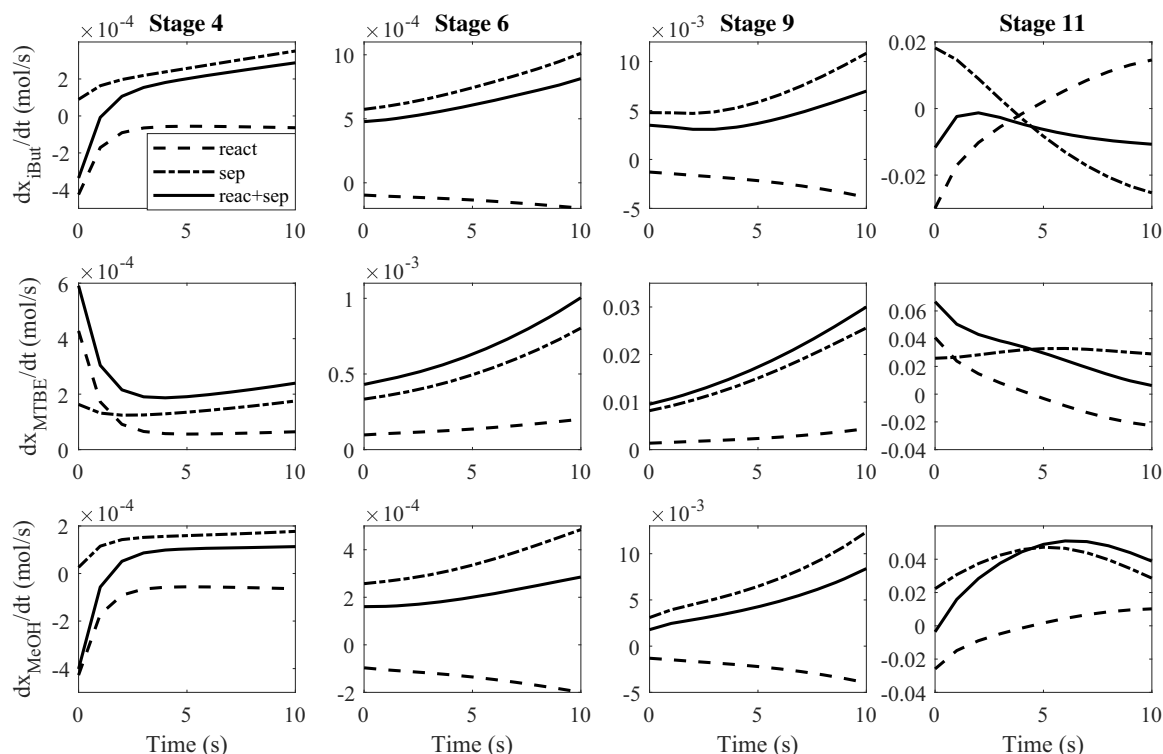


Fig. 4. Reactive, separation and combined contributions to $\frac{dx_{n,i}}{dt}$ for stage 4, 6, 9 and 11. Top plots are for isobutene, middle for MTBE and bottom for methanol.

With the high conversion in the cyclic case there is an issue with consumption of MTBE in stage 11 after approximately 4 seconds of VFP. Despite this the overall conversion with periodic operation was still considerably higher than with conventional operation.

5. Analysis of the effect of key design variables

For a reactive cyclic distillation column many variables must be considered in order to propose a design. First of all the number of stages, reactive and non-reactive, must be determined. Currently, there are no specific design methods for reactive cyclic distillation columns, however, the backwards integration method by Toftegård et al. [29] can be used for the stripping and rectifying stages, as also done by Pătruț et al. [14]. The reactive stages can then be estimated. With the number of stages determined there are still many design decisions to be made, the feed locations, feed specifications, reflux, boilup and duration of the VFP and LFP. If the cyclic column design is based on an existing reactive conventional column, such as the MTBE case shown here, the feed locations and reactive stages can be chosen as the same. Otherwise the feed locations can be found from other methods, e.g. graphical, heuristic or optimisation methods [26]. The feed flow rate, composition and temperature are usually determined from the process, i.e. desired throughput, conversion of reactants and outlets from processes before the reactive distillation column.

In order to better understand the reactive cyclic distillation process and identify the variables that are important to keep in mind, when designing a reactive cyclic distillation column, the key design variables must be found. When these key design variables are identified it is easier to study the effect of each and propose suitable settings for them. When the effect of each of these key variables are known, it is possible to suggest a column design, although not necessarily an optimised column design.

From the above results for the reactive cyclic distillation process, it can be seen that the cyclic column is overdimensioned. Figure 2 shows that there are three stripping stages, 12-14, where little change in compositions and temperatures occur. These stages could potentially be removed without significant loss in overall separation efficiency. The rectifying stages, 2-3, also seem to undergo very low change in composition and temperature. Regarding the reactive stages, it is clear from Figure 3 that the bottom stage in the reactive zone, stage 11, is not optimally designed since there is a negative production of MTBE, meaning a shift in the equilibrium towards the reactants. It is further evident that the MTBE produced per cycle per total holdup in stage 11 in the cyclic column is not as high as in the conventional case, due to the consumption of MTBE after approximately 4 seconds. However, this is the stage in the column where both the butene vapour feed and methanol liquid feed mixes, so it is an important reactive stage and it might not necessarily be a benefit to remove this reactive stage. In the top of the reactive zone, stage 4, there is very low production of MTBE, and as shown in Figure 2 and 3 the liquid compositions here do not change significantly either, so this might be a possibility for a reduction of the reactive zone.

The reflux and boilup ratios must also be determined. The reflux can almost be freely chosen to ensure a high purity product as long as the vapour flow rate from the reboiler is chosen carefully as well [14]. In a cyclic operated process the reflux flow is the liquid holdup on stage 2 after a LFP, i.e. the amount added to the column from the condenser over a LFP. The reflux will affect the boilup and vice versa. Thus in order to choose a reflux and boilup ratio, it might be a good idea to first determine a suitable reflux value, and then find the corresponding boilup that gives a high purity product. In the case of MTBE there are multiple states of reactant conversions [5], so it is necessary to keep this in mind when choosing the boilup and reflux and ensure the chosen values give the high state of reactant conversion. One approach is to initially keep the boilup and reflux ratios from the conventional column, and gradually decrease or increase them until the desired product purity is reached.

The duration of the LFP and VFP should also be chosen. The liquid flow period duration, t_{LFP} , is determined from the draining time of the stages. It should be at least set to the time it takes to drain the slowest draining tray to ensure all liquid is drained in the LFP, thus avoiding back-mixing of the holdups. When setting the t_{LFP} it must also be remembered that this is also where liquid feed and reflux are added and products are removed. The duration of the vapour flow period is more difficult to determine, one must take account of the reaction time and separation, while considering the liquid holdup and vapour flow rate. In the case of MTBE studied in this paper, it was assumed the liquid and vapour feed were scaled with regards to the cycle time, i.e. a higher cycle time means higher feed, which in turn means higher liquid holdups on the stages. The duration of the VFP will influence both the reaction and separation. A long VFP will mean more time for the reaction to occur. In the case of MTBE, which is a fast reaction, this meant that the MTBE will be consumed after approximately 4 seconds in stage 11. For slower reactions it might be a benefit to set a long VFP. A long VFP will also influence the separation, so more components will experience mass and energy transfer between the phases. This could lead to problems with more heavy components transferring to the vapour phase. On the other hand, a short t_{VFP} will reduce the reaction and separation time, so that there might not be a suitable conversion in the reactive stages or not enough mass transfer between the liquid and vapour phases.

A new column design of the cyclic operated reactive distillation process for MTBE is proposed based on the above observations. This new realisation is not an optimal design, however, it shows improvements with regards to reduction in column size without loss of product purity. For this new realisation it was decided to only keep the bottom product purity of 99.2 mol% as a hard constraint. Without a systematic method for designing a reactive cyclic distillation column the other outputs were allowed to have softer constraints, without decreasing the performance significantly in terms of conversion, top product purity and product flow rates. A total of four stages were removed by trial and error, of which one was a rectifying, one was a reactive and two were stripping stages. The liquid and feed locations are kept at the stage above and below the bottom reactive stage, respectively. The duration of both VFP and LFP were kept, despite the consumption of MTBE after approximately four seconds in stage 11. It was deemed that the overall conversion of the reactants in the reactive zone was still high enough to compensate for this. By keeping the duration of the VFP and LFP the improved column can be compared to the conventional and equivalent column. The boilup and reflux ratios were increased slightly compared to the equivalent cyclic column. The specifications for this new realisation is shown in Table 5.

The vapour-liquid ratio V/L for this improved cyclic distillation is slightly higher than the larger cyclic column in Table 4. With these specifications from Table 5 it was shown the target bottom product purity of 99.2 mol% for MTBE could be reached, without significant reduction in the other output parameters and conversions relative to the equivalent cyclic operated column. Figure 5 and Table 6 shows the column profiles and outputs of the improved realisation of the cyclic column.

As can be seen in Figure 5 the improved realisation of the cyclic column does not have the stripping stages with low degree of separation, as shown in the equivalent cyclic column profiles for stage 12-14 in Figure 2. This implies the stages where a low degree of separation and reaction occurs can be removed with a significant reduction in performance. Comparing the results from the smaller cyclic column in Table 6 and the cyclic column in Table 4 with 17 stages, it shows that while the bottom product purity of MTBE is maintained at 99.2 mol%, the reactant conversions, top product purity and bottom product flow rate are slightly reduced while the top product flow rate and energy consumption are slightly increased from reducing the number of trays.

For the design of this short cyclic column there is a trade-off regarding column size and energy consumption. The increase in energy requirement for the smaller cyclic column is, however, small

Table 5

Design specifications for the improved realisation of the cyclic distillation column.

Parameter	Improved cyclic column
No. of trays (NT)	13
Rectifying stages	1
Reactive stages (NR)	7 (3:9)
Stripping stages	3
Condenser type	Partial
Reboiler type	Total
Overhead pressure (P)	1110 kPa
Column pressure drop (ΔP)	31.25 kPa
Boilup ratio (BR)	0.225
Reflux ratio (RR)	6.047
V/L	0.619
Duration of VFP (t_{VFP})	10 s
Duration of LFP (t_{LFP})	5 s
First feed (liquid)	
Flow rate (L^f)	2970 mol/cyc
Composition (x_i^f)	Pure MeOH
Temperature (T^{LF})	320 K
Feed to above stage (NF)	8
Second feed (vapour)	
Flow rate (V^f)	8205 mol/cyc
Composition (y_i^f)	36 mol% iBut 64 mol% nBut
Temperature (T^{VF})	350 K
Feed to above stage (NF)	10

compared to the large cyclic column. Compared to the conventional reactive column the small cyclic column has a lower energy requirement. This new proposed realisation of a cyclic column for the MTBE production is not an optimal realisation, as is it derived from observations of the cyclic column equivalent to a conventional column. The backwards-integration method used by Pătruț et al. [14] could also have been used, however, this approach would only estimate the number of

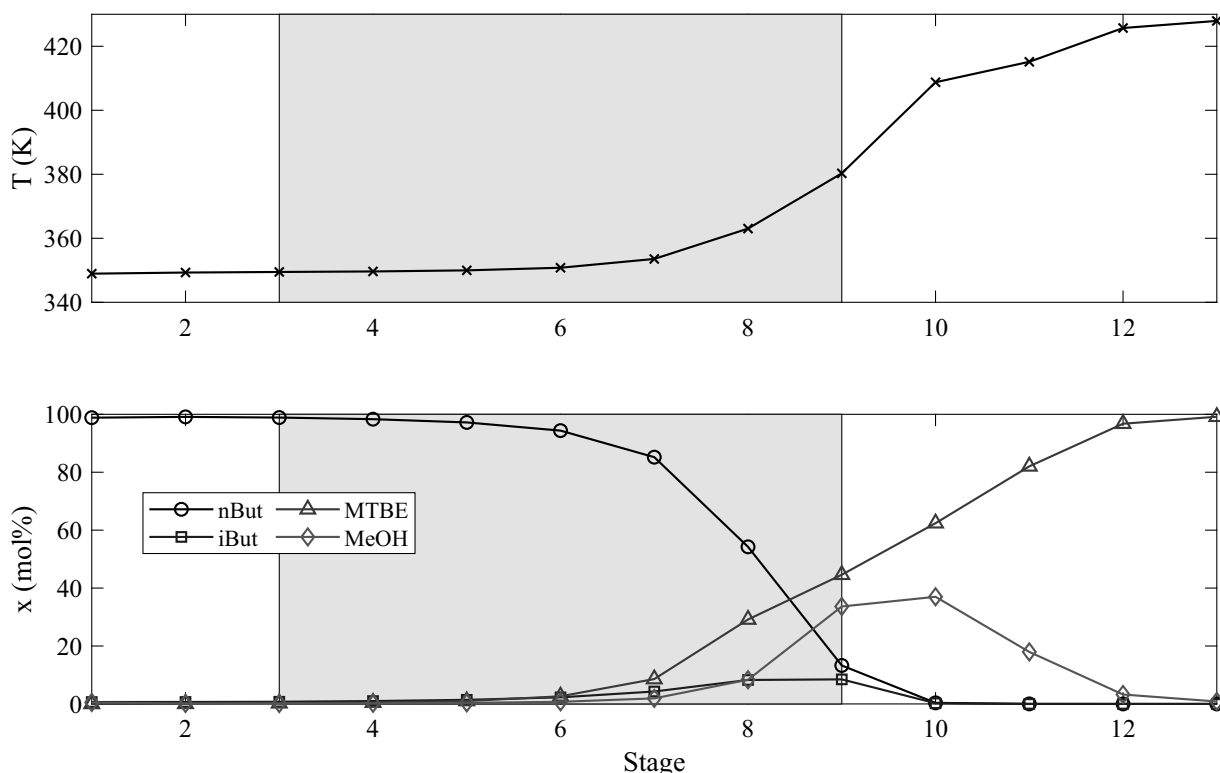
the non-reactive stages followed by an estimation or trial-and-error approach to find the number of reactive stages. In this case a good initial estimate would be to keep the number of reactive stages as in the conventional case and from that try to remove one stage at a time. Alternatively, if the total amount of catalyst necessary to achieve the overall conversion of reactants is known the number of reactive stages can be estimated by dividing the catalyst load with a suitable number of reactive stages. The study by Wang et al. [11], which was used as basis for this paper, does not provide catalyst load as it assumes an equilibrium reaction. Jacobs and Krishna [5], who studied the MTBE reactive distillation assuming reaction kinetics, mentioned catalyst loads of 1000 kg and 10^6 kg catalyst per stage.

It is expected that other reactive separation processes than the MTBE production can benefit from moving to periodically operated distillation. This was also the case for the DME production shown by Pătruț et al. [14]. However, based on the current available literature and the observations made in this study, it is difficult to make any general conclusions for other cases, as each reactive distillation case behaves differently.

Table 6

Summary of reactive distillation with the improved cyclic column. The cycle time is 15 seconds, of which 10 seconds is the vapour flow period.

	Improved Cyclic Column
B (mol/cycle)	2943
D (mol/cycle)	5313
x_{nBut}^D (mol%)	98.8
x_{MTBE}^B (mol%)	99.2
χ_{iBut} (%)	98.8
χ_{MeOH} (%)	98.3
Q_B (MJ/cycle)	625
Q_C (MJ/cycle)	775

**Fig. 5.** Column profiles, temperature (top) and liquid composition (bottom) for the proposed realisation of an improved cyclic column after the VFP.

6. Future perspectives for reactive cyclic distillation

The presented model for reactive cyclic distillation is a general model that can be used for different case studies. It is a general applicable model, with the possibility of incorporating either equilibrium or non-equilibrium reaction, multiple vapour or liquid feed locations and side draws. In this section some of future possibilities with the proposed model are discussed.

The presented dynamic reactive cyclic distillation model is suitable for other case studies. The model is intentionally made general and can handle fast reactions, described by reaction equilibrium as the MTBE case, and slower reactions that are described by reaction rate kinetics. Other conventional reactive distillation cases could also be investigated using the proposed model for cyclic operation, for example a case such as the production of methyl acetate, which can be described by rate kinetics, could be interesting to analyse in a cyclic operated distillation column. As mentioned previously the production of DME has been previously studied in a reactive cyclic distillation column [14], although with a stage model that neglects the energy transfer between the liquid and vapour phases.

The proposed dynamic model can be used for more in-depth column design with regards to finding and optimal design. With the stage performance analysis in this paper the key design variables have been identified for the design of a reactive cyclic distillation column. However, determining a design algorithm for a reactive cyclic distillation is not simple. In order to propose such a design method one would need to account for the simultaneous reaction and separation to determine the column specifications, i.e. number of stages, number of reactive stages and vapour and liquid reactant feed locations. The cyclic distillation specific design variables, that is the duration of the liquid and vapour flow period duration, must also be accounted for.

The design of a control strategy of a reactive cyclic distillation process, such as the MTBE production shown in this paper, is an extensive task. The proposed rigorous dynamic model for reactive cyclic distillation gives the possibility for accounting for many controlled and manipulated variables, such as feed and product specifications, energy consumption (condenser and reboiler duty) and the duration of the two flow periods, t_{VFP} and t_{LFP} . The design of such a control structure requires in-depth analysis of dynamic response to different input disturbances, degree of freedom analysis, controller pairing and tuning.

7. Conclusion

In this study a model for reactive cyclic distillation was presented, accounting for both mass and energy transfer between the liquid and vapour phases and applicable to either chemical equilibrium or rate kinetic reactions. For the presented case study the reaction has been assumed to be described as an equilibrium reaction. This implies a fast reaction, which will reach equilibrium at each time step. The separation is also assumed to be in equilibrium, meaning that a vapour liquid equilibrium model is used to describe the mass and energy transfer

Appendix A. Appendix

A1. Conventional reactive distillation model

A conventional steady state reactive distillation model has been set up and solved in order to ensure comparable results with data available from literature. The steady state model is based on the MESH equations [30,31] shown below.

The mass and heat model equations for a steady state reactive conventional distillation are as follows:

$$0 = V_{n+1} + L_{n-1} + L_n^F + V_n^F - V_n - L_n + \sum_{i=1}^{NC} R_{n,i}^R \quad (\text{A.1})$$

$$0 = V_{n+1}y_{n+1,i} + L_{n-1}x_{n-1,i} + L_n^F x_{n,i}^F + V_n^F y_{n,i}^F - V_n y_{n,i} - L_n x_{n,i} + R_{n,i}^R \quad (\text{A.2})$$

between the phases on each stage.

Here the production of MTBE from isobutene and methanol was investigated, assuming chemical equilibrium reaction. This study of a chemical equilibrium reaction is the first of its kind in a reactive cyclic distillation process. Based on an existing column design for the conventional reactive distillation of MTBE, the equivalent cyclic column was simulated. The results showed that with the cyclic column it was possible to lower the energy requirements, increase the conversions of the reactants and increase the throughput of the bottom product MTBE. The reboiler duty was reduced by 4.48% and the condenser duty by 23.21%. Looking at the column profiles, it seems the equivalent cyclic column is overdimensioned, which means there could be a potential for improving the cyclic process further.

By analysing the stage performance in the reactive section of the column, it was found that the overall production of MTBE was indeed higher in the cyclic case. This is due to the cyclic operation, which does not have back-mixing of the liquid holdups and thus have a higher separation efficiency, which in turn favours the desired reaction.

Despite the lack of a proper design method, an attempt was made to propose a new design of a cyclic column, based on the observations from the performance of the cyclic column equivalent to a conventional column. No systematic design method have been used, as the current methods for reactive cyclic distillation is still reliant on estimation of reactive stages. This new proposed realisation can give similar product specifications and conversions in a smaller column. Compared to the conventional column the energy requirement in the reboiler was reduced by 3.55% and in the condenser a 22.81% reduction in the energy requirement was achieved. Compared to the equivalent cyclic column a small increase in the energy requirement for the reboiler and condenser were necessary, 0.97% and 0.52% in the reboiler and condenser, respectively. While the number of stages were reduced and the boilup and reflux ratios slightly increased, the duration of both the LFP and VFP were kept. This was despite the issue in stage 11 of the equivalent cyclic column, where MTBE is consumed instead of produced after 4 seconds of VFP, since the overall reaction in the reactive zone still favoured high conversions.

In this paper, it was shown how the cyclic operation of the MTBE reactive distillation process affects both the reaction and separation. With the MTBE case study an equilibrium reaction was assumed, which simplifies the process and made the analysis of the effect of periodic operation on the reactive distillation easier. Cyclic distillation has previously been shown to have an increase in separation efficiency compared to a conventional distillation. This higher separation efficiency was also shown in the MTBE case, and furthermore it helped push the extent of reaction, so that a high conversion of reactants was reached.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

$$0 = V_{n+1}H_{n+1} + L_{n-1}h_{n-1} + L_n^F h_n^F + V_n^F H_n^F - V_n H_n - L_n h_n + Q_n + \Delta H_n^{reac} \sum_{i=1}^{NC} R_{n,i}^{rt} \quad (\text{A.3})$$

For the total condenser the following applies: $V_n = L_{n-1} = I_n^F = V_n^F = 0$, and $Q_n = Q_C$, and for the partial reboiler: $V_{n+1} = I_n^F = V_n^F = 0$, and $Q_n = Q_B$. The reboiler and condenser duties are calculated as:

$$Q_C = V_2(H_2 - h_1) \quad (\text{A.4})$$

$$Q_B = V_{NT}(H_{NT} - h_{NT}) \quad (\text{A.5})$$

The VLE equations (7)-(9) must also be accounted for.

This steady state model can be solved in MATLAB® with the *lsqnonlin* command or a similar algebraic equation solver. The *lsqnonlin* command is an algebraic least square nonlinear equation solver that can handle upper and lower boundaries for all the variables. For L_n , V_n and T_n the lower bounds are 0 and the upper bounds are infinite. The molar compositions must be between 0 and 1. The steady state solution is found for $NT(3 + 2NC)$ variables, i.e. L_n , V_n , T_n , $x_{n,i}$ and $y_{n,i}$. The total number of the above equations is $NT(4 + 2NC)$ with the total mass balance, see equation (Appendix A.1). The total mass balance is derived from combination of equations (7)-(8) and summation of equation (Appendix A.2). In order to solve this nonlinear algebraic equation system initial estimates for the output variables must be determined.

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