Understanding process intensification in cyclic distillation systems

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ARTICLE INFO

Volume 50, Issue 7,
July 2011, pages 655-664

ABSTRACT

The most effective separation possible in distillation columns takes place in the hydrodynamic regime where there is perfect displacement of the liquid and vapor streams. This can be achieved in distillation equipment with separate phase movement (SPM). Such an innovative route for process intensification in distillation is called cyclic distillation. The required process conditions are the lack of liquid outflow from the tray during vapor admission and the lack of liquid mixing in adjacent trays upon outflow of liquid. Remarkably, the throughput of such a column that operates in a controlled cycle mode is two or more times higher than the throughput reachable with conventional operation, at equivalent separation performance.

In this study, a theoretical stage model with perfect displacement is proposed and the theory of the process working lines is developed. An adequate mass transfer model is also described along with the mode of calculation of tray columns operating in the cyclic operation mode. Sensitivity analysis was used to determine the effect of the key model parameters. The theoretical developments were implemented at industrial scale and subsequent testing showed an increase in the separation efficiency of 2–3 times as compared to the standard process.

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1. Introduction

Process intensification in distillation [1] has received much attention in the last decades, following various integration routes such as: internal heat-integrated distillation columns [2], dividing-wall columns [3–5], reactive distillation [2,6] and even reactive dividing-wall columns [7]. Consequently, the design and control of such integrated systems is considered of utmost importance [2,3,6,8–10].

Another route for process intensification in distillation is cyclic distillation that presently receives revived attention. Cannon et al. [11,12] proposed an innovative method of operating various types of existing distillation towers, namely the controlled cycling distillation mode. Basically, a cyclic distillation column has an operating cycle consisting of two key parts: (1) a vapor flow period when vapor flows upwards through the column and liquid remains stationary on each plate, and (2) a liquid flow period when vapor flow is stopped, reflux and feed liquid are supplied, while the liquid holdup is dropped from each tray to the one below (Fig. 1). Remarkably, the throughput of such a column using the controlled cycle mode of operation is two or more times higher than the throughput reachable with conventional operation [13].

Although the Murphree vapor efficiency of a plate at any instant of time is assumed to be constant and equal to the local point efficiency, the effective plate efficiency based on the liquid-phase plate compositions is usually significantly greater than the point efficiency [14]. This leads to the improved separating ability achieved in controlled cyclic operation. A precise analogy exists between cyclic and conventional distillation with liquid-phase concentration gradients across the plates of the column. Basically, this analogy reduces to the substitution of time as the independent variable in case of cyclic distillation, for distance in the case of conventional distillation. Note that the concept could be further extended to catalytic cyclic distillation (CCD), a novel setup that can add – on top of the benefits of reactive distillation (RD) – also the ones of the cyclic distillation operation mode.

This study gives a clear overview of previous work on cyclic distillation, and presents a novel model of a theoretical stage with perfect displacement as well as the operating lines theory. Two relevant case-studies illustrate the theoretical findings and applications of our work.

2. Overview of cyclic distillation processes

The following comprehensive literature review gives – in historical order – a good overview of the previously reported studies on cyclic operation mode of various distillation systems.

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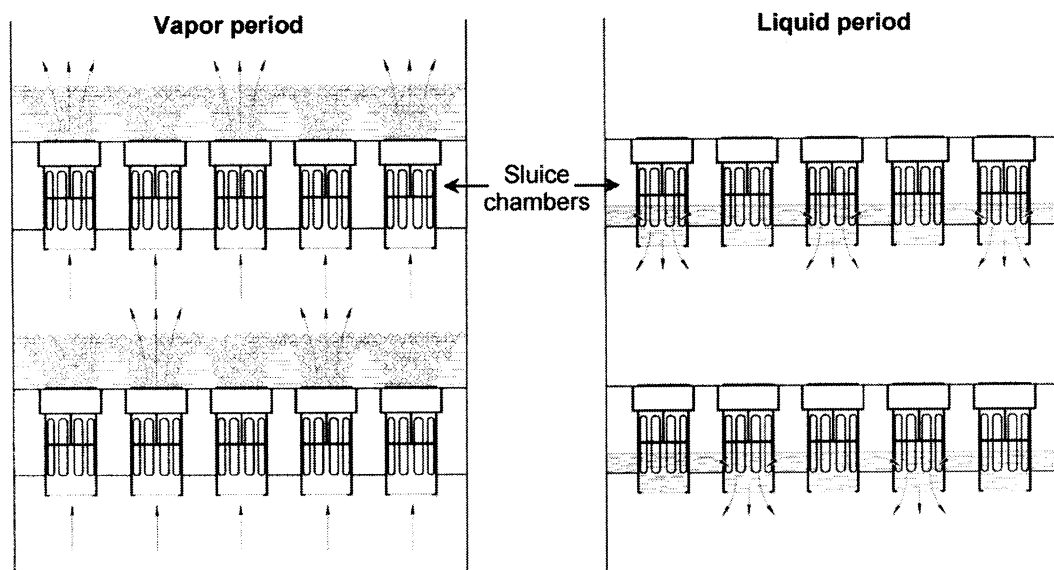E-mail addresses: Tony.Kiss@akzonobel.com, tonykiss@gmail.com (A.A. Kiss).

Fig. 1. Schematics of the cyclic mode operation: vapor period followed by liquid period.

Controlled cycling distillation, in sieve and screen plate towers, was proposed by Cannon et al. [11,12] as a new method of operating various types of existing equipment. This also permits new types of equipment to be designed for many conventional processes with key advantages such as: no downcomers needed on plates that are operated with controlled cycling and greater capacity than that attainable conventionally. Cannon et al. [11,12] also reported the results of applying controlled cycling to several types of plates in distillation towers. Remarkably, a 48% increase in the total vapor load was possible at a fixed pressure drop. Their data illustrate an interesting fact, namely that the maximum rate of the phase flow is not dictated by physical dimensions of the equipment and the properties of the system only, but it is also a function of the method of operation employed. Thus, the authors [12] believe that the capacity of existing bubble-cap plate towers as well as other types can be increased by use of controlled cycling.

Sommerfeld et al. [14] studied the controlled cyclic distillation and reported their computer simulations and the analogy with the conventional operation. At the same time, Chien et al. [15] provided an analytical transient solution and reported the asymptotic plate efficiencies. These solutions were used then to establish asymptotic expressions for the compositions at the pseudo-steady-state condition of the cycling column. A method of numerical iterative solution for a nonlinear equilibrium relationship was demonstrated, and a simplified graphical method for calculating the number of stages required for a given separation was presented.

Robinson and Engel [16] performed a theoretical analysis to demonstrate the advantages of cycled mass transfer operations, in which only one phase flows at any given time and where the phases use the same interstage flow passages during their respective flow periods.

Schrodt et al. [13] carried out a plant-scale study of controlled cyclic distillation. A dual-purpose column (15 perforated trays, 305 mm diameter) for testing the controlled cycling concept was designed, installed and operated successfully. The throughput for the column using the controlled cycle mode of operation was well over two times the throughput obtainable with conventional operation—at equivalent separation performance.

Gel'perin et al. [17] reported the similar operation of a bubble-cap fractionating column in a cyclic regime. Subsequently, Rivas [18] showed that simple analytical equations can be used to calcu-

late the ideal number of trays for cyclic countercurrent processes such as cyclic distillation. These equations represent an accurate solution of the set of ordinary differential equations that result from making material balances on each plate of a cyclic column. They simplify greatly the preliminary design of these columns since they are easy to use and similar to the well known Kremser–Souder–Brown equations that are applied in conventional processes.

Furzer [19] reported the discrete residence time distribution of a distillation column operated with microprocessor controlled periodic cycling. The fluid flow in a distillation column was studied by measurements of the discrete residence time distribution. The column was fitted with 5 sieve plates of 100 mm diameter, 14.8% free area, 6.1 mm hole diameter, and 635 mm plate spacing. The periodic control was obtained using a JOLT microprocessor system. An analysis of the discrete residence time distribution yielded the parameters in the (2S) model that describes the fluid flow. Modifications to the column internals were required to alter these parameters, if the maximum separation improvements were to be obtained.

Goss and Furzer [20] studied then the mass transfer in periodically cycled plate columns containing multiple sieve plates. A five plate distillation column (100 mm diameter) was used to study both the fluid mixing and the mass transfer separations of mixtures of methylcyclohexane and n-heptane, under periodically cycled conditions. Both the fluid mixing and mass transfer could be successfully analyzed using the (2S) model to describe the liquid movement in the column. However, only moderate improvements in separating ability could be obtained with sieve plates and packed sieve plate columns operated in the cycled mode.

Baron et al. [21] investigated the stepwise periodic distillation under total reflux operation. They found a new periodic operating mode where the liquid flow was manipulated directly, and not indirectly through pulsations of the vapor flow rate (as in controlled cycling). Baron et al. [21] presented also the theory of stepwise periodic distillation, under assumptions allowing a fair comparison with known results for controlled cycling. They showed that the two processes have the same asymptotic efficiencies for large values of the number of trays, while periodic stepwise distillation is slightly more efficient than controlled cycling for a finite number of trays. Soon after, Baron et al. [22] described the stepwise periodic operation of a distillation column in which a binary mix-

ture was separated. A simple but realistic model and a simulation algorithm were proposed for both stepwise periodic and controlled cycling operations. The results of an extensive parametric study of stepwise periodic operation were presented along those for ideal controlled cycling (i.e. no axial mixing). For reasonable tray efficiencies and difficult separations, stepwise periodic operation can compare favorably or be superior to ideal controlled cycling [22].

Thompson and Furzer [23] reported the hydrodynamic simulation and the experimental confirmation of periodic cycled plate columns. Szonyi and Furzer [24] investigated the periodic cycling of distillation-columns using a new tray design. The simulations of a periodically cycled columns predicted improvements in column performance of greater than 200% for systems with nonlinear equilibrium curves. The experiments of distilling various methanol-water mixtures validated the theoretical predictions for periodic cycling with a single plate. Moreover, a new tray design consisting of a sieve plate and inclined surfaces was introduced to get an effective liquid time delay. Remarkably, a wide range of operating conditions provided overall column efficiencies of over 140% [24].

Matsubara et al. [25] investigated the binary periodic distillation scheme with enhanced energy conservation. They proposed a composite scheme in which the beneficial features of the Cannon [12] and Baron et al. [21] schemes were combined with each other. The construction of the scheme and its superiority to conventional steady-state operation scheme was ascertained first through some numerical analyses [25]. Afterward, a laboratory-scale periodic distillation column using the idealized Cannon scheme was constructed and some basic experiments were carried out to examine its performance [26]. The system employed was the binary mixture water–methanol in a five-stage distillation column. The average vapor rate that is roughly proportional to the energy requirements rate, was 20–50% lower than the vapor rate required for achieving the same separation by use of a conventional continuous column.

Toftegard and Jorgensen [27] proposed an integration method for the dynamic simulation of cycled processes. The method is based on an efficient algorithm for dynamic simulation of non-singular periodically cycled chemical processes. The application of the algorithm was successfully demonstrated on a dynamic simulation of controlled cycling distillation. Other dynamic optimization methods can be applied to find the optimal profiles for all possible control variables. For an ideal ternary mixture separated into two or three fractions, it was demonstrated that appropriate control profiles can reduce the required energy supply compared to steady-state conditions [28].

More recently, Maleta et al. [29] have shown the use of a theoretical stage model with perfect displacement in a tray column with separate movement of the vapor and liquid phases. This current study presents the complete theoretical model, the operating lines theory as well as two relevant applications. Note also that during the past years the authors also published several patents based on the work described in this study [30–32].

3. Problem statement

According to the work of Lewis [33] the use of combinations of various hydrodynamic modes of liquid and vapor phases enhances the efficiency of component separation. The maximum effect is achieved upon perfect displacement of liquid and vapor, at single direction movement of the liquid on adjacent trays. Under such conditions, the Murphree efficiency of the tray may significantly exceed the local point efficiency and reach values of 200–300%.

Cannon et al. [11,12] suggested the way of phase interaction: during the passage of vapor through the column the liquid does not overflow from tray to tray, and upon liquid overflow it does not mix on adjacent trays (cyclic process). In a series of works by

Sommerfeld et al. [14,15] and Thompson and Furzer [23] it was shown that upon comparison of stationary and cyclic processes, the cyclic process is similar to the stationary process upon single-direction movement of liquid on adjacent contact levels and perfect displacement of liquid and vapor.

The aim of obtaining separation efficiencies above the theoretical stage proposed by McCabe and Thiele [34], promoted the development of constructive solutions—for stationary mode towards longitudinal sectioning on the tray, and for the cyclic regime to provision the liquid overflow on the trays with minimum mixing of liquid on the adjacent trays.

The problem is that in spite of the many papers tackling this topic (see also previous section) there is still no straightforward model describing the cyclic distillation process, and consequently there are no design methods for cyclic distillation columns. To solve this problem, we developed and present in this paper an adequate mass transfer model and a simple graphical mode for designing tray columns operating in a cyclic mode—thus providing valuable insight to the process intensification in a cyclic distillation process.

4. Process description

In the first attempts of industrial implementation, the mass transfer technology suggested by Cannon et al. [11,12] used the ordinary overflow trays accompanied by changeable or cyclic supply of contacting phases to the column. The use of conventional trays in a non-conventional (cyclic) operation mode was unsuccessful. As shown in the literature review, the subsequent creation of special contact devices allowed obtaining a broad range of the required technical solutions with various options of discrete and even uninterrupted flow inputs.

Therefore, in our humble opinion, the term of *separate phase movement* (SPM) reflects the essence of this phenomenon in the most integral manner and it may be used as a synonym to the term of the *cyclic distillation process*. Basically, the cyclic process of mass transfer in tray columns reduces to satisfying the requirements of the liquid flow dynamics: (1) Lack of the liquid overflow on the trays during the vapor supply period, and (2) Lack of mixing of liquids on adjacent trays during liquid overflow period (Fig. 1). The constructive solution of such tasks automatically brings to attention the enhancement of mass transfer efficiency and the reduction of energy requirement in such a distillation process. So far, the authors obtained a series of patents [30–32] that allowed the implementation of all advantages of cyclic distillation at industrial scale.

The algorithm of engineering the design of such a special tray is relatively simple. The lack of liquid overflow on the trays during vapor supply is achieved by using perforated trays while the vapor velocity exceeds the column flooding. The lack of liquid mixing on adjacent trays during liquid overflow is realized by means of a sluice chamber located under the tray. This installed system works as described hereafter. The liquid streams (e.g. feed supply, reflux) are continuously supplied to the corresponding tray. During the vapor supply period, the liquid does not overflow from tray to tray (in contrast to conventional operation) as the vapor velocity exceeds the column flooding. The vapor fed to the column controls the liquid overflow from tray to tray. When the vapor supply is cut for a few seconds, it allows the liquid to overflow from the tray to the sluice chamber. Subsequent vapor supply opens the sluice chamber and the liquid flows by gravitation to the empty tray below. Such sequence of actions takes place synchronically on all trays in the column. In practice, no complication related to increasing the number of trays was observed in the column operability.

Description of the liquid flow hydrodynamics can be clearly subdivided in two major stages: (1) vapor supply stage and (2) liquid overflow stage (Fig. 1). In the first case, during the mass transfer
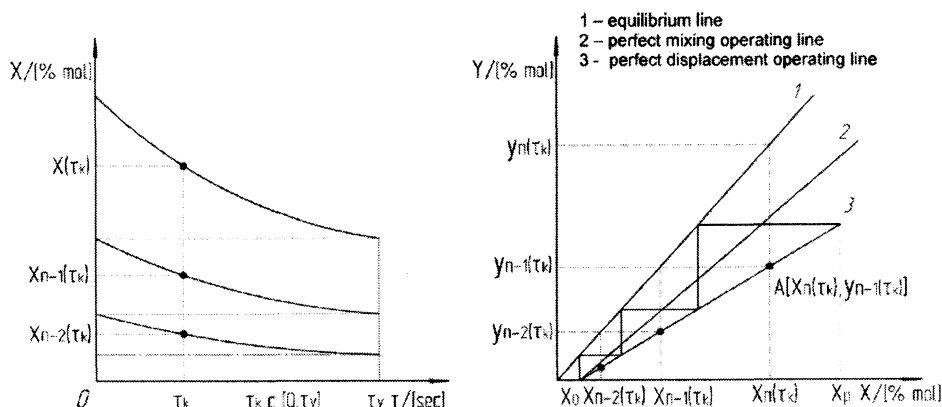
Fig. 2. Methodology of construction of the perfect displacement mode operating line: temporary concentration profiles in liquid (left) and depiction of the perfect displacement operating line in coordinates (right).

between vapor and liquid, the liquid is located on the tray only and it does not overflow from one tray to another. Hence, we can disregard the transfer of liquid to the tray below. The volume of liquid on the tray can be considered as a closed circuit hence not a single droplet of liquid leaves this volume. As the liquid inside this volume is perfectly mixed under the influence of the vapor flowing through, there is no gradient of concentration and temperature at a certain point in time. Moreover, all the liquid on the tray has the same residence time, and there is equal speed of movement of the liquid volume—which equals to zero in fact.

Such conditions are typical to only one hydrodynamic mode, the perfect displacement mode. This can be achieved also in actual circumstances, and not only in a hypothetic piston-flow. Therefore, during the transfer of vapor through the column (vapor period), the hydrodynamic model of the liquid flow on the tray in real circumstances is the perfect displacement model.

5. Mathematical model of cyclic distillation

5.1. Theoretical model

The formalized description of a tray column with separate phase movement is provided by the mathematical model of the process that makes use of the following equations.

(1) Mass balance of the volatile component (VC) on the contact stage, during the vapor supply:

$$\frac{dx_n}{d\tau_v} = -\frac{G}{H}(y_n - y_{n-1})$$ (1)

where n is the tray number, x_n is the molar fraction of VC in the liquid on the tray n, y_n is the mol fraction of VC in vapor leaving tray n, y_{n-1} is the molar fraction of VC in vapor coming from tray $n-1$, H is the amount of liquid on the tray (mol); G is the vapor flowrate (mol/s), and τ_v is the vapor supply time (s).

(2) Liquid flow hydrodynamics during the liquid period (liquid overflow from tray to tray):

$$x_n(0) = Fx_{n+1}(\tau_v) + (1 - F)x_n(\tau_v)$$ (2)

$$F = \frac{H_l}{H} \quad \text{and} \quad < F \leq 1$$

where F is the multiplication factor of liquid transfer delay, H_l is the amount of liquid holdup flowing from the tray (mol), and τ_v is the vapor supply time (s).

(3) Mass transfer kinetics, determined by the local point efficiency (E_{OG}):

$$E_{OG} = \frac{y_n(\tau_k) - y_{n-1}(\tau_k)}{y_n^*(\tau_k) - y_{n-1}(\tau_k)}$$ (3)

where τ_k is a random point in time: $\tau_k \in [0, \tau_v]$

(4) Equilibrium line (vapor composition as function of liquid composition):

$$y^* = f(x)$$ (4)

This system of equations can be also solved analytically (Robinson and Engel [16]). Consequently, the concentration profiles on each stage can be described as follows:

$$x_n(\tau) = e^{(-(Gm/H))\tau} \sum_{i=1}^{n} C_i \frac{((Gm/H)\tau)^{n-1}}{(n-i)!}, \quad i = \overline{1, n}$$ (5)

with the boundary condition:

$$x_i(0) = C_i$$ (6)

Note that for tray columns, the most widespread model is the theoretical stage introduced by McCabe and Thiele [34]. The model is based on the column material balance by distributed components and it is postulated as follows. (1) The concentration of the volatile component on the contact stage is constant. (2) The vapor leaving the stage is in equilibrium with the liquid leaving the same stage. Therefore, the hydrodynamic models of liquid and vapor flows are expressed as *perfectly mixed models*. The process operating line determines the concentrations of the distributed component in the liquid/vapor on each tray. Moreover, it is discrete and the coordinates of the operating line points (trays) in the $Y - X$ coordinates are given by $A(x_n, y_{n-1})$.

In this work, we use a similar technique in order to obtain the cyclic process operating line, as previously suggested by Maleta et al. [35]. Upon knowing the interim concentration profiles in the liquid and vapor on all trays, at a random point in time $\tau_k \in [0, \tau_v]$, one can determine the operating line point coordinates as: $A[x_n(\tau_k), y_{n-1}(\tau_k)]$.

Fig. 2 illustrates the methodology of constructing the perfect displacement mode operating line: temporary concentration profiles in liquid (left) and the perfect displacement operating line in coordinates (right). By changing the time points – $\tau_k \in [0, \tau_v]$ – one can find graphically any number of points referring to the operating line (line 3 in Fig. 3). Therefore, the operating line of the cyclic process is built on the basis of differential equations of the material balance by distributed component on the contact stages. It is drawn by definition as a line of points where the vapor rising from the tray below meets the liquid located on the tray above. The line
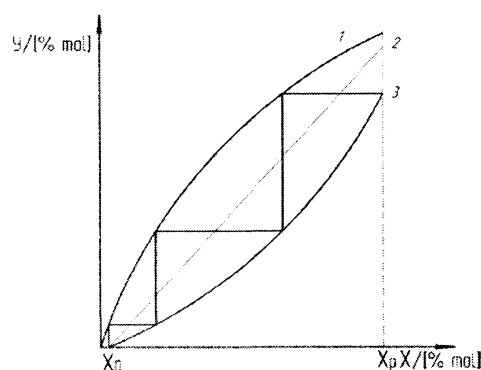
Fig. 3. Influence of model parameters on the position and shape of the operating line: (1) equilibrium line, (2) operating line (L/G), and (3) perfect displacement operating line $(F=1; E_{OG}=1)$.

is uninterrupted and straight for $y^* = mx$. The tangent of the perfect displacement operating line inclination is less than the values of L/G. Using this line one can determine the values of the concentration of the distributed component in vapor and liquid for each tray and any point in time.

The contact stage built on this line may be called a *theoretical contact stage of perfect displacement*, since its operation conditions are the same as those of the hydrodynamic mode of perfect displacement of liquid and vapor in a single-direction liquid movement on adjacent trays suggested by Lewis [33]. The difference between the cyclic and the stationary process consists in changing the coordinate system: for the cyclic process during vapor supply $dx_n/d\tau$, and for the stationary distillation process dx_n/dl, along the liquid movement route on the tray.

5.2. Hydrodynamic model

In the previous section, upon constructing the theoretical stage of perfect displacement we considered the case of lack of liquid mixing on adjacent trays, $F=1$. According to the theoretical stage model with perfect displacement, the liquid flow hydrodynamics upon overflow results in the distribution of components on contact stages during vapor supply, as given by Eq. (2). In other words, this is equivalent to the determination of C_i in Eq. (4). Therefore, the task of describing the imperfect flows is significantly simplified.

One can use the simplest – historically the first – cell model, in which the only parameter is the number of cells. To determine the actual stage of liquid mixing, one needs to study the distribution of separate liquid volumes according to their residence time on the tray—i.e. to determine what share of the liquid flow resides on the tray at a certain point in time. The data on the residence time distribution of separate liquid volumes on the tray are obtained by plotting the system disturbance source (tracer agent input) and analysis of the dependence curves of the tracer agent concentration on time $C(\tau)$ in the liquid outlet.

For the analysis of the mixing degree, one can use three values: (1) average residence time of the liquid on the tray, (2) dispersion of the residence time of the liquid on the tray, and (3) the number of perfect mixing cells. The modeling of the liquid flow hydrodynamics, in the range of $0 < F \leq 1$, allows obtaining the following dependencies:

(1) Average residence time of the liquid on the tray:

$$\bar{\tau} = \frac{\tau_v}{F} \tag{7}$$

(2) Degree of dispersion around the mean value:

$$\sigma^2 = 1 - F \tag{8}$$

(3) Hydrodynamic cell model:

$$N = \frac{1}{(1 - F)} \tag{9}$$

The validity of the obtained dependency of the cell model on the liquid flow hydrodynamics can be determined by studying their behavior upon extreme values of F. When $F=1$ the average residence time $\bar{\tau}$ is equal to the vapor supply time (τ_v), the dispersion is $\sigma^2 = 0$ and the number of cells is $N \to \infty$, so these are the *perfect displacement* conditions. Similarly, when $F=0$, the average residence time is $\bar{\tau} \to \infty$, the dispersion is $\sigma^2 = 1$, and the number of cells is $N = 1$, which are in fact the *perfect mixing* conditions.

When the number of cells is sufficiently high $(N \geq 10)$, it is considered that the cell model approximates very well the perfect displacement. In this case, the condition is met in the range of $0.9 < F \leq 1$. Therefore, the liquid flow hydrodynamics determines the theoretical stage—from the theoretical stage with perfect mixing to the theoretical stage with perfect displacement. For the cyclic operation mode, the physical interpretation of transfer of the theoretical stage with perfect displacement into the theoretical stage model results in an increase of the amount of liquid on the tray up to infinity, $N \to \infty$, and in this case the concentration of volatile component on the tray during the vapor supply time will not change.

6. Results and discussion

Sensitivity analysis is used as a powerful tool to explore the effect of several key parameters of the cyclic distillation model developed in the previous section. Moreover, two industrial case studies are presented to demonstrate the practical applications of cyclic distillation. Note that practically, cyclic distillation could be used in batch or continuous distillation, absorption and reactive distillation. However, some restrictions are imposed on the velocity of the gas (steam) in the column (0.3–2 m/s) and the load of liquid (1–30 m³/m²h).

6.1. Sensitivity analysis

Eqs. (1)–(4) represent a mathematical description of the cyclic distillation process. The model parameters include the values of the multiplication factor of liquid delay transfer, $0 < F \leq 1$, and the local point efficiency of contact $0 < E_{OG} \leq 1$. The mathematical model includes also the system of non-linear differential equations that can be solved only numerically. Any continuous phenomenon may be considered as a limit to which the discrete phenomenon tends to, if the interval between component events tends to zero. In this case, instead of describing the object with differential equations one can use the system of finite differences. The continuous signal (concentration of volatile component in vapor and liquid phases) can be presented as a sequence of discrete signals quantified simultaneously by level and time. This is the so called *double quantification* that presents the signal in the form of a sequence of numbers and their delivery at discrete moments of time. Using the above technique, a calculation algorithm can be created and implemented based on iterative methods. The solution of the mathematical description represents a limit of a certain sequence of approximations. The calculation results in the form of the number of trays, tray efficiency according to Murphree, distribution of concentration of volatile component in liquid and vapor on the trays and the operating lines in coordinates $Y - X$.

The influence of the equilibrium line shape on the position and shape of the operating line was applied to an equimolar binary mixture ethanol–water. The modeling results are presented in Fig. 4. The perfect displacement operating line (line 3, $F=1$, $E_{OG}=1$) is not a straight but a concave continuous line that is in fact a mirror reflection of the equilibrium line.
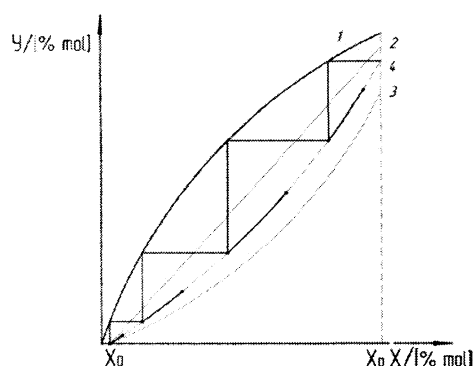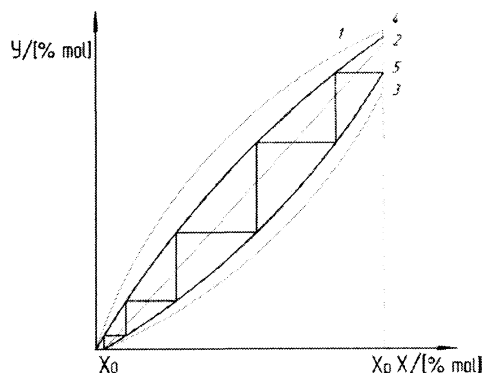
Fig. 4. Influence of model parameters on the position and shape of operating line: (1) equilibrium line, (2) operating line (L/G), (3) perfect displacement operating line ($F = 1$; $E_{OG} = 1$), and (4) perfect displacement operating line ($F \neq 1$; $E_{OG} = 1$).

Fig. 5. Influence on model parameters on position and shape of the operating line: (1) equilibrium line, (2) operating line (L/G), (3) perfect displacement operating line ($F = 1$, $E_{OG} = 1$), (4) kinetic curve, and (5) perfect displacement operating line ($F = 1$; $E_{OG} \neq 1$).

The liquid flow dynamics, expressed through the value of the multiplication factor of liquid delay transfer (F) influences the mass transfer process as follows. At $F < 1$ (line 4, Fig. 5), the operating line has a discrete nature, while the solid parts are determined by the dependency expressed in Eq. (2). When $F \to 0$, the average residence time of liquid on the tray tends to infinity ($\overline{\tau} \to \infty$), the mixture separation efficiency reduces and the operating parts are converged into a single point. In this case the process operating line coincides with operating line of perfect mixing with the inclination tangent L/G (line 2, Fig. 5). For linear equilibrium dependency $y^* = mx$, the above position is proven analytically if the VC concentration on the tray is not changed. According to the suggested calculation technique, this condition is met when the amount of liquid on the contact stage is $H \to \infty$, $F \to 0$, and $\overline{\tau} \to \infty$. Using Eq. (4) one can create an equation for the operating line:
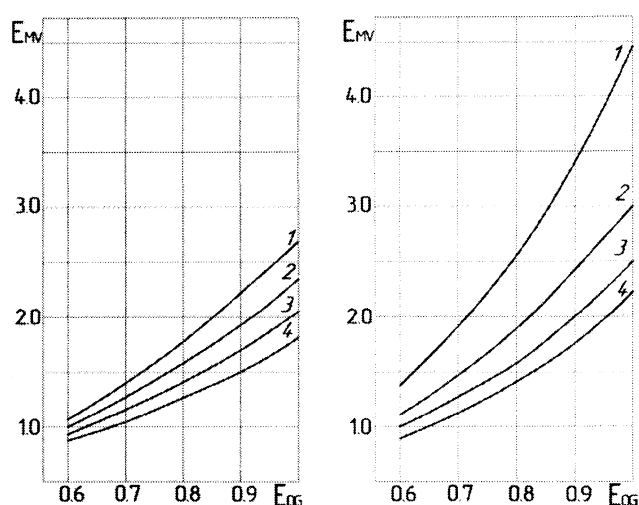
$$y = Ax + b \tag{10}$$

where

$$A = \frac{(x_n - x_{n-1})m}{x_{n+1} - x_n} \quad \text{and} \quad b = \frac{m(x_{n-1}x_n - x_n^2)}{x_{n+1} - x_n} \tag{11}$$

Fig. 6. Dependency of efficiency of stage according to Murphree E_{MV} from point efficiency of E_{OG}, for various stripping factor values (1: $\lambda = 2.2$, 2: $\lambda = 1.9$, 3: $\lambda = 1.6$, and 4: $\lambda = 1.3$) at $F = 0.7$ (left) and $F = 1$ (right).

Table 1
Influence of the diffusion potential factor ($\overline{\lambda} = mG/L$), local point efficiency (E_{OG}) and the liquid transfer delay factor (F) on the Murphree efficiency ($\overline{E_{MV}}$) and the number of trays (N) in a cyclic distillation column for ethanol concentration.

| L, kmol/h (feed)	X_F %mol (feed)	G, kmol/h (steam)	Y_F, %mol	L/G	$\lambda = mG/L$	E_{OG} (point effic.)	$F = H_l/H$	X_B, %mol (bottom)	X_D, %mol (distillate)	E_{MV} (Murphree efficiency)	N trays
617	3.29	152.78	0	4.04	2.2	1	1	0.003	13.269	4.91	3
617	3.29	138.89	0	4.44	2	1	1	0.001	14.61	4.29	4
617	3.29	125	0	4.94	1.8	1	1	0.003	16.22	3.64	4
617	3.29	111.11	0	5.55	1.6	1	1	0.002	18.25	3.19	5
617	3.29	97.22	0	6.35	1.4	1	1	0.002	20.866	2.77	7
617	3.29	83.33	0	7.4	1.2	1	1	0.003	24.345	2.35	10
617	3.29	111.11	0	5.55	1.6	1	1	0.002	18.25	3.19	5
617	3.29	111.11	0	5.55	1.6	0.9	1	0.002	18.254	2.68	6
617	3.29	111.11	0	5.55	1.6	0.8	1	0.002	18.255	1.82	7
617	3.29	111.11	0	5.55	1.6	0.7	1	0.003	18.252	1.48	8
617	3.29	111.11	0	5.55	1.6	0.6	1	0.003	18.257	1.12	10
617	3.29	111.11	0	5.55	1.6	0.5	1	0.002	18.267	0.79	13
617	3.29	111.11	0	5.55	1.6	0.1	1	0.003	18.898	0.1	84
617	3.29	111.11	0	5.55	1.6	1	1	0.002	18.25	3.19	5
617	3.29	111.11	0	5.55	1.6	1	0.9	0.001	18.258	2.81	6
617	3.29	111.11	0	5.55	1.6	1	0.8	0.002	18.253	2.45	6
617	3.29	111.11	0	5.55	1.6	1	0.7	0.004	18.246	2.13	6
617	3.29	111.11	0	5.55	1.6	1	0.6	0.002	18.225	1.89	7
617	3.29	111.11	0	5.55	1.6	1	0.5	0.004	18.249	1.67	7
617	3.29	111.11	0	5.55	1.6	1	0.1	0.001	18.388	1.05	12
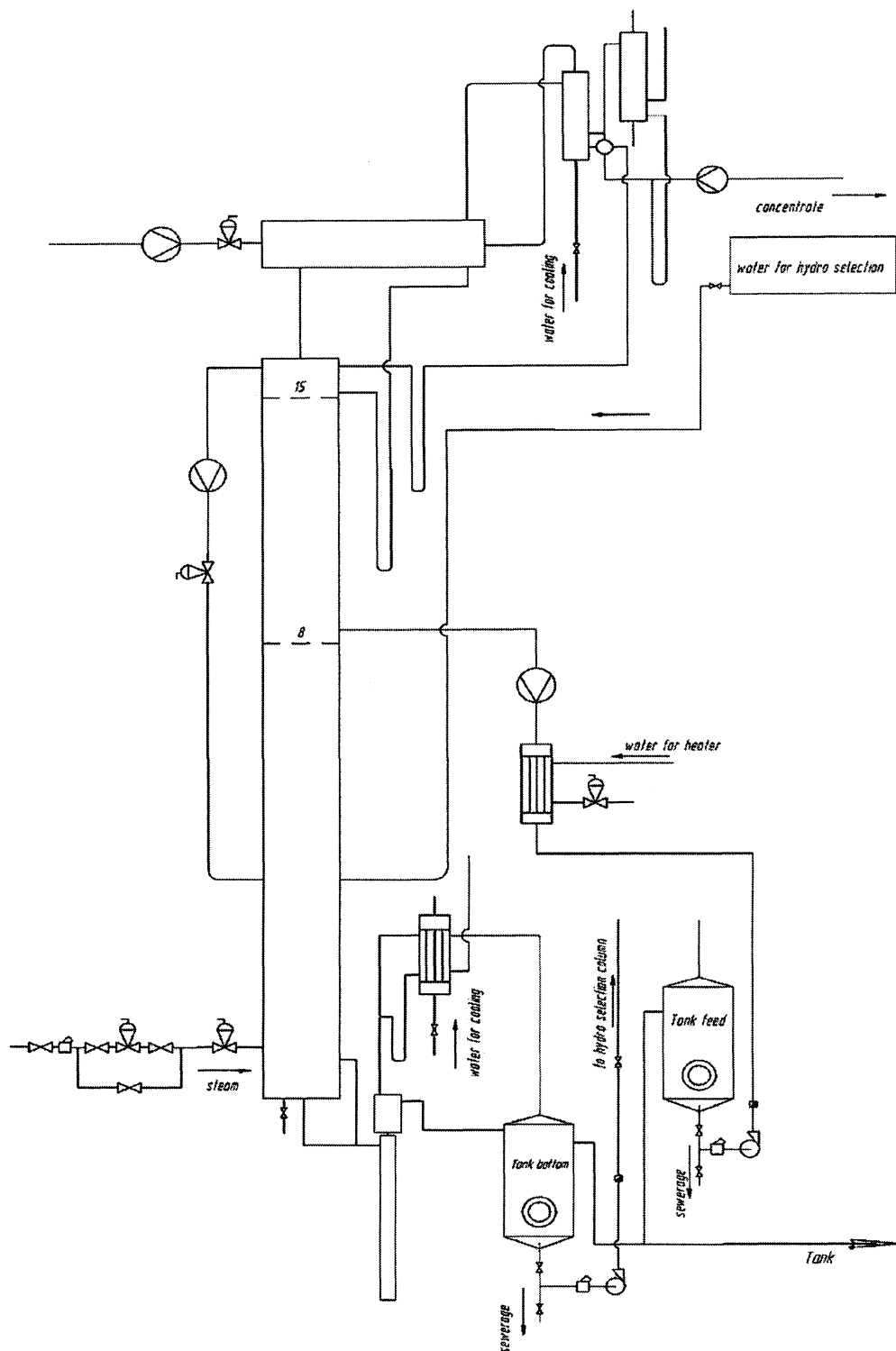
Fig. 7. Flowsheet of a cyclic distillation column for concentration of impurities.

By means of serial transformations, it is clear that when $F \to 0$ the tangent of this line is equal to L/G at any values of τ_k in the interval $\tau_k \in [0, \tau_v]$. The limit is given by:

$$\lim_{F \to 0} A = \lim_{F \to 0} \frac{mF}{a\tau_v} = \frac{mFL}{mGF} = \frac{L}{G}, \quad \tau_k \in [0, \tau_v] \qquad (12)$$

The leading role in the separation process is played by the local point efficiency value (E_{OG}). According to Fig. 6 it becomes clear that E_{OG} influences not only the degree of equilibrium – this known fact is used upon calculation of stationary process columns – but also the position of the operating line. In view of E_{OG} reduction, the kinetic curve 4 and the operating line 5 get close to each other thus

Table 2
Impurity content (ppm) in the feed and product streams for a capacity of 30,000 l/day.

Component	Group	Hydro selection column $D = 1000$ mm, 56 trays, $W = 550$ kW			Column concentrating the impurities, cyclic mode $D = 400$ mm, 15 trays, $W = 50$ kW		
		Feed	Bottom	Top	Feed	Bottom	Top
Ethylic ether	Ether	–	–	0.223	0.223	–	1.404
Acetic aldehyde	Aldehyde	88.29	0.461	660.38	660.382	0.36	17730
Methyl acetate	Ester	6.597	–	103.72	103.727	–	2394
Acetone	Ketone	0.727	–	7.3	7.3	–	192.2
Ethyl acetate	Ester	261.5	–	3806	3806.69	–	94527
Methanol	Alcohol	0.038	0.005	0.15	0.150	0.009	1.94
2-Butanone	Ketone	–		5.38	5.383	–	115.37
2-Propanol	Alcohol	5.77	1.339	75.17	75.178	2.93	1796
Isobutyl acetate	Ether	2.00	0.393	57.85	57.856	0.17	1465
1-Propanol	Alcohol	13762	2289	83.76	83.763	80.04	1192
Croton aldehyde	Aldehyde	0.655	0.075	5.22	5.226	0.201	143.6
Isobutyl alcohol	Alcohol	23,476	2661	84.64	84.642	139.86	57.6
Isoamyl acetate	Esther	–	–	57.17	57.175	–	1272
1-Butanol	Alcohol	130.4	18.72	–	–	0.744	6.62
Isoamyl alcohol	Alcohol	42,982	4295	3.43	3.431	205.64	78.49
1-Pentanol	Alcohol	11.82	1.193	–	–	–	3.64
1-Hexanol	Alcohol	20.20	1.936	–	–	0.142	0.26
Benzaldehyde	Arom. aldeh.	6.42	0.809	–	–	0.309	–
2-Phenyl ethanol	Arom. alcohol	518.5	42.43	–	–	1.088	–

reducing the separation efficiency. The ultimate position of both lines at $E_{OG} \rightarrow 0$ will be the operating line L/G.

Fig. 6 presents the quantitative characteristics of the cyclic process in the form of dependency of the Murphree efficiency (E_{MV}) of the tray on the local point efficiency (E_{OG}), the liquid transfer delay factor (F) and the diffusion potential factor ($\lambda = mG/L$).

The Murphree efficiency (E_{MV}) continuously increases, subject to the increase of E_{OG}, F, and λ. When $F \rightarrow 0$, the Murphree efficiency tends to the local point efficiency ($E_{MV} \rightarrow E_{OG}$). The obtained results are in line with the theoretical stage model when the point efficiency and the Murphree efficiency of the tray have the same value. Significant differences between the efficiency of the stationary and the cyclic distillation processes can be observed at higher values of $F \rightarrow 1$, and $E_{OG} \rightarrow 1$. The conclusion points to the right direction in the engineering developments of contact devices for cyclic distillation processes. The influence of model parameters on efficiency is clearly illustrated by the analysis of the mass transfer rate equation:

$$n_A = k_c A \ \Delta c_A \tag{13}$$

where A is the effective mass transfer area, k_c is the mass transfer coefficient, and Δc_A is the driving force concentration difference.

The local point efficiency (E_{OG}) determines the product $k_c A$, while the value of λ along with the multiplication factor of liquid delay transfer F determine the process driving force Δc_A. Obviously, the increase of each term of the right side of the mass transfer rate equation results in an increase of the amount of mass transferred from one stage to another.

6.2. Case studies

6.2.1. Modeling of an ethanol–water stripping column

In this section we briefly describe as case study the modeling of a cyclic distillation column implemented at industrial scale in the food industry (Lipnitsky Alcohol Plant, Ukraine). The cyclic distillation column described hereafter acts mainly as a stripper that increases the alcohol concentration to a higher grade. In the beer production process, a mixture of mainly ethanol–water is obtained by fermentation. Here we model the stripping (beer) column for the real plant production of 30,000 l/day ethanol food grade. There are

also additional components (~30 impurities) but these constitute less than 0.2 mol% in the feed stream.

The concentration of alcohol in the feed stream is 10 vol%—equivalent to 3.29 mol%. The feed stream is supplied on the top tray of the cyclic distillation column (stripping column), while direct steam injection is used in the bottom of the column. The specification for the ethanol concentration in the top distillate varies between 13 and 24 mol%, with a typical value of ~18.25 mol%, while the concentration of ethanol in the bottom product must not exceed 0.004 mol%. For this system we carried out the simple modeling of the cyclic distillation column, based on the theoretical background presented in this study.

Table 1 illustrates the influence of the diffusion potential factor ($\overline{\lambda} = mG/L$), local point efficiency (E_{OG}) and the liquid transfer delay factor (F) on the Murphree efficiency ($\overline{E_{MV}}$) and the number of trays (N) in a cyclic distillation column for ethanol concentration. Consequently, a lower number of trays and a higher efficiency are possible when the perfect displacement mode of operation is achieved.

6.2.2. Column for concentration of impurities

The column for concentrating impurities is also part of an industrial plant producing food grade alcohol (Lipnitsky Alcohol Plant, Ukraine). Fig. 7 shows the flowsheet of the ethanol concentration section, with the cyclic distillation column as the key operating unit. The wastes from this column are 5% of capacity of the plant. The column concentrating the impurities recycles waste back to the plant. Remarkably, the wastes of this column are only 0.5% of the plant capacity, so an additional alcohol output (4.5% of the total plant capacity) is possible.

Note that the hydro-selection column and the column for concentrating impurities are the same type of column, performing the same task of removing the volatile components, while sharing identical impurities and working under the same conditions. The main difference between them lies in the fact that the concentration of impurities in the cyclic distillation column is much higher than in the hydro-selection column. This makes it possible to increase the yield of the desired product. The efficiency of both columns is compared under conditions close to the ones determined by Fenske. For both columns, the reflux ratio is about 50 mol/mol. Table 2 presents the concentration of impurities (ppm) in the liquid stream for the

hydro-selection column and also for the column concentrating the impurities.

For example, a simple comparison of the key components listed in Table 2 shows that in the conventional hydro selection column (56 trays) the concentration of acetic aldehyde in the bottom is 0.461 ppm and in the top is 660.38 ppm. In case of the cyclic distillation column (15 trays) the bottom concentration of acetic aldehyde is 0.36 ppm while the top concentration reaches 17730 ppm. A similar trend is observed for the other components in the hydro selection column: methyl acetate (conventional: bottom 0 ppm and top 103.72 ppm, cyclic distillation: bottom 0 ppm and top 2394 ppm), acetone (conventional: bottom 0 ppm and top 7.3 ppm, cyclic distillation: bottom 0 ppm and top 192.2 ppm), ethyl acetate (conventional: bottom 0 ppm and top 3806 ppm, cyclic mode: bottom 0 ppm and top 94527 ppm). According to the reported industrial data (Lipnitsky Alcohol Plant, Ukraine) we can conclude that the separation efficiency in the cyclic distillation column (15 trays) is much higher as compared to the conventional bubble cap trays column (56 trays)—exceeding 200–300%.

The two industrial case studies included here demonstrate that cyclic distillation could be considered now as proven technology. Whenever process intensification methods are introduced, more challenging and complex control might be required. However, from the standpoint of practical control of the process, cyclic distillation is relatively simple and robust—similar to conventional distillation. Additional optimal control (dynamic optimization) problems could be conveniently solved by employing model based control techniques such as Model Predictive Control [36–40], but this is out of the scope of the current study.

7. Conclusions

The novel model of a theoretical stage with perfect displacement and the operating lines theory proposed in this work provide significant insight in understanding process intensification in cyclic distillation, and make available adequate tools for designing tray distillation columns operated in a controlled periodic mode.

The process operating line is a continuous concave line that reflects the shape of the equilibrium line. The mixing of liquid during liquid overflow from tray to tray enhances the separation efficiency. The operating line bears the discrete nature and at its limit, upon perfect mixing, can be approximated as the operating line L/G. The mass transfer kinetics expressed through the local point efficiency (E_{OG}) influences not only the position of the kinetic curve but also the position and the shape of the operating line. The ultimate position of both lines at $E_{OG} \rightarrow 0$ is the operating line L/G. The material differences between the efficiency of the stationary and the cyclic processes are observed at high values of $F \rightarrow 1$, and $E_{OG} \rightarrow 1$. The Murphree efficiency of a tray continuously increases, subject to the increase of the local point efficiency, stripping factor and hydrodynamic conditions of liquid overflow on the trays.

The mass transfer mode described in this work has several features that compare it favorably against the conventional steady-state one. The separation efficiency does not depend on the diameter of the column. The load of a column does not lead to an increase in the hydraulic resistance, as the quantity of a liquid on a plate remains constant while only the cycle frequency is being changed. The effect of secondary self-evaporation of a liquid is observed. Moreover, the mass transfer technology with separate movement of phases (SPM) has more degrees of freedom that contribute to a better process control. The introduction of this mass transfer mode at industrial scale can provide considerable benefits in terms of:

- Lower capital expenditure (CapEx) due to the lower number of trays required.
- Reduced energy requirements and significant savings in operating costs (OpEx).
- Increased quality of the products, due to higher separation efficiency.
- Higher yield and equipment productivity as compared to conventional distillation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cep.2011.04.002.

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