I&EC research
Industrial & Engineering Chemistry Research

Article

pubs.acs.org/IECR

Batch Distillation Targets for Minimum Energy Consumption

Nana Y. Asiedu,* Diane Hildebrandt,* and David Glasser*

Centre of Materials and Process Synthesis, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private bag x3, Wits 2050, Johannesburg, South Africa

ABSTRACT: Distillation technology, which is applied in most chemical and process industries in general, is an energy-intensive process, and this has a significant effect on the overall cost of production. Batch distillation, in particular, is one of the most important unit operations for small-scale production of specialty and fine chemicals. This unit operation is a strong unifying factor and the main support of pharmaceutical and perfume industries. This paper investigates a novel approach of minimizing energy consumption of a simple conventional binary batch distillation process by applying the attainable region theory for a binary batch boiling process. The fundamental processes considered are boiling and mixing. It is shown that the trajectory of a simple batch distillation process is convex in the concentration−energy space and that there is no room for minimizing energy consumption by any simple mixing policy.

■ INTRODUCTION

In its latest report, the intergovernmental panel on climate change warns that inefficient use of fossil fuels pose a threat to continued economic growth and prosperity. Even China is now talking about slowing the pace of its economic growth in order to rein in its enormous energy consumption and halt environmental degradation.[1] For all branches of industry and trade, both public and private-sector, the fastest and most economical sustainable path to greater climate protection and security of energy supply is to conserve energy by making greater use of existing and new high efficiency technologies. For purely economic reasons, it is imperative that industrialized countries increase their energy productivity, market energy efficiency, and cutting-edge technologies; if we fail to do this at this time, the global economic growth engine will grind to a halt. This is why the Hannover Fair 2007 created the world energy dialogue, a central forum designed to promote important energy technology innovations and pressing issues of energy policy at the highest levels of industry and government. Energy-efficient technologies translate directly into improved climate protection. Energy cost and the ability to conserve energy will soon become critical success factor for industries.[1]

Maximizing energy efficiency will, thus, become crucial to the competitiveness of industrial productivity.[1] Distillation operations are responsible for about 40% of the energy use in the chemical process industries. The technology that can reduce this energy requirement significantly will represent a major breakthrough in energy efficiency and give significant competitive edge to the companies that adopt it. Heat-integrated distillation columns are such a technology. By combining rectifying and stripping columns in an annular arrangement so that they exchange heat along their lengths and elevating pressure in the rectifying, highly significant energy savings can be achieved. However, despite the obvious potential, this very promising concept has not yet developed into successful industrial-scale applications. This is partly because it is difficult to test its applicability to specific mixtures to be separated, leading to a high perceived risk in deploying such innovative technology. In particular, the practical deployment of heat-integrated distillation columns technology is hampered by the difficulty of proving that it is possible to start up and operate the unit as intended. There is a relatively narrow window of feasibility operation, outside of which the heat-integrated distillation columns systems is either not fully efficient or suffers from liquid drying in certain regions. About 50% of industrial processes,[2] and chemical production,[3] are batch processes. Energy consumption of production processes contributes significantly to overall resource use. Moreover, about 75% of man-made air pollution is caused by energy use.[4] Therefore, minimizing energy consumption is listed as the sixth principle of green chemistry.[5] The chemical industry is a large and, in certain sectors, intensive user of energy. Chemical industries in North America accounted for about 20% of the total manufacturing primary energy consumption in 1994 (about 5.4 EJ);[6] this value is even greater if oil and gas are added. Thus, the U. S. chemical industry sets in their "vision 2020" the clear target to reduce energy consumption of chemical production and to improve energy efficiency.[7] Energy consumption of plants engaged in continuous productions has been investigated extensively in the past by pinch technology.[8] Similar methods for batch production are not yet well established. Other studies account for time-varying temperatures[9] and rescheduling.[10] The use of these methods in batch production is limited because most of them are considered too complicated, lengthy, demanding, and complex to be of practical interest for most of the cases encountered in batch productions.[2] The fact that energy cost amounts to about 5−10% of total production costs from common chemicals produced in batch operation[11] limits the effort undertaken in achieving high energy efficiency. Energy models for batch plants are lacking in industry. It is known that energy consumption is related to production output, but exactly

Received: July 9, 2013
Revised: January 26, 2014
Accepted: January 27, 2014
Published: January 27, 2014

 © 2014 American Chemical Society

where energy is used is not known. Energy consumption models are therefore needed for providing consumption forecasts to the energy supplier and for calculating total production costs. A helpful overview of energy consumption and management in batch production is provided by Grant.[12]

OBJECTIVES

This paper discusses how the attainable region concept could be used in optimizing energy consumption in simple binary batch distillation process.

BRIEF LITERATURE REVIEW OF THE ATTAINABLE REGION (AR) THEORY

The attainable region (AR) concept has successfully been used simultaneously to solve optimization problems and in process synthesis formulations for reactor systems. The AR theory considers all fundamental processes involved in a system (e.g., reactors, batch distillation systems, ball mills), determines all the possible outputs from the system, and uses these outputs to optimize a process objective function and predict the optimal process configuration. Optimizing process configurations has been a problem in process synthesis. Techniques such as mixed integer, nonlinear, and dynamic optimization have been applied to optimize process configurations.[13] These techniques are complex and time consuming, and the possibility of missing the optimal configuration is high. Horn[14] proposed that for a given kinetic equation and feedstock, it is possible to determine all possible output concentrations from all possible reactor systems, which he called attainable region (AR). If one can determine this region or boundary, then a search over the region for an output can be used to optimize a given objective function with respect to the system. Glasser and Hildebrandt[15] were able compliment Horn's[14] proposal by developing a technique to construct the AR by taking into consideration the fundamental physical processes occurring within the system (reactor), thus reaction and mixing. They considered these fundamental processes as operational vectors in concentration space. By a logical step-by-step procedure, they were able to formulate a set of necessary and sufficient conditions needed to determine the candidates of AR. Hence, they were able to optimize output concentrations of several well-known problems in literature. Another result of their work was that they were able to use their method for flow sheet development and the reactor type required for a particular duty. Hence, optimal equipment was found as part of their solution. There has been a fair amount of work devoted to attainable region (AR) over the past decade. Most of the early work in AR research was based on geometrical interpretations of the fundamental processes such as reaction, mixing ,and heat exchange. Subsequent work in AR research has relied on properties and results from geometric interpretations and include publications by Glasser, Hildebrandt and Crow,[16] Glasser, Hildebrandt, and Glasser,[17] Nicol, Hildebrandt and Glasser,[18] and Glasser and Hildebrandt.[19]The AR technique has been applied to synthesis problems such as isothermal reactor network synthesis (Hildebrandt and Glasser),[20] optimal temperature control problems (Godorr, Hildebrandt, Glasser, and McGregor)[21] classical variation and dynamic problems (Glasser, Hildebrandt, Godorr, and Jobson).[22]

ATTAINABLE REGION THEORY

The AR theory is a technique that allows the design engineer to solve process synthesis and optimization problems by providing guidelines for the construction of the attainable region as well as providing some necessary conditions to check the results. The attainable region as defined above is the set of all possible outcomes for the system under consideration that can be achieved using the fundamental processes operating within the system and that satisfies all constraints placed on the system. The following needs to be performed in order to complete an attainable analysis:

- Choose the fundamental processes.
- Choose the state variables.
- Define the process vectors.
- Determine the geometry of the process units.
- Determine the necessary conditions.
- Construct the region.
- Interpret the boundary as process flow sheet.
- Determine the optimum of your objective.

Some necessary conditions for AR derived from the work of Glasser and Hildebrandt[16] can be summarized as follows:

- The AR includes all feeds to the system.
- The AR is convex.
- No process vector point out of the AR boundary.
- No rate vectors in the complement of the AR when extended backward intersects the AR.

The procedure entails finding all possible achievable outputs from the process feed for a given system, from the trajectory describing the system operation. These trajectories are used to construct convex hulls and these regions are tested against the necessary conditions and recursively update so that any violated necessary conditions is eliminated. The process ceases when all necessary conditions are satisfied, namely that all process vectors along the boundary are either tangent, zero, or point inward. When the tangency criteria are satisfied, the complement of AR is searched for rate vectors pointing back into the AR. If no rate vector exists, then the resulting AR is considered to satisfy the necessary conditions, Glasser and Hildebrandt.[16]

APPLICATION OF AR APPROACH TO MINIMIZE ENERGY IN BINARY BATCH DISTILLATION PROCESSES

Fundamental Processes in a Binary Batch Distillation Process. The AR approach requires the fundamental processes taking place in the system be identified. Various fundamental processes can occur within a system. Such fundamental processes may include

- mixing
- mass tranfer
- boiling
- heat transfer
- reaction

The following two fundamental processes are identified to be associated with the system binary batch distillation:

- boiling
- mixing

State Variables in the Binary Batch Distillation Process. These are variables required to characterize the state of the system, in this case, a batch distillation process. The variables stated must be sufficient to describe the dynamics of

all the fundamental processes occurring within the system and must incorporate all the variables in the objective function. These variables would include component A (x_A), component B (x_B), time parameter (τ), energy parameter (η). These variables when grouped together form a vector called the characteristic vector ($\vec{C}$). The dimensionality of the optimization problem is determined by the dimension of $\vec{C}$. The higher the dimensionality, the more complex the problem to be solved. In this case, the following characteristic vectors will be considered; $\vec{C}_1 = [x_A, \tau]$, $\vec{C}_2 = [x_A, \eta]$ and $\vec{C}_3 = [\tau, \eta]$. These variables [x_A, x_B, τ, η] are independent and completely describe the state of the system. Many objective functions for common optimization problems for binary batch distillation processes are likely to be functions of these variables. Considering $\vec{C}_1$ and $\vec{C}_2$, we therefore have a 2-D optimization problem with the objective of minimizing [τ], time parameter and [η], an energy parameter.

Process Vectors: Separation Vector and the Mixing Vector. *Separation Vector.* Once the characteristic vector has been defined, the next step is to define the process vectors. The fundamental process vectors are defined in such a way that they give an instantaneous change in the state C when the fundamental process occurs.

During the boiling process, separation occurs as a result of differences in boiling points and relative volatilities; the separation vector $\vec{S}$ is therefore given by

$$\vec{S} = \frac{dS}{d\tau} \tag{1}$$

where τ is a dimensionless scalar variable.

Mixing Vector. The mixing vector $\vec{V}(\vec{C}^o,\vec{C}^*)$ gives the change in the direction of state $\vec{C}^*$ if material of state $\vec{C}^*$ is added. The mixing vector is given by:

$$\vec{V}(\vec{C}^o, \vec{C}^*) = (\vec{C}^* - \vec{C}^o) \tag{2}$$

The mixing therefore obeys the linear mixing rule such that the mixing vector describing this $\vec{V}(\vec{C}^o,\vec{C}^*)$ is defined by:

$$\vec{C} = \alpha\vec{C}^o + (1 - \alpha)\vec{C}^* \tag{3}$$

where $\vec{C}$ is the resultant constant of the system when mixing material $\vec{C}^o$ with $\vec{C}^*$. $\vec{C}$ lies on the straight line between $\vec{C}^o$ and $\vec{C}^*$.

■ BOILING PROFILE AND THE SEPARATION VECTOR EQUATION

In this paper, the following assumptions are considered in all derivation and discussions:

1. No reflux.
2. No reboiler.
3. No cascade.
4. No countercurrent flow.

Consider a simple batch distillation unit as shown in Figure 1. The still consists of a an ideal binary mixture of compounds A and B with volatilities α_A and α_B, respectively, where $\alpha_A < \alpha_B$. Initially, the amount L^o moles of materials (A and B) are charged in the still consisting of x_A^o moles of A and x_B^o moles of B. Energy is introduced to cause boiling of the mixture. During the boiling process, separation is induced as a result of differences in the boiling points and relative volatilities of the materials A and B. The rate of change of material A in the still during the boiling process is governed by the first-order differential equation given below:

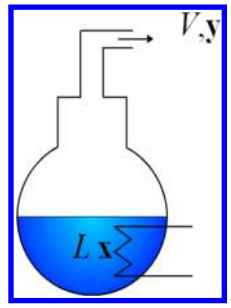

Figure 1. Simple batch distillation set-up.

$$\frac{dx_A}{d\tau} = \vec{S}_A = (x_A - y_A) \tag{4}$$

where $\vec{S}_A$ is the vector separation for component A, y_A is the amount of A in the vapor phase leaving the still and it is given by the expression below:

$$y_A = \frac{\alpha_A x_A}{\alpha_A x_A + \alpha_B(1 - x_A)}$$

where

$$x_B = (1 - x_A) \tag{5}$$

According to Dorherty and Malone,[23] eq 4 can be rewritten as

$$\frac{dx_A}{\frac{V}{L}dt} = \frac{dx_A}{d\tau} \tag{6}$$

Let us consider the quantity $(V/L)\ dt$

$$d\tau = \frac{V}{L}dt \tag{7}$$

but

$$V = -\frac{dL}{dt} \tag{8}$$

thus

$$d\tau = -\frac{dL}{L} \tag{9}$$

Integrating eq 9 over the intervals $[\tau_o, \tau]$ and $[L_o, L]$ gives an expression that describe material remaining at some value of τ during boiling process as

$$[\tau - \tau_o] = -\ln\left(\frac{L}{L_o}\right) \tag{10}$$

If the amount of material evaporated from the still within the time span $[\tau - \tau_o]$ is φ, then we can write that

$$\phi = \frac{L_o - L}{L_o} = \left(1 - \frac{L}{L_o}\right) \tag{11}$$

It can be inferred that the amount of material evaporated (φ) is directly proportional to the amount energy input into the system. From eq 11, let

$$\frac{L_o}{L} = \eta \tag{12}$$

and then we can rewrite eq 11 as follows:

$$\phi = \left(1 - \frac{1}{\eta}\right) \tag{13}$$

Thus, from eqs 11−13, the following limiting conditions can be deduced:

$$\phi \to 1,\ \eta \to \infty,\ \text{and}\ L \to 0 \tag{14}$$

$$\phi \to 0,\ \eta \to 1,\ \text{and}\ L \to L_0 \tag{15}$$

From the limiting conditions, we can conclude that because φ is proportional to the amount of energy input to the system, minimization of the energy of the process requires the minimization of the quantity φ and, thus, trying to achieve a value of η as close to unity as possible.

RELATIONSHIP BETWEEN η AND τ

The relationship between η and τ is given by eq 16

$$\eta = \frac{1}{\exp[-(\tau - \tau_o)]} \tag{16}$$

Appendix A1 provides the derivation of eq 16.

MIXING PROCESS

Consider the following batch processes:

- Batch 1 consists of material of quantity L_1^o and with composition x_1^o.
- Batch 2 consists of material of quantity L_2^o and with composition x_2^o.

After boiling the batches for some time (γ) we obtain the following quantities and compositions:

Batch 1

$$[L_1^o,\ x_1^o]\frac{\text{boiling}}{\text{for } \gamma_1}[L_1,\ x_1],\ \text{with } \eta_1 = \frac{L_1^0}{L_1} \tag{17}$$

or

$$[\eta_1^o,\ x_1^o]\frac{\text{boiling}}{\text{for } \gamma_1}[\eta_1,\ x_1] \tag{18}$$

Batch 2

$$[L_2^o,\ x_2^o]\frac{\text{boiling}}{\text{for } \gamma_2}[L_2,\ x_2],\ \text{with } \eta_2 = \frac{L_2^0}{L_2} \tag{20}$$

or

$$[\eta_2^o,\ x_2^o]\frac{\text{boiling}}{\text{for } 2}[\eta_2,\ x_2] \tag{21}$$

By mixing the products from Batches 1 and 2 to produce material of composition x^* and $\eta^* = [(L_1^o + L_2^o)/(L_1 + L_2)]$ it is shown in Appendix A2 that the parameter η^* (the energy parameter) obeys the mixing rule.

RELATIONSHIP BETWEEN η AND X_A

The relationship between η and x_A that was used to create the 2-dimensional space for the graphical optimization is given by eq 22.

From eq 4 and 16, it can be shown that

$$\frac{dx_A}{d\eta} = \frac{(x_A - y_A)}{\eta} \tag{22}$$

Appendix A3 provides the derivation of eq 22.

PROBLEM FORMULATION FOR A SIMPLE BINARY BATCH DISTILLATION PROCESS WITH CONSTANT RELATIVE VOLATILITIES

Case 1: The Boiling−Separation Profile. Let us use the result we have derived to do some examples. Consider a simple binary batch distillation process. The system consists of components A and B with relative volatilities of α_A and α_B, respectively, with the aim of using the minimum amount of energy for separating component A, the more volatile component, from the mixture. Assume that α_A = 3.0 and α_B = 1.0 and that component A has a higher boiling point than component B. Initially, material of L^o moles are charged in the still consisting of x_A^o moles of A and x_B^o moles of B. Energy is introduced at the rate of q, as shown in Figure 1, to cause boiling in the system. During the boiling process, separation is induced as a result of differences in the boiling points and the relative volatilities of the components A and B. The rate of change of component A in the still during the boiling−separation process is governed by the first-order differential equation shown in eq 4. The vapor and liquid compositions of component A can be determined by eq 5. The simultaneous solutions of eqs 4 and 5 yields the 2-dimensional profile for the boiling−separation the process. For flexibility, Matlab (2010a) program ode45 was used to produce values of the independent time variable (τ) in the range [0,10], from composition (x) values in the range [0,1], respectively, starting with initial feed consisting of C_A^o = 98% A and C_B^o = 2% B to generate the profile shown in Figure 2.

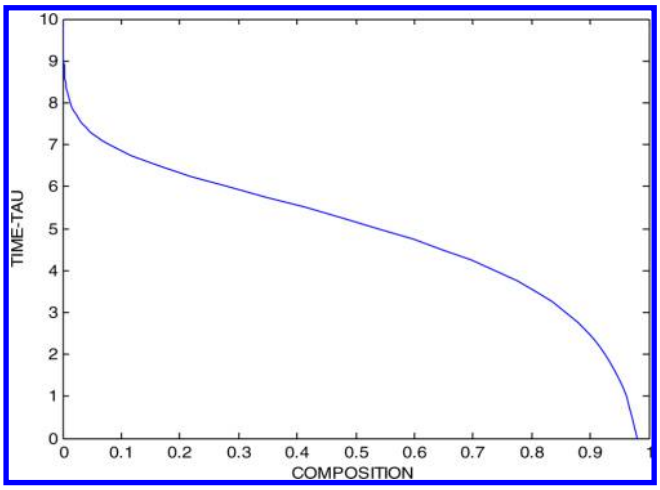

Figure 2. Time (tau, τ) as a function of composition.

Case 2: The Graphical Relationship between x_A and η. We recall the relationship derived in eq 13 and the limiting conditions deduced from it. The limiting conditions gave the idea that in order to minimize energy by simple mixing for the process, one needs to minimize the quantity φ, which is related to energy by making η, the energy parameter, as close to 1 as possible. Thus, for one to minimize energy by mixing, it implies that the parameter η must obey the mixing rule as shown in Appendix A2. We were then able to show the relationship that exists between x_A and η as in eq 22. Equation 22 then indicates how boiling−separation with simple mixing varies with energy. It is then expected that one should be able to determine the minimum energy required for the process from the profile of

the solution of the first-order differential of eq 22. The graphical solution of eq 22 is shown in Figure 3.

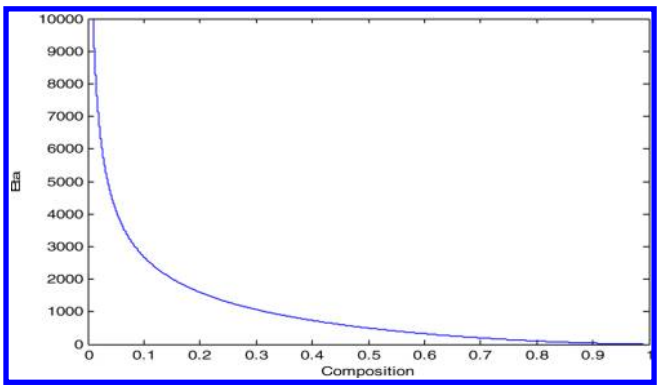

Figure 3. Eta (η) as a function of liquid composition.

DISCUSSION

A graphical illustration of energy minimization based on the theory of attainable region has been presented. The separation of any binary mixture by batch distillation process that employs the fundamental process of boiling can be describe by the profile shown in Figure 2. The figure shows three major sections that describe the boiling process. The first section begins from the feed point (C_A^o). This section shows a very steep curvature, indicating a very high slope starting from the feed point. The separation process at this section is very slow because the rate of composition change with time is very slow. From the figure, this section occurs from time $\tau = 0$ to $\tau = 4$. This section is an energy-consuming step, very little separation is achieved. Ranging from $\tau = 4$ to about $\tau = 7$ is the second separation step of the distillation process. The slope within this time span is a considerably more gentle slope, and this is the section in the distillation process where most of the material separation occurs. The area above $\tau = 7$ describes the third part of the boiling process curve. Here, the slope changes considerably to a very high level, therefore giving slow separation. This part of the boiling process has very little practical significance with respect to the separation process. From the boundary of the trajectory of Figure 2, there is a concavity clearly define by the curve. Thus, the boundary of the region satisfies the necessary conditions of the AR. However, because τ does not obey the mixing rule, the region cannot be extended by simple mixing. When Figure 3 is considered, the trajectory described by [composition (x) − eta (η)] shows convexity. Thus, the minimum energy consumption is achieved by a simple boiling process and mixing, and by the nature of the curve, one cannot reduce the energy consumption by any simple mixing policy.

CONCLUSION

Energy minimization of a binary distillation process has been investigated using the attainable region theory. It has been shown that minimum energy consumption occurs with a simple batch distillation process. This is in contrast to continuous distillation columns, where it can be shown that mixing can decrease the cost of separation. This is an interesting result and is probably not totally unexpected. For simple first-order reactions, the plug-flow reactor is always the best, in that mixing cannot improve its performance. A plug-flow reactor and a batch reactor have the same equations governing them, so one would expect no simple mixing would improve the batch reactor performance. A batch distillation process with constant relative volatilities is the simplest distillation process and so one might not be surprised by our results that simple mixing cannot improve it. However, it is interesting that for countercurrent distillation, which is at infinite reflux, is equivalent to batch distillation; it can be shown that mixing can improve its performance. For reactors, however, systems with more complex kinetics do provide opportunities for mixing to improve their performance, and the same might hold true for more complex vapor−liquid equilibrium models.

APPENDICES

A1: Relationship between η and τ

Recall from eq 10 that $[\tau - \tau_o] = -\ln (L/L_o)$, thus

$$\frac{L}{L_o} = \exp[-(\tau - \tau_o)] \tag{1A}$$

Hence, from eq 12 we can write equation 1A as follows:

$$\eta = \frac{1}{\exp[-(\tau - \tau_o)]}$$

A2: Derivation of the Mixing Rule

Consider the following batch processes:

- Batch 1 consists of material of quantity L_1^o and with composition x_1^o.
- Batch 2 consists of material of quantity L_2^o and with composition x_2^o.

After boiling the batches for some time (γ) we obtain the following quantities and compositions:

Batch 1

$$[L_1^o,\ x_1^o]\frac{\text{boiling}}{\text{for } \gamma_1}[L_1,\ x_1],\ \text{with } \eta_1 = \frac{L_1^0}{L_1} \tag{17}$$

or

$$[\eta_1^o,\ x_1^o]\frac{\text{boiling}}{\text{for } \gamma_1}[\eta_1,\ x_1] \tag{18}$$

Batch 2

$$[L_2^o,\ x_2^o]\frac{\text{boiling}}{\text{for } \gamma_2}[L_2,\ x_2],\ \text{with } \eta_2 = \frac{L_2^0}{L_2} \tag{20}$$

or

$$[\eta_2^o,\ x_2^o]\frac{\text{boiling}}{\text{for 2}}[\eta_2,\ x_2] \tag{21}$$

By mixing the products from Batches 1 and 2 to produce material of composition x^* and $\eta^* = [(L_1^o + L_2^o)/(L_1 + L_2)]$ we can formulate the following mathematical expressions

$$L_1x_1 + L_2x_2 = (L_1 + L_2)x^*$$

$$x^* = \left(\frac{L_1}{L_1 + L_2}\right)x_1 + \left(\frac{L_2}{L_1 + L_2}\right)x_2$$

$$\eta_1 + \eta_2 = \eta^*$$

Thus, for the composition x^* to follow the linear mixing rule we can write

$$L_1^o + L_2^o = L^{*o}$$

$$\eta_1 L_1 + \eta_2 L_2 = \eta^*(L_1 + L_2)$$

Thus

$$\eta^* = \left(\frac{L_1}{L_1 + L_2}\right)\eta_1 + \left(\frac{L_2}{L_1 + L_2}\right)\eta_2$$

Hence, η^* thus follows the linear mixing rule.

A3: Relationship between η and x_A

Recall from eq 4 and 16 that

$$\frac{dx_A}{d\tau} = \vec{S}_A = (x_A - y_A)$$

and $\eta = 1/\exp[-(\tau - \tau_o)]$. Differentiating η with respect to τ gives

$$\frac{d\eta}{d\tau} = \frac{1}{\exp(-\tau + \tau_o)}$$

$$d\eta = d\tau\left(\frac{1}{\exp(-\tau + \tau_o)}\right)$$

$$\frac{1}{\exp(-\tau + \tau_o)} = \frac{1}{\exp[-(\tau - \tau_o)]} = \eta$$

Thus

$$d\eta = d\tau^*\eta$$

and

$$d\tau = d\eta/\eta$$

By substituting for $d\tau$ in eq 4 and rearranging, we can, therefore, write

$$\frac{dx_A}{d\eta} = \frac{(x_A - y_A)}{\eta}$$

AUTHOR INFORMATION

Corresponding Authors

*N. Y. A. E-mail: nasiedusoe@yahoo.co.uk.
*D. H. E-mail: Diane.Hildebrandt@wits.ac.za.
*D. G. E-mail: David.Glasser@wits.ac.za.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

N.A. would like to thank the NRF and Centre of Material Processing and Synthesis (COMPS), University of the Witwatersrand, Johannesburg, South Africa for financial support of this work.

NOTATION

AR = attainable region
Q_B = heat input to the still
x_A = moles of liquid A in the still
y_A = mole of vapor A leaving the still
τ = time parameter
S = separation vector
α_A = volatility of A
α_B = volatility of B
α = positive constant
L = amount of liquid at any time in the still
V = vapor flow rate from the still
C_{AO} = initial composition of A
τ = time parameter
η = energy parameter
q = energy required for the distillation process
L_o = amount of liquid mixture in the still at the initial time

REFERENCES

(1) Smrζka, K. Hannover Fair 2007. *Creamer Media's Eng. News* **2007**, *27*, 15, 73.
(2) Stoltze, S.; Mikkelsen, J.; Lorentzen, B.; Petersen, P. M.; Qvale, B. Waste-Heat Recovery in Batch Processes Using Heat Storage. *Trans. ASME: J. Energy Resour. Technol.* **1995**, *117* (2), 142−149.
(3) Philips, C. H.; Lauschke, G.; Peerhoussaini, H. Intensification of Batch Chemical Processes by Using Integrated Reactor Heat Exchangers. *Appl. Therm. Eng.* **1995**, *17* (8), 809−824.
(4) Wang, Y.; Feng, X. Energy Analysis Involving Resources Utilization and Environmental Influence. *Compt. Eng.* **2000**, *24*, 1243−1246.
(5) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
(6) Worrel, E.; Price, L.; Ruth, M. Policy Modeling for Energy Energy Efficiency Improvement in US Industry. *Annu. Rev. Energy Environ.* **2001**, *26*, 117−143.
(7) Eissen, M.; Metzger, J. O.; Schmidt, E.; Schneidewind, U. 10 Years after Rio-Concepts on the Contribution of Chemistry to Sustainable Development. *Angew. Chem., Int. Ed.* **2002**, *41*, 414−436.
(8) Linnhoff, B. Pinch Analysis − a State-of-the-Art Overveiw. *Trans. IChemE, Part A* **1993**, *71* (6), 503−522.
(9) Vaselenak, J. A.; Grossmann, I. E.; Westerberg, A. W. Heat Integration in Batch Processing. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25* (2), 357−366.
(10) Vaselenak, J. A.; Grossmann, I. E.; Westerberg, A. W. An Embedding Formulation for the Optimal Scheduling and Design of Multipurpose Batch Plants. *Ind. Eng. Chem. Res.* **1987**, *26* (1), 139−148.
(11) Vaklieva-Bancheva, N.; Ivanov, B. B.; Shah, N.; Pantelides, C. C. Heat Exchanger Network Design for Multipurpose Batch Plants. *Comput. Chem. Eng.* **1996**, *20* (8), 989−1001.
(12) Grant, C. D. *Energy Management in Chemical Industry. Kirk-Othmer: Encylopedia of Chemical Technology*; Kroschwitz, J. I., Ed., John Wiley & Sons: New York, 1996; 12-1−12-16.
(13) Kokossis, A. C.; Floudas, C. A. Optimization of Complex Reactor Networks II: Non-isotherml Operation. *Chem. Eng. Sci.* **1994**, *49* (7), 1037.
(14) Horn, F. Attainable and Non-attainable Regions in Chemical Reaction Techniques. *Chem. React. Eng., Eur. Symp., 3rd*; Pergamon Press Ltd.: Oxford, U. K., 1964.
(15) Glasser, D.; Crowe, C.; Hildebrandt, D. A. Geometric Approach to Steady Flow Reactors: The attainable Region and Optimization in Concentration Space. *Ind. Eng. Chem. Res.* **1987**, *26*, 1803−1810.
(16) Glasser, D.; Hildebrandt, D.; Crowe, C. M. The geometry of the attainable region generated by reaction and mixing: with and without constraints. *Chem. Eng. Sci.* **1990**, *29* (1), 49−58.
(17) Glasser, B.; Hildebrandt, D.; Glasser, D. Optimal mixing for exothermic revesible reactions. *Ind. Eng. Chem. Res.* **1992**, *31* (6), 1541−1549.
(18) Nicol, W.; Hildebrandt, D.; Glasser, D. Process synthesis for reaction systems with cooling via finding the attainable region. *Comput. Chem. Eng.* **1997**, *21* (1001), s35−s40.
(19) Glasser, D.; Hildebrandt, D. Reactor and process synthesis. *Comput. Chem. Eng.* **1997**, *21*, s775−s783.
(20) Hildebrandt, D.; Glasser, D. The attainable region and optimal reactor structures. *Ind. Eng. Chem. Res.* **1990**, *35* (4), 2161−2168.
(21) Godorr, S.; Hildebrandt, D.; Glasser, D.; McGregor, C. Choosing optimal control policies using the attainable region approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 639−651.

(22) Glasser, D.; Hildebrandt, D.; Godorr, S.; Jobson, M. Geometric approach to variational optimization: finding the attainable region. *Chem. Eng. Sci.* **1993**, *5*, 37−43.
(23) Doherty, M. F.; Malone, J. D. *Conceptual Design of Distillation Systems*, 1st ed.; McGraw Hill: New York, 2001; Chapter 2, pp 37−42.