

## ON THERMODYNAMICS OF EVAPORATION PROCESSES IN NONEQUILIBRIUM SYSTEMS

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Thermodynamic theory of phase equilibrium is the main base for the development of the methods of fluid mixtures separation. Thermodynamic approach has a lot of advantages in the practical application when conditions of separation processes are close to the equilibrium. For nonequilibrium processes these advantages fail and one should use another methods including empirical relationships and models. The nonequilibrium thermodynamic seems to be a good approach but the practical applications meet many difficulties. On the other hand there are a number opportunities to use equilibrium thermodynamic relationships for the treatment of systems or processes that are nonequilibrium as a whole but some parts and stages of them could be considered as equilibrium. For example it could be the case of equilibrium phase transitions in the system with nonequilibrium chemical reaction. In this paper we consider some thermodynamic regularities and singularities of the structure of diagrams of phase transitions in nonequilibrium multi-component systems vapour – condensed phases.

The lack of equilibrium in the evaporation could be caused by a numerous reasons. In a general case the gradients of intensive variables are driving forces for phase processes, and the affinity is the driving force for the chemical reactions in nonequilibrium system. Gradients of the temperature, of the pressure and of the chemical potentials also effect on the rate of the processes in a nonequilibrium system.

The topology of diagrams in the case of the absence of vapour–liquid equilibrium was considered in the work [1]. The mass balance in both equilibrium and nonequilibrium evaporation can be described by the Rayleigh equations:

$$\left( \frac{dx_i^L}{d \ln m^L} \right)_{\text{evap}} = x_i^V - x_i^L.$$

Therefore the structure of residue curve map for nonequilibrium evaporation is similar to the ordinary residue curve map (the case of equilibrium simple distillation) [1]. The fluxes from liquid to vapour phase can be also described by well-known linear

phenomenological laws:

$$Y_i = \sum_{k=1}^n L_{ik} X_k$$

which are valid for the sufficiently small deviations from the equilibrium [2]. Thermodynamic forces  $X_k$  are usually the functions of gradients of intensive thermodynamic variables; thermodynamic fluxes (thermodynamic flows)  $Y_i$  are the time derivatives of extensive variables. In general case  $n$  Cartesian coordinates of independent forces and fluxes should be considered. In the nonequilibrium evaporation fluxes across the vapour–liquid interface could be caused by temperature or pressure gradient. The vacuum pervaporation is an example of the nonequilibrium evaporation when the driving force of the process is a pressure gradient. In this case liquid and vapour phases are separated by the membrane that keeps up the difference of the pressure. Formally the natural interphase border between vapour and liquid can be also considered as membrane and relationships of nonequilibrium thermodynamics of membrane processes can be apply. On the other hand in the absence of phase equilibrium the opportunities to apply the classical methods of equilibrium thermodynamic are limited.

Another type of the systems that should be considered is a type of equilibrium evaporation when the liquid is in the nonequilibrium state. The most important example is the equilibrium evaporation in systems with nonequilibrium chemical reaction (chemically nonequilibrium systems). This is well-known case of partly equilibrium systems. In comparison with non-reactive systems the diagram of the process in such systems includes some new elements (lines or surfaces of constant affinity, reaction or stoichiometric lines). In the case of the evaporation of homogeneous liquids the topological structure of diagrams of combined process (coupled reaction and mass transfer) significantly depends on the reaction rate. In partly immiscible mixtures some additional complications should be taken into account due to liquid–liquid phase transitions and the difference of reaction rates in coexisting liquid phases. The vapour–liquid phase transitions in reactive systems were the object of the study during few last decades. First significant works in this area belong to Zharov, Serafimov, Doherty and co-workers (e.g. [3–10]). Most of these research deal with phase equilibrium in systems with reversible chemical reaction, i.e. simultaneous phase and chemical equilibrium.

Analysis of singular points is a main aspect of topological consideration of phase diagrams. The conditions of reactive azeotrope for the first time were obtained in works [4, 8, 11]. Let us obtain one more form of these conditions that can be derived on the base of thermodynamic approach proposed in works [12, 13]. For the sake of simplicity we may consider the ternary system with the chemical reaction:



According to [13] the equation of the chemical equilibrium curve at constant temperature may be presented as following:

$$(dP)_T = \frac{(d^2g^L)_{P,T}[v_1D(LVR_1) + v_2D(LVR_2) + v_3D(LVR_3)]}{-v^V[v_1D(L'LR_1) + v_2D(L'LR_2) + v_3D(L'LR_3)]} \quad (2)$$

where  $D(L'LV)$ ,  $D(LVR_i)$ ,  $D(L'LR_i)$  are symbols of determinants. Elements of each determinant are coordinates of points of liquid (L), vapour (V) and pure specie  $R_i$  in composition triangle; points of liquid  $L'$  correspond to the solution obtained from the initial one by infinitesimal shifting of the state. For example

$$D(LVR_1) = D(R_1LV) = \begin{vmatrix} 1 & 0 & 0 \\ x_1^L & x_2^L & x_3^L \\ x_1^V & x_2^V & x_3^V \end{vmatrix} = \begin{vmatrix} x_2^L & x_3^L \\ x_2^V & x_3^V \end{vmatrix}$$

$$D(L'LV) \equiv \begin{vmatrix} x_1^L + dx_1^L & x_2^L + dx_2^L & x_3^L + dx_3^L \\ x_1^L & x_2^L & x_3^L \\ x_1^V & x_2^V & x_3^V \end{vmatrix} = \begin{vmatrix} dx_1^L & dx_2^L & dx_3^L \\ x_1^L & x_2^L & x_3^L \\ x_1^V & x_2^V & x_3^V \end{vmatrix}.$$

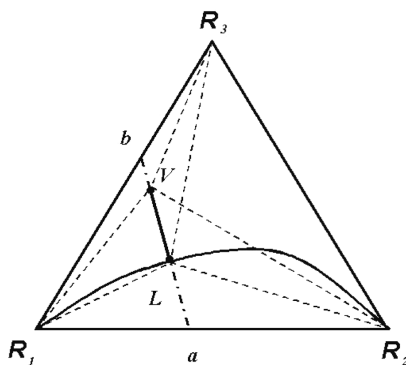
In equation (2) the molar volume of the vapour  $v^V$  is positive and according to stability condition  $(d^2g^L)_{P,T} > 0$ . Determinant values are proportional to the square of triangles  $L'LV$ ,  $LVR_i$ ,  $L'LR_i$  and their signs depends on the disposition of tops of these triangles. For example if the direction of the passing the tops L, V,  $R_i$  of triangle  $LVR_1$  is clockwise and  $LVR_2$  counterclockwise the values of squares  $S(LVR_i)$  are of opposite sign:

$$S(LVR_1) > 0, S(LVR_2) < 0 \quad \text{or} \quad S(LVR_1) < 0, S(LVR_2) > 0.$$

As a result, equation (2) has a clear geometrical sense. In particular equation (2) determines the change of the pressure along the chemical equilibrium line. The direction of the pressure change depends on the mutual disposition of tie-lines and tops of the composition triangle. In a stationary point of the vapour pressure the following relationship for the sum of squares of triangles is valid:

$$v_1S(LVR_1) + v_2S(LVR_2) + v_3S(LVR_3) = 0. \quad (3)$$

This result can be considered as generalized Gibbs–Kononov rule for the reactive system (Figure 1).



**Figure 1.** Stationary point of vapour pressure on the chemical equilibrium curve: vapour–liquid tie-line ( $L-V$ ) coincides with stoichiometric line (stroke-dotted line  $a-b$ ). Dotted lines – sides of triangles  $LVR_1$ ,  $LVR_2$  и  $LVR_3$ . Curve  $R_1LR_2$  – chemical equilibrium line

Equation (3) can be transformed into the following forms:

$$\frac{x_1^V - x_1^L}{x_2^V - x_2^L} = \frac{\nu_1 - x_1^L \sum_{i=1}^3 \nu_i}{\nu_2 - x_2^L \sum_{i=1}^3 \nu_i} \quad (4)$$

and

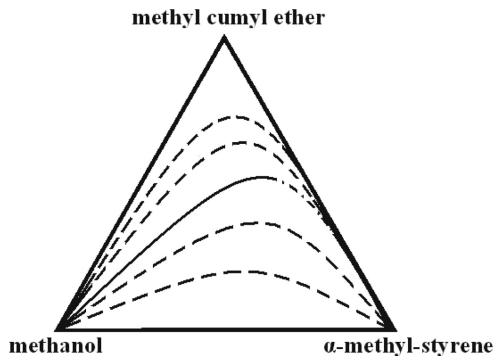
$$\begin{vmatrix} x_1^L & x_2^L & x_3^L \\ x_1^V & x_2^V & x_3^V \\ \nu_1 & \nu_2 & \nu_3 \end{vmatrix} = 0 \quad (5)$$

Equation (5) is a well-known necessary condition of reactive azeotrope [8, 14]. According to equation (4) the tie-line coincides with stoichiometric line in the stationary point of the pressure. The type of pressure extremum depends on the disposition of tie-lines in the vicinity of stoichiometric line in composition triangle.

Now let us consider the case of the absence of chemical equilibrium. Equation (2) should be valid also for the manifolds of constant affinity in chemically nonequilibrium systems. Accordingly, for these manifolds the regularities of the change of thermodynamic properties and the conditions of the stationary point can be obtained in the way similar to chemical equilibrium case. The affinity of reaction is the quantity

$$A = - \sum_i \nu_i \mu_i, \quad (6)$$

where stoichiometric numbers  $\nu_i$  are positive for products and negative for reactants. In an isothermal ternary system with a chemical reaction (1) isoaffinity manifolds



**Figure 2.** Lines of chemical equilibrium, data [15], and constant affinity (dotted lines) in the system methanol– $\alpha$ -methyl-styrene–methyl cumyl ether,  $T = 328$  K

represent a set of curves that are similar to chemical equilibrium line. The qualitative arrangement of isoaffinity curves for the system methanol– $\alpha$ -methyl-styrene–methyl cumyl ether with the reaction of the methyl cumyl ether synthesis is illustrated in Figure 2. The location of chemical equilibrium curve is constructed on the base of the data [15]. The arrangement and singularities of isoaffinity curves and stoichiometric lines are important elements for the analysis of the topological structure of chemically nonequilibrium systems.

The important results concerning phase transitions and thermodynamic properties of reacting systems in chemically nonequilibrium states were obtained by Zharov and Pervukhin [16–19]. Now we will derive some relationships for reacting systems on the base of the classical form of the Storonkin–Van-der-Waals differential equation [20]. For the sake of simplicity the ternary system with the reaction



will be considered. At constant temperature the Storonkin–Van-der-Waals differential equation for the ternary system has the following form [20]:

$$\begin{aligned} v^{LV} dP = & (x_1^V - x_1^L) \left[ \frac{\partial(\mu_1 - \mu_3)}{\partial x_1^L} dx_1^L + \frac{\partial(\mu_1 - \mu_3)}{\partial x_2^L} dx_2^L \right] + \\ & + (x_2^V - x_2^L) \left[ \frac{\partial(\mu_2 - \mu_3)}{\partial x_1^L} dx_1^L + \frac{\partial(\mu_2 - \mu_3)}{\partial x_2^L} dx_2^L \right] \end{aligned} \quad (8)$$

where

$$v^{LV} = v^V - v^L - \sum_{i=1}^{n-1} (x_i^V - x_i^L) \left( \frac{\partial v}{\partial x_i} \right)^L.$$

The following conditions should be valid for the states that are far from a vapour-liquid critical point and if vapour nonideality may be neglected:

$$v^V \gg v^L, \quad v^{LV} dP \cong RT d \ln P. \quad (9)$$

As usual we can neglect the pressure influence on a chemical potential in condensed phases. According to the reaction equation (7) the following equations for the affinity and the extent of reaction take place:

$$A = - \sum_{i=1}^3 \nu_i \mu_i = \mu_1 + \mu_2 - 2\mu_3 \quad (10)$$

$$d\xi = \frac{dm_i}{\nu_i} = \frac{dx_i}{\nu_i} = \frac{dx_1}{-1} = \frac{dx_2}{-1} = \frac{dx_3}{+2} \quad (11)$$

Taking into account (9), (11) and Maxwell reciprocal relationships, Equation (8) can be written as

$$\begin{aligned} RT d \ln P = d\xi \left\{ \nu_1 (x_1^{(2)} - x_1^{(1)}) \left[ \frac{\partial(\mu_1 - \mu_3)}{\partial x_1^{(1)}} + \frac{\partial(\mu_2 - \mu_3)}{\partial x_1^{(1)}} \right] + \right. \\ \left. + \nu_2 (x_2^{(2)} - x_2^{(1)}) \left[ \frac{\partial(\mu_1 - \mu_3)}{\partial x_2^{(1)}} + \frac{\partial(\mu_2 - \mu_3)}{\partial x_2^{(1)}} \right] \right\} \end{aligned} \quad (12)$$

Substituting equation (10) for the affinity into equation (12) we obtain:

$$\frac{d \ln P}{d\xi} = -(x_1^{(2)} - x_1^{(1)}) \frac{\partial A}{\partial x_1^{(1)}} - (x_2^{(2)} - x_2^{(1)}) \frac{\partial A}{\partial x_2^{(1)}}. \quad (13)$$

Equation (13) describes the change of the pressure on the stoichiometric lines of the reaction (7) for the chemically nonequilibrium states. In a stationary point  $d \ln P / d\xi = 0$

and the following relationship holds:

$$\frac{(x_1^{(2)} - x_1^{(1)})}{(x_2^{(2)} - x_2^{(1)})} = -\frac{\frac{\partial A}{\partial x_2^{(1)}}}{\frac{\partial A}{\partial x_1^{(1)}}} = \left(\frac{dx_1}{dx_2}\right)_{A=\text{const}} \quad (14)$$

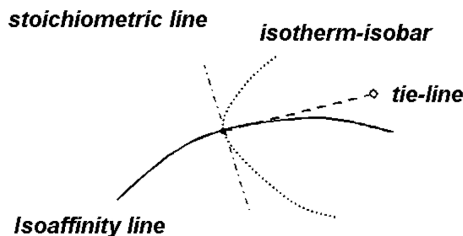
According to (13) and (14) we obtain three alternative conditions of the stationary point of the pressure on the stoichiometric lines:

- i. compositions of vapour and liquid are equal (ordinary azeotropic point);
- ii. derivatives of affinity with respect to the concentration are equal to zero;
- iii. tie-line touches isoline of affinity.

The third case is of most interest as a nontrivial one. The first and the second cases correspond to the special conditions of the stationary point. These conditions coincide with results of Zharov and Pervukhin for multicomponent reacting systems [16–19] and also may be generalized for the n-component system with non-equilibrium chemical reaction.

Figure 3 illustrates the third condition of the stationary point. The extremum of the pressure corresponds to the touching of isotherm-isobar curve by stoichiometric lines as well. The equation (14) may be also interpreted as the touching of isoaffinity curve and simple distillation line. On the other hand in the case of nonequilibrium reaction the residue curve map cannot be considered as a diagram of simple distillation line: preferably to call such diagrams as “a residue curve map for the coupled reaction–evaporation process”. Strictly speaking equation (14) corresponds to the touching of isoaffinity line and residue curve only if the reaction is frozen.

The liquid phase splitting adds extra elements to the topological structure of diagrams of reacting systems. Now we only briefly describe some problems. For example different cases of the crossing of binodal and isoaffinity curves (including chemical equilibrium



**Figure 3.** Mutual disposition of isoaffinity line, tie-line (o – vapour composition), stoichiometric (reaction) line and isotherm-isobar in the stationary point of the pressure on the stoichiometric line.

line) can be considered. According to Ung and Doherty the tie-line corresponding to the intersection of the liquid–liquid envelope with chemical equilibrium line can be called unique reactive liquid–liquid tie-line [21]. Recently we had considered possible types of diagrams that differ in the mutual disposition of the liquid–liquid envelope and chemical equilibrium line in ternary systems [22]. Another problem is connected with the effect of the reaction kinetics. The mass balance of the coupled reactive–evaporation process usually is described with the use of the Damköhler number that helps to take into account the value of the reaction rate. In systems with the liquid splitting the reaction rates in coexisting phases could significantly differ. Accordingly different Damköhler numbers for every liquid phase should be taken into consideration. The problems of reactive distillation in the systems with limited miscibility are discussed in recent papers, e.g. [21–25].

The nonequilibrium evaporation in the systems with nonequilibrium liquid phases is the most general case of the subject under consideration. The reacting systems would be also a good example. The chemical equilibrium takes place if the reaction rate is much more than the rate of evaporation (or, in a special case – when the composition of condensed phases in the evaporation process is shifting along the surface of chemical equilibrium). Diagrams of the coupled reaction and mass transfer nonequilibrium process may include points of equal compositions that are analogous to the reactive azeotrope. When the values of reaction and evaporation rates are close, the point like a kinetic azeotrope may exist. One of the most significant examples of nonequilibrium evaporation in the systems with nonequilibrium liquid phases is a reactive pervaporation. Because this membrane process is out of the scope of our conference we confine ourselves to references on some recent papers [26–29].

In spite of the well-known industrial significance of coupled reactive and mass transfer processes the experimental thermodynamic and kinetic data base on the evaporation in nonequilibrium reacting systems is very limited. The most of experimental works concern systems with equilibrium esterification reaction. Only few works deal with ternary reactive vapour–liquid systems. The quoted study of Heintz and Verevkin [15] is the best research in this area.

Unfortunately theoretical study of the evaporation in nonequilibrium reacting systems usually is not based on the methods of thermodynamics of irreversible processes. The opportunity of an application and advantages of the nonequilibrium thermodynamic approach for the study of vapour–liquid phase transitions in nonequilibrium systems are indisputable. Nevertheless ordinary thermodynamic methods combined with the kinetic approach were also successful in the analysis of such complex systems. The further development both these methods and nonequilibrium thermodynamic approach will require the extension of experimental data base on the evaporation in nonequilibrium systems.

## CONCLUSION

Some aspects of thermodynamic approach for the study of evaporation processes in nonequilibrium system are discussed. The main examples are singularities of the reacting system diagrams. New form of reactive azeotrope conditions is presented. The conditions



of a stationary point of the pressure on the stoichiometric lines are considered for chemically nonequilibrium systems.

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### NOMENCLATURE

|           |                               |
|-----------|-------------------------------|
| A         | affinity                      |
| g         | molar Gibbs energy            |
| P         | pressure                      |
| R         | gas constant                  |
| $R_i$     | symbols of reacting species   |
| T         | temperature                   |
| $v^{(2)}$ | molar volume of the vapour    |
| $x_i$     | molar fraction of component i |
| $X_k$     | thermodynamic force           |
| $Y_i$     | thermodynamic flux            |

### GREEK SYMBOLS

|         |                                      |
|---------|--------------------------------------|
| $\mu_i$ | chemical potential of a component i  |
| $\nu_i$ | stoichiometric number of a species i |
| $\xi$   | extent of reaction                   |

### SUBSCRIPTS

1, 2, i indexes components

### SUPERSCRIPTS

|   |              |
|---|--------------|
| L | liquid phase |
| V | vapour phase |

### REFERENCES

1. L.A. Serafimov, Classification of the phase diagrams of real batch distillation, *Theor. Foundations of Chem. Eng.* 35 (2001) 237–241.
2. H.J. Kreuzer, *Nonequilibrium Thermodynamics and its Statistical Foundations*, Clarendon Press, Oxford, 1981.
3. V.T. Zharov, Processes of open evaporation of solutions of substances with chemical interaction, *Zh. Fiz. Khim. (J. Phys. Chem. USSR)* 44 (1970) 1967–1974 (in Russian).

4. V.T. Zharov, On thermodynamics of vapour–liquid equilibrium and open evaporation processes for systems with chemical reactions, in: *Thermodynamics of Heterogeneous Systems and Theory of Surface Phenomena, Issue 2*, Publishing House of Leningrad University, Leningrad, 1973, pp. 35–53 (in Russian).
5. L.A. Serafimov, M.I. Balashov, Reactive Distillation Processes, additional chapter in Astarita, G., *Massoperedacha s khimicheskoi reaktsiei* (Mass Transfer with Chemical Reaction), Leningrad: Khimiya, 1971 (in Russian).
6. M.I. Balashov, L.A. Serafimov, Principles and technological expedients of organization of continuous coupled reactive distillation processes, *Teor. Osn. Khim. Tekhnol. (Theor. Foundations of Chem. Eng.)* 14 (1980) 515–521.
7. A.V. Solokhin, S.A. Blagov, L.A. Serafimov, V.S. Timofeev, Processes of open evaporation accompanied by chemical reaction in the liquid phase, *Teor. Osn. Khim. Tekhnol. (Theor. Foundations of Chem. Eng.)* 24 (1990) 163–169.
8. D. Barbosa, M.F. Doherty, Theory of phase diagrams and azeotropic conditions for two-phase reactive systems, *Proc. R. Soc. Lond. A* 413 (1987) 443–458.
9. D. Barbosa, M.F. Doherty, The influence of equilibrium chemical reactions on vapor-liquid phase diagrams, *Chem. Eng. Sci.* 43 (1988) 529–540.
10. D. Barbosa, M.F. Doherty, The simple distillation of homogeneous reactive mixtures, *Chem. Eng. Sci.* 43 (1988) 541–550.
11. Yu.A. Pisarenko, L.A. Serafimov, Stationary states of a reactive distillation process, *Teor. Osn. Khim. Tekhnol. (Theor. Foundations of Chem. Eng.)* 25 (1991) 422–426.
12. B.I. Gorovits, A.M. Toikka, Vapor pressure and chemical potentials in bivariant liquid–vapor systems, *Russian J. Phys. Chem.* 77 (2003) 186–189.
13. B.I. Gorovits, A.M. Toikka, Changes in thermodynamic parameters in heterogeneous systems with a chemical reaction in the liquid phase, *Doklady Phys. Chem.* 405, Part 1 (2005) 244–247.
14. A.S. Shuvalov, Yu.A. Pisarenko, Chemiazeotropes: formation conditions and properties, *Theor. Foundations of Chem. Eng.* 35 (2001) 133–141.
15. A. Heintz, S.P. Verevkin, Simultaneous study of chemical and vapour–liquid equilibria in the reacting system of the methyl cumyl ether synthesis from methanol and  $\alpha$ -methylstyrene, *Fluid Phase Equilibria* 179 (2001) P. 85–100.
16. V.T. Zharov, O.K. Pervukhin, On vapour–liquid equilibrium in chemically nonequilibrium systems. II, *Vestnik Leningrad State Univ.* 10 (1977) 102–108 (in Russian).
17. V.T. Zharov, O.K. Pervukhin, On thermodynamics of vapour–liquid equilibrium and kinetic investigations of chemical processes, in: *Thermodynamics of Heterogeneous Systems and Theory of Surface Phenomena, Issue 5*, Publishing House of Leningrad University, Leningrad, 1979, pp. 3–28 (in Russian).
18. O.K. Pervukhin, Vapour–liquid equilibrium in multicomponent chemically nonequilibrium system, *Zh. Fiz. Khim. (Russian J. Phys. Chem.)* 69 (1995) 1754–1757 (in Russian).
19. O.K. Pervukhin, Phase equilibrium in the systems with irreversible chemical reaction, in: *Thermodynamics of Heterogeneous Systems and Theory of Surface Phenomena, Issue 10*, Publishing House of St. Petersburg University, St. Petersburg, 1996, pp. 55–98 (in Russian).

20. A.V. Storonkin, *Termodinamika Geterogennyh System (Thermodynamics of Heterogeneous Systems)*, Parts 1 and 2, Publishing House of Leningrad University, Leningrad, 1967 (in Russian).
21. S. Ung, M. Doherty, Theory of phase equilibria in multireaction systems, *Chem Eng. Sci.* 50 (1995) 3201–3216.
22. V.V. Kocherbitov, A.M. Toikka, On the structure of state diagrams of chemically nonequilibrium ternary systems liquid–liquid, *Vestnik St. Petersburg State Univ.* 3 (1998) 120–124.
23. M.J. Okasinski, M.F. Doherty, Prediction of heterogeneous reactive azeotropes in esterification systems. *Chem. Eng. Sci.* 55 (2000) 5263–5271.
24. Z. Qi, A. Kolah, K. Sundmacher, Residue curve maps for reactive distillation systems with liquid-phase splitting, *Chem. Eng. Sci.* 57 (2002) 163–178.
25. Z. Qi, K. Sundmacher, Bifurcation analysis of reactive distillation systems with liquid-phase splitting, *Comp. Chem. Eng.*, 26 (2002) 1459–1471.
26. Y.-S. Huang, K. Sundmacher, Z. Qi, E.-U. Schlunder, Residue curve maps of reactive membrane separation, *Chem. Eng. Sci.* 59 (2004) 2863–2879.
27. Q. Liu, Z. Zhang, H. Chen, Study on the coupling of esterification with pervaporation, *J. Membrane Sci.* 182 (2001) 173–181.
28. D. Nemeč, R. van Gemert, Performing esterification reactions by combining heterogeneous catalysis and pervaporation in a batch process, *Ind. Eng. Chem. Res.* 44 (2005) 9718–9726.
29. S. Steinigeweg, J. Gmehling, Transesterification processes by combination of reactive distillation and pervaporation, *Chem. Eng. Proc.* 43 (2004) 447–456.