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# EQUIPARTITION OF FORCES: REVIEW OF A NEW PRINCIPLE FOR PROCESS DESIGN AND OPTIMIZATION

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## Abstract

We present a general proof for a design principle developed during the last two years: The principle of equipartition of forces. The principle is derived for parallel, coupled transport processes without restrictions on the phenomenological coefficients. Minimum entropy production is obtained for the total system, when the thermodynamic forces of transport are the same over all parallel paths in the system. We review some of the results obtained so far by application of the principle to distillation columns.

*Keywords:* entropy production, energy efficiency, irreversible thermodynamics, distination.

## 1. Introduction

Energy optimization is important in the process industry. Energy optimization of a process means determination of minimum entropy production. Already in his works on the symmetry relations, ONSAGER stated (1931a, b) that entropy production is minimum in the stationary state, that is a state with constant fluxes. BEJAN (1982) has described how minimum entropy production can be obtained in practice for several cases of heat and mass transfer. In a heat exchanger for example, he found a sharp minimum for the entropy production for certain flow conditions in the tube. For constant transport coefficients, TONDEUR – KVAALEN (1987) showed that minimum entropy production is obtained when the entropy production rate is constant through the apparatus. As a consequence of this, a heat exchanger with countercurrent flow dissipates less energy than one with concurrent flow; a well-known engineering observation.

The results of TONDEUR – KVAALEN are in accordance with the results from finite time thermodynamics. In a recent review on finite time thermodynamics, ANDRESEN (1996) states: Constant rate of entropy production is the path or operating strategy which produces the least overall entropy in the system. In his elaboration on the topic in 1990, TONDEUR writes: 'With a constant coefficient (of transport), the distribution of driving forces, which minimize the entropy production of the system under the constraint of a specified duty, is a uniform distribution.'

The present work summarizes our recent results in this field (KJELSTRUP RATKJE et al., 1995, SAUAR et al., 1995, 1996, 1997a). We have been able to generalize the results of TONDEUR (1990) and show that the last statement is true for parallel processes, also when the coefficients are *not* constant. We call our general result *the principle of equipartition of forces.* The principle has bearings on apparatus design. We review some which we have found for distillation columns.

## 2. The Principle of Equipartition of Forces

We repeat our derivation of conditions for minimum entropy production in a system of $k$ parallel transport paths. Consider for simplicity that each path $n$ has the coupled fluxes, $J_{1,n}$ and $J_{2,n}$, with their conjugate forces $X_{1,n}$ and $X_{2,n}$. The entropy production rate for path number $n$ is $\theta_n$:

$$\theta_n = \sum_{i=1}^{2} J_{i,n} X_{i,n} \ , \tag{1}$$

and the fluxes are:

$$J_{1,n} = L_{11,n} X_{1,n} + L_{12,n} X_{2,n} \ , \tag{2}$$

$$J_{2,n} = L_{21,n} X_{1,n} + L_{22,n} X_{2,n} \ . \tag{3}$$

Onsager's reciprocal relation, $L_{12,n} = L_{21,n}$, applies. All $k$ paths are adding to the total entropy production rate, $\Theta$:

$$\Theta = \sum_{n=1}^{k} \theta_n = \sum_{n=1}^{k} \sum_{i} J_{i,n} X_{i,n} \ . \tag{4}$$

We are interested in a certain total output and demand that the sums of fluxes over all paths are constant:

$$J_1 = \sum_{n=1}^{k} J_{1,n} = C_1 \ , \tag{5}$$

$$J_2 = \sum_{n=1}^{k} J_{2,n} = C_2 \ . \tag{6}$$

The minimum value of *Eq.* (4) for the conditions (5) and (6) is found by using the Lagrange method for constant multipliers $\lambda_1$ and $\lambda_2$ for all paths:

$$-\frac{\partial \sum_n \theta_n}{\partial X_{1,n}} = \lambda_1 \frac{\partial \sum_n J_{1,n}}{\partial X_{1,n}} + \lambda_2 \frac{\partial \sum_n J_{2,n}}{\partial X_{1,n}} , \tag{7}$$

$$-\frac{\partial \sum_n \theta_n}{\partial X_{2,n}} = \lambda_1 \frac{\partial \sum_n J_{1,n}}{\partial X_{2,n}} + \lambda_2 \frac{\partial \sum_n J_{2,n}}{\partial X_{2,n}} . \tag{8}$$

The derivatives in these equations can be identified from *Eqs* (2) and (3) so that:

$$-2J_{1,n} = \lambda_1 L_{11,n} + \lambda_2 L_{12,n} , \tag{9}$$

$$-2J_{2,n} = \lambda_1 L_{21,n} + \lambda_2 L_{22,n} . \tag{10}$$

Comparison of *Eqs* (9) and (10) with *Eqs* (2) and (3) gives:

$$X_{1,n} = -\frac{\lambda_1}{2} , \tag{11}$$

$$X_{2,n} = -\frac{\lambda_2}{2} . \tag{12}$$

The result is that *the forces for each path must be constant in order to give minimum entropy production rate.* Increasing the number of forces and fluxes will simply add more terms to *Eqs* (9) and (10), and give more results like *Eqs* (11) and (12).

The result is valid independently of the nature of the fluxes and forces. The conjugate fluxes and forces may be scalars, vectors or tensors. This means that the fluxes subject to the constraints of *Eqs* (5) and (6) can be fluxes of heat, mass, charge, and of chemical reactions. The driving forces of transport for these cases are, respectively, the thermal force, $\nabla(1/T)$, the chemical force, $\nabla(\mu_i/T)$, (where $\mu_i$ is the chemical potential of component $i$), the electric force, $\nabla\phi/T$, (where $\phi$ is the electric potential), and the force of a chemical reaction is $\Delta_r G/T$ (where $\Delta_r G$ is Gibbs energy of reaction). For a constant vectorial force, condition (10) means that components of the vector are different constants.

The proof for equipartition of forces is independent of $L_{ij,n}$. This means that we need not assume constant coefficients. The phenomenological coefficient is normally a function of state variables, and the proof allows $L_{ij,n}$ to vary between the paths. By introducing *Eqs* (2), (3), (11) and (12) into *Eq.* (4), we have the following expression for the minimum entropy production rate of the system:

$$\Theta_{\min} = X_{1,n}^2 \sum_{n=1}^{k} L_{11,n} + X_{1,n}X_{2,n} \sum_{n=1}^{k} (L_{12,n} + L_{21,n}) + X_{2,n}^2 \sum L_{22,n} . \tag{13}$$

The expression shows that the paths of high conductivity contribute more than other paths to the entropy production. This must be understood on the background of *Eqs* (5) and (6). The high conductivity path also have a high flux.

One scalar and two vectorial forces are common in chemical reactors, namely the scalar reaction force, and the vectorial forces $\nabla(1/T)$ and $\nabla(\mu_i/T)$. We have minimum entropy production for a constant sum of all local chemical reactions (i.e. yield of the reactor), when all forces in the reactor are constant. The cross coefficients between the scalar and vectorial forces are zero. The two vectorial forces therefore contribute to the entropy production rate of the total system by an expression like *Eq.* (13), while the chemical reactor contributes by a single term.

In many industrial processes, the fluxes are not of equal importance. In separations, for instance, usually one of several fluxes is of primary interest. An interesting question to ask is then: Does a combination of two forces give a lower entropy production than one force alone for the same constraints, *Eq.* (5) and *Eq.* (6)? More specifically: can mass transport be better promoted by a combination of gradients in chemical potential and in temperature, than by a gradient in chemical potential alone. By taking away one of the constraints of *Eqs* (5) and (6), say the second one, the optimization problem reduces, so the last term in *Eqs* (9) and (10) disappears. We obtain the solution:

$$X_{1,n} = -\frac{\lambda_1}{2} , \qquad X_{2,n} = 0 . \tag{14}$$

In words: the result is that it is better to use only $X_{1,n}$ to promote $J_{1,n}$ instead of a combination of $X_{1,n}$ and $X_{2,n}$ when $J_1$ is of interest, as long as the $L_{ij}$'s are the same.

We have not so far discussed how we understand the $k$ parallel processes. In some unit operations, like in a distillation tower there is a discrete stepwise addition to the total yield of the process (the flux) from each stage in the tower. The output of the product in the gas increases stepwise as the gas rises from stage to stage in the column. In this system the stages of the column are the $k$ paths of the equations above (see *Eq.* (2)). Each stage has a share, $A_n$, of the total 'transfer area' of the column: $A = \sum_{n=1}^{k} A_n$. The non-intersecting streamlines for mass transfer across the interface of all are gas bubbles, however, also parallel paths, meaning that also $J_n$ can be seen as composed of parallel contributions. This means that the force, $X_{i,n}$, should be constant not only for all the stages of the column, but also for all bubbles on each stage.

In the heat exchanger, there is a flux of heat both along and perpendicular to the transfer area in the exchanger, $A$. The direction along the area is the $x$-coordinate, and the direction perpendicular to the area is the $y$-coordinate. The area for heat exchange, $A$, can then be compared to the transfer area of one stage in a distillation tower. The thermal force across all parts of this area (i.e. the $y$-component of the total force) must be constant in the optimal situation. Furthermore, we must also have that the $x$-component of the thermal force as well as the mechanical force is constant, in an optimal heat exchanger.

The parallel paths and their forces need not be distributed in space only. Paths can also be distributed in time. The optimization problem is then to find the minimum of *Eq.* (4) given *Eqs* (5, 6) when all equations are integrated over time. The mathematical formulation of the problem is otherwise the same as above. This means that the optimum operation of a continuous process with constant $L_{ij}$'s is a stationary state operation with time-independent driving forces. In the special case where we have only one path, this stationary state result is the same as that obtained by PRIGOGINE (1947): A stationary state for linearly coupled fluxes is a state of minimum entropy production. The premises for the derivations differ, however.

Chemical reactors can be dealt with in a new way by means of these results. According to these results, vectorial and scalar forces should be constant in space and in time in the optimal reactor. The chemical reaction must accordingly be kept at the same distance from equilibrium, as the reaction proceeds in space and/or in time. When the heat of reaction changes the temperature of the system, we obtain that heat must be supplied to the reaction site in a manner which keeps the components of the thermal force constant in space.

The principle of equipartition of forces is, according to this discussion, applicable to most chemical engineering unit operations, for instance chemical reactors, drying cascades, adsorption units or distillation towers. It does not lead to new results for simple processes, i.e. processes described by one flux and one force with a constant transport coefficient. New results are expected for coupled transport processes and processes with varying coefficients. So far we have applied the principle of equipartition of force to distillation columns. We shall shortly review this work below. The application to chemical reactors is in progress (SAUAR, et al. 1997).

## 3. Applications to Distillation Columns

In this section we describe some results obtained for distillation of binary mixtures in adiabatic and diabatic columns. A schematic illustration of a distillation column with stages is shown in *Fig. 1.* We shall first see that we are able to predict a favourable stage for location of one additional heat exchanger for a column which is adiabatic at the outset, using the principle of equipartition of forces.

Simple engineering design of distillation towers is done on the basis of the Mc Cabe–Thiele diagram. This diagram contains the compositional

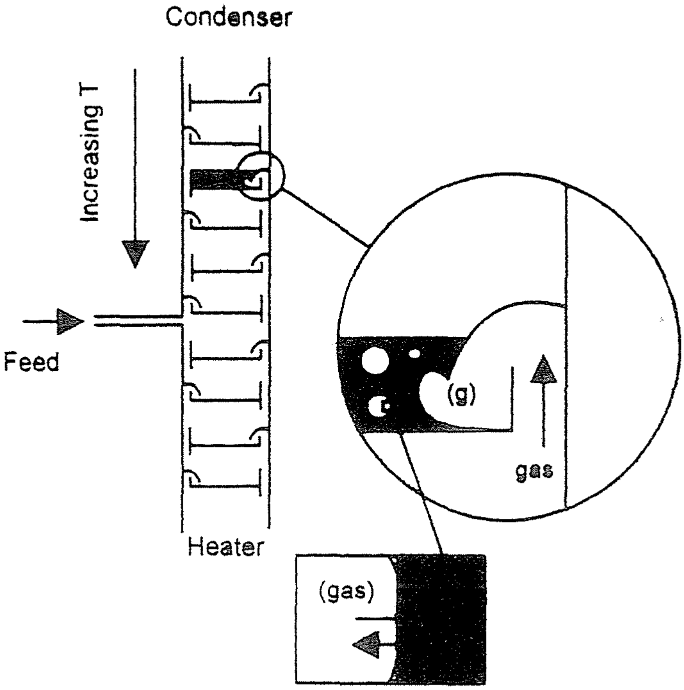

*Fig. 1.* A schematic illustration of the distillation column with stages. Mass and heat is exchanged between the up-coming gas and the down-falling liquid streams

phase diagram for the mixture to be separated, and an operating line, which relates the composition of the vapour and liquid in the column to the phase diagram. We have introduced the *isoforce operating line* for use in Mc Cabe–Thiele diagrams as a design tool for new columns.

### *3.1. Minimizing Entropy Production for Existing Distillation Columns*

In a distillation column separating a binary mixture there are two independent forces of transport, one chemical force, and one thermal force. For each stage in the column we have (KJELSTRUP RATKJE et al., 1995):

$$\theta_n = -J_q' \frac{1}{T^2} \frac{\mathrm{d}T}{\mathrm{d}x} - \frac{1}{T} J_d \frac{y_l \mathrm{d}\mu_{l,T}}{\mathrm{d}x} \,. \tag{15}$$

Here $J_q'$ is the measurable heat flux, and $J_d$ is the separation flux:

$$J_d = \left( \frac{J_l}{y_l} - \frac{J_h}{y_h} \right) \,. \tag{16}$$

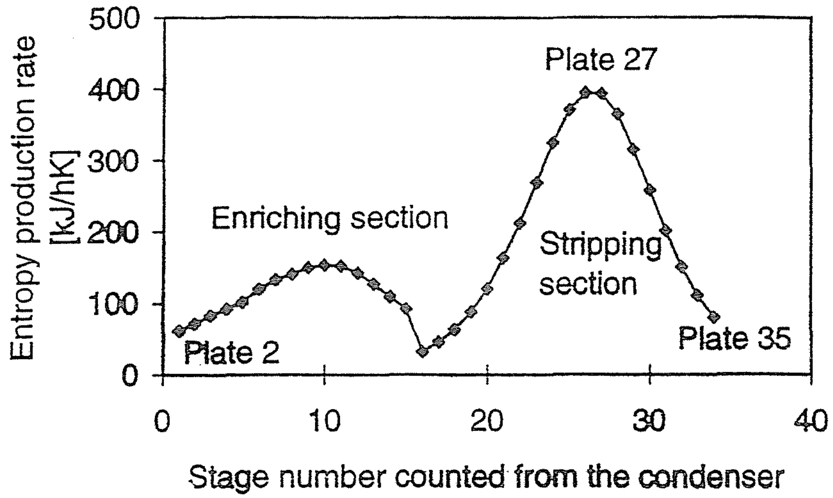

*Fig. 2.* The entropy production as a function of stage number in an adiabatic distillation column separating benzene and toluene

The fluxes of the light ($l$) and heavy ($h$) components are $J_l$ and $J_h$, respectively, and $y_l$ and $y_h$ are their mole fractions in the gas phase. The force $y_l \mathrm{d}\mu_{l,T}/\mathrm{d}x$, does not include the temperature dependent term of the chemical potential. The interchange of the two components takes place over the gas/liquid interface, and we have assumed that mass transfer is limited by transport into the gas phase in our numerical example. The positive direction of transport is from the liquid to the gas. The flux equations are:

$$J_q' = -l_{qq}\frac{1}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x} - l_{ql}\frac{1}{T}\,\frac{y_l \mathrm{d}\mu_{l,T}}{\mathrm{d}x}\,, \tag{17}$$

$$J_d = -l_{lq}\frac{1}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x} - l_{ll}\frac{1}{T}\,\frac{y_l \mathrm{d}\mu_{l,T}}{\mathrm{d}x}\,. \tag{18}$$

In order to have numerical estimates for the entropy production on the stage, we need information on the fluxes and forces or of the phenomenological coefficients and the forces. The entropy production for a stage was estimated for the separation of benzene and toluene, from the following equation:

$$\theta_n = -\frac{\Delta T}{T^2}\int_{A_n} J_q' \mathrm{d}A_n - \frac{y_l \Delta\mu_{l,T}}{T}\int_{A_n} J_d \mathrm{d}A_n\,, \tag{19}$$

where $A_n$ is the transfer area of one stage. The forces of transport were taken to be constant on the stage and the flux was integrated across the stage. In practice the process is not stationary, because the continuous evaporation and condensation of components lead to a varying composition both

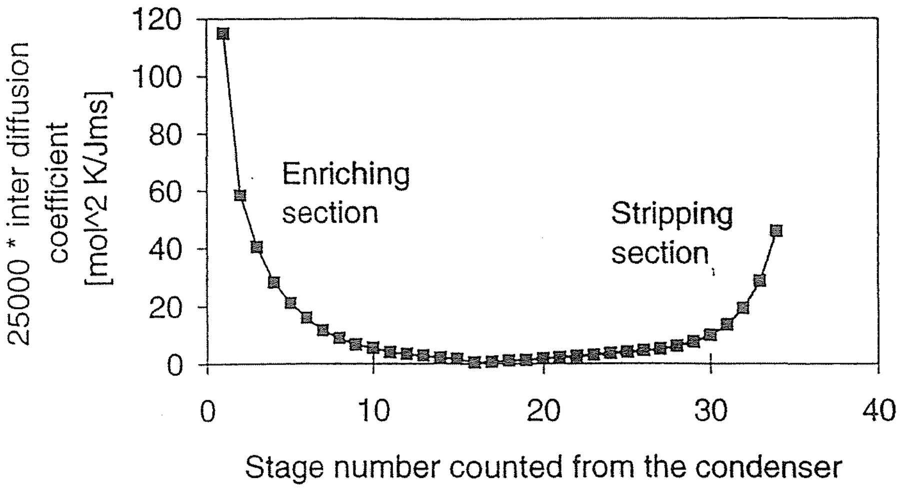

*Fig. 3.* The phenomenological coefficient for mass transfer (interdiffusion coefficient) as a function of stage number in the column of *Fig. 2*

in the vapour and in the liquid phases. For this reason we must consider small changes for which the approximation *Eq.* (19) is good (i.e. when there are several stages in the column). We choose to analyze a column with 36 stages, see *Table 1* for further specifications. For details of the calculations, it is referred to KJELSTRUP RATKJE et al. (1995). The entropy production in the adiabatic column as a function of stage number is given in *Fig. 2*. We found that the dissipation due to the thermal force was negligible in this column, since the components have boiling points which are close. The phenomenological coefficient for mass transfer was calculated as a function of stage number, see *Fig. 3*. In a column which has a uniform distribution of chemical forces, the entropy production should then ideally have the same variation with stage number as the phenomenological coefficient, see *Eq.* (13). By comparing *Figs 2* and *3* we see that this is far from the case for the adiabatic column. The question is then: Given that the investments for additional apparatus are limited, where will it be most favourable to supply (or withdraw) heat to (from) the column? According to *Figs 2* and *3* the forces will get a more uniform distribution when we increase the driving force at a place where the coefficient is relatively large, and reduce it where the coefficient is small. Increased driving forces near the end of the column are impossible without increasing the total reflux ratio (i.e. the dimensions of the column). We therefore chose to add a heat exchanger at stage no 22, and performed a new column simulation. In order to keep the total outlet conditions (nearly) constant, we had to increase the column by one stage in the process (see *Table 1*).

*Table 1.* Column specification for separation of benzene–toluene in an adiabatic column

| System | Adiabatic column | Column with heat exchanger |
|---|---|---|
| Stage numbers | 36 | 37 |
| Feed stage | 17 | 17 |
| Mole fraction in feed, $x_l$ | 0.54 | 0.54 |
| Reflux ratio | 1.58 | 1.58 |
| Stage efficiency | 0.7 | 0.7 |
| Distillate composition, $x_l$ | 0.9896 | 0.9889 |
| Bottom composition, $x_l$ | 0.0105 | 0.0114 |

The results for the entropy production for the column with the extra heat exchanger and stage are given in *Fig. 4.* The variation in the bottom composition is small compared to that in the composition of the feed which, however, means that we can compare the entropy production for the two columns. We see that the peak of the entropy production around stages 27 – 28 is reduced compared to that of *Fig. 2.* The change in area under the curve and the change in entropy production in the equipment, leads to a reduction in total entropy production by 7%, a relatively large number for distillation of ideal mixtures. This example of binary distillation therefore demonstrates how the principle can be used as a design tool for modification of existing distillation columns. In practical situations, the question arises whether the extra apparatus investments can be compensated for by the lower energy required by the process. We have also shown how the principle can be used to improve the performance in multicomponent distillation (SAUAR et al., 1995).

### *3.2. Isoforce Operating Lines in Mc Cabe–Thiele Diagrams*

The principle of equipartition of forces is a relatively easy design criterion for energy efficient columns, because it can be translated into controlling compositions at different stages in the column. The sequence of compositions, which defines constant forces of operation everywhere in the column, was used to define the *isoforce operating line* in the Mc Cabe–Thiele diagram (SAUAR et al., 1995). Examples of such lines for the benzene–toluene phase diagram are shown in *Fig. 5.* Isoforce lines were constructed using a constant chemical force:

$$\frac{y_l \Delta \mu_l}{T} = C \qquad (20)$$

for two values of $C$. It appears that the isoforce line is nearly parallel with the equilibrium line in the phase diagram, which relates compositions in the liquid and vapour phases. We explain this for the present mixture which is

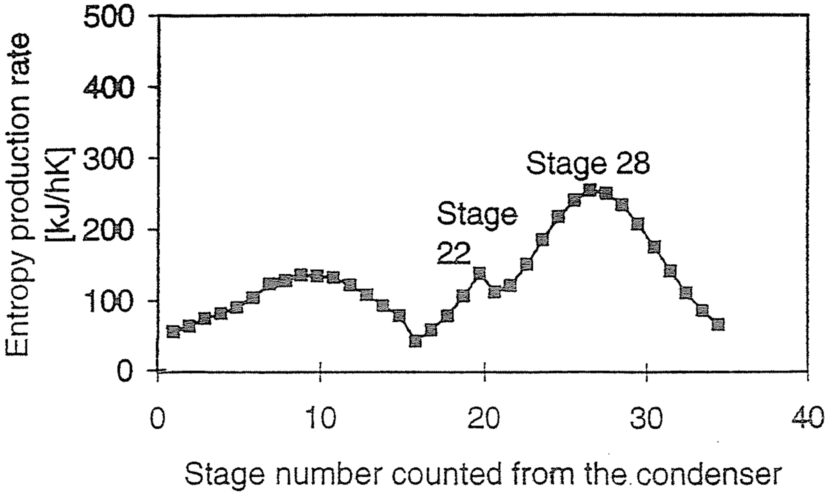

*Fig. 4.* The entropy production as a function of stage number in the modified adiabatic column

close to being ideal. Activity coefficients which deviate largely from unity make the lines less parallel. The choice of the constant $C$ is a trade-off between energy costs and investment costs. A large $C$ means higher energy costs and lower investment costs, and vice versa for a small $C$. We choose its value according to column height and other practical limitations. It may be difficult in practice to keep a constant force throughout the whole column. Isoforce lines can also be defined for multicomponent mixture distillations. Their illustration in the phase diagram then becomes more complicated.

The common operating line, which has a constant ratio between gas and liquid streams in the column, is for comparison a straight line. It follows that distributed heat exchange is needed to maintain uniform forces over the whole column. RIVERO (1995) found the optimum operating line of a diabatic column, from a numerical analysis of lost exergy. The diabatic column has a distributed heat exchange. This operating line followed an isoforce line for large parts of the Mc Cabe–Thiele diagram (SAUAR et al., 1997b).

### 3.3. Conclusions

We have shown that equipartition of forces over parallel paths gives minimum entropy production when there is a constant yield in the process. The parallel paths are non-intersecting streamlines, with arbitrary conductivi-

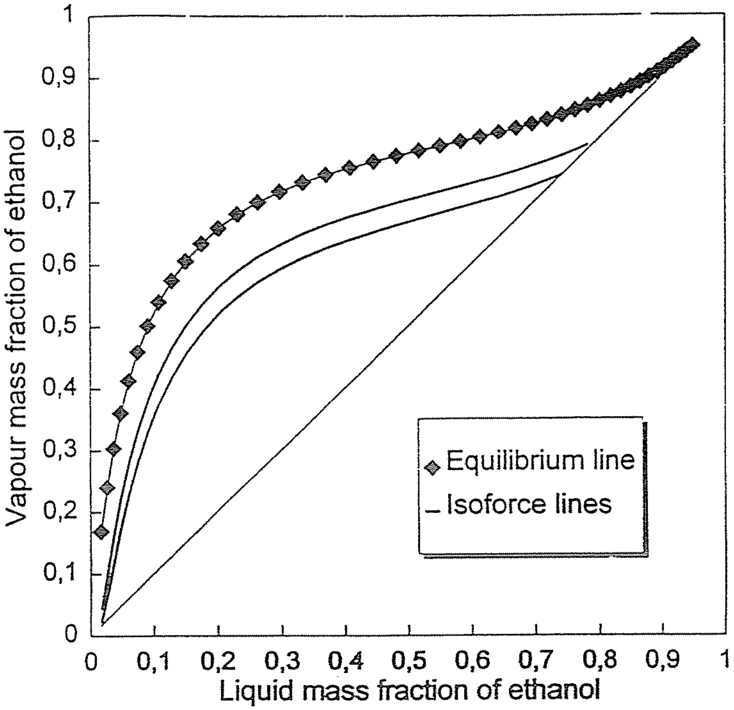

*Fig. 5.* Examples of isoforce lines in a Mc Cabe–Thiele diagram for the separation of benzene and toluene. A standard operating line is also shown

ties, distributed in space or time. We have demonstrated the value of the principle for distillation, expect that it may be useful also in other contexts.

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