

# Dynamic modelling of a fractionation process for a liquid mixture using supercritical carbon dioxide

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## Abstract

This work presents a simple dynamic modelling of a process of separation of a quaternary mixture using supercritical CO<sub>2</sub>. Thermodynamic description is accomplished using efficient available models (SRK equation of state with MHV2 mixing rules). An approximate approach was compared to the rigorous resolution of the system of algebro-differential equations, and was shown to enable a correct description of the dynamic behaviour. The modelling was compared to experiments performed on a small pilot composed of one 200-ml contactor and a cascade of three cyclonic separators. Good results were obtained for the contactor, although they were not very satisfactory for the description of the fractionation in the cyclonic separators. Even if discrepancies between experimental and calculated results may probably originate from the experimental procedure, the hydrodynamic description of the separators here is likely to be oversimplified. The cyclonic separator cannot be regarded as a simple theoretical stage (TSM), and we have proposed an alternate description (EPSM), that, although more suitable, still needs to be improved.

*Keywords:* Supercritical CO<sub>2</sub>; Dimethyl carbonate; Dynamic modelling; Liquid mixture fractionation

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## 1. Introduction

Using supercritical fluids and especially carbon dioxide as a solvent and/or as a reagent in chemical synthesis appears nowadays as a very attractive field of application for supercritical fluids. Many reactions, using mainly supercritical carbon dioxide (SCCO<sub>2</sub>) or supercritical water, are under study and results are very promising, as shown in recent literature [1,2]. Performing reactions with supercritical CO<sub>2</sub>, in addition to an obvious environmental advantage, may alleviate mass transfer limitations and has been shown to provide better control of selectivity [3]. Moreover, it is often argued that recovery of products, and even fractionation, is likely to be easily done by temperature and/or pressure changes, avoiding separation set-ups like distillation or extraction columns.

In this context, we are interested in the separation of the mixture involved in the direct synthesis of dimethyl carbonate (DMC) from methanol and supercritical CO<sub>2</sub>, the latter acting, in this case, as a reagent and as a solvent. Studies of this reaction [4–8] have shown a severe limitation because of the decomposition of the organotin catalyst by water produced by the reaction itself, as well as due to the reverse hydrolysis of DMC. Several attempts have been made in order to avoid the detrimental effect of water. For example, Kizlink and Pastucha [6,7], performing this reaction with gaseous CO<sub>2</sub>, proposed to use chemical scavengers for water, like trimethyl phosphate or dicyclohexylcarbodiimide, enabling increase of the reaction yield from 260 to 330 mol% with respect to the organotin compound. For the same purpose, using SCCO<sub>2</sub>, Sakakura et al. [5] proposed the pre-dehydration of methanol. We may also think that continuous elimination of water from the reactor, as the reaction proceeds, would constitute another attractive solution. It implies that the reaction is undertaken in a continuous or a semi-continuous process configuration.

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In this work, in a first step, the feasibility of the fractionation of a mimicked post-reactional mixture has been investigated by simple changes of temperature and pressure in a semi-continuous process. The aim is to propose the dynamic modelling of this operation. The present study does not involve the reaction synthesis itself, it only attempts to describe the thermodynamic behaviour of the system constituted of reagents and products, i.e. the CO<sub>2</sub>–methanol–DMC–water mixture. In the field of supercritical extraction, the dynamic modelling of fractionation of the extracts has been the subject of relatively few studies. For example, Cesari et al. [9] have been interested by the modelling of a semi-batch process of extraction–separation using a system of differential and algebraic equations, but they have focused their work on the mathematical model representing the extraction, thanks to SCCO<sub>2</sub>, of methanol from a methanol–water mixture, and citral from lemon oil. They have pointed out that major difficulties were encountered in the modelling of the thermodynamics of the mixture, and not in the application of a numerical method of integration. A similar study has recently been done by Benvenuti et al. [10], relative to the extraction of terpenic compounds from lemon essential oil, but results representing the behaviour of the system in the post-extraction single stage of separation were not presented.

In the present work, we have considered a contacting vessel, acting here as an extractor (in the future synthesis process, it will be the reactor), and three stages of separation by pressure and temperature changes, as available in our experimental pilot. The mathematical model is based on mass balance equations and equilibrium relations giving a system of algebraic and dif-

ferential equations. This system can be solved with a conventional numerical method, but we also proposed a simplified approach where the system is considered as steady state over an increment of time,  $\Delta t$ . This approach is very likely to be valid because the dynamics of the system are slow. This modelling is very useful to test the possibility of the post-reactional fractionation, that is expected to be quite difficult due to similar volatility of the components (methanol, DMC, water), and because of strong molecular interactions existing between them.

## 2. Materials and methods

Runs were carried out in a SEPAREX SF200 pilot (Separex Company, Nancy, France) represented in Fig. 1. This apparatus is composed of a 200-ml contacting vessel, that could be used as a reactor, or, as is the case here, as a simple liquid-fluid contactor. CO<sub>2</sub> is introduced via a specific device consisting of a filter mesh screen from a commercial HPLC pump. This allows for a good dispersion of the CO<sub>2</sub> in the liquid mixture (methanol–water–DMC), when a biphasic system is present. This dispersion is also improved by magnetic stirring within the contactor. A cascade of three 20-ml cyclonic separators is present at the contactor outlet. Pressure in each vessel is adjusted by depressurization valves.

Subcooled liquid CO<sub>2</sub> is pumped by a volumetric membrane pump (Milton Roy, max. 4 kg/h), then heated to the desired temperature and continuously introduced into the contactor. Experiments can be carried out in open-loop or closed-loop configuration, in

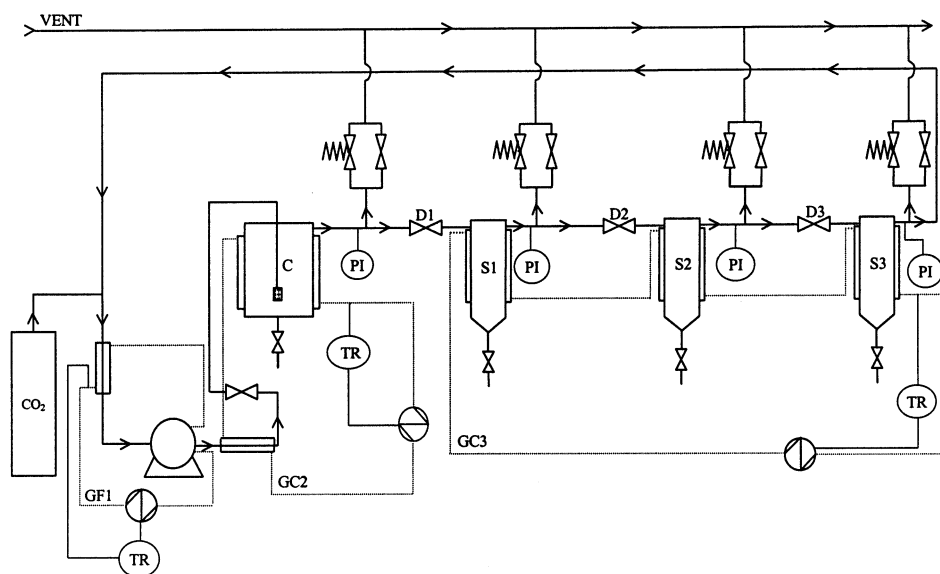


Fig. 1. Pilot SF200. C, contactor; S1, S2, S3: separators; GF1, cooling group; GC2, GC3: heating groups; PI, pressure indicators; TR, temperature regulators; D1, D2, D3: depressurisation valves.

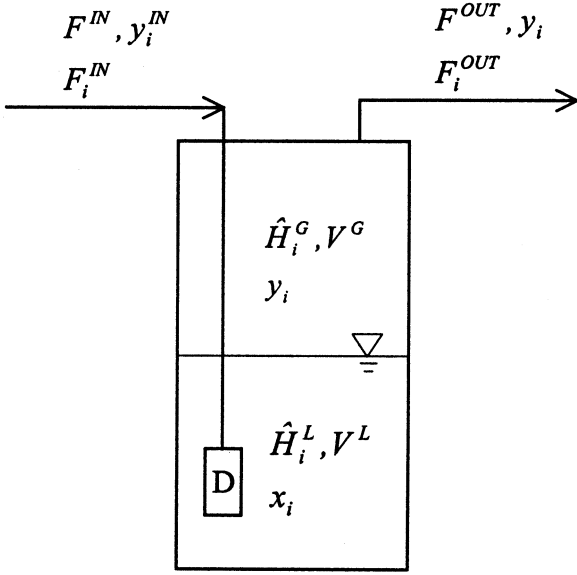


Fig. 2. Schematic representation of the contactor; D, distributor of CO<sub>2</sub>.

which case, after condensation, CO<sub>2</sub> is recycled at the head of the pump. Temperatures and pressures are controlled in each unit of the pilot, pressure being limited to 30 MPa and temperature around 333 K.

Before starting an experiment, the pilot is filled with CO<sub>2</sub> at bottle pressure (4.9 MPa) and air is flushed out. The mixture to be separated is then directly introduced into the contactor by a HPLC pump (Gilson, model 302). The desired pressure is reached in the contactor by pumping CO<sub>2</sub> in. CO<sub>2</sub> is then fed at a constant flow rate into the system. The liquid composition of each vessel is analysed, as a function of time, giving the evolution of composition of the mixture in the process.

Analyses are done by gas chromatography with a Hewlett-Packard 5890 series II chromatograph equipped with a Supel-QTM Plot capillary column (30 m, 0.53 mm i.d.) from SupelCo (USA) and a TCD detector.

Synthetic mixtures are prepared from distilled water, DMC (Aldrich, 99%, D15, 292-7), and methanol (Pro-labo Chromanorm, min.99.8%, 20834.291).

### 3. Mathematical model

#### 3.1. The contactor

Fig. 2 shows a schematic representation of the contactor. The description of the dynamic behaviour of the contactor is based on the following assumptions

- it is regarded as a theoretical stage. Thus, at each moment in time, thermodynamic equilibrium is considered between effluent and liquid hold-up. This

condition of coexistence of two phases is not always met and depends mainly on the quantity of water. It may occur that the system shifts from mono to biphasic (or the reverse) within one experiment;

- homogeneity of concentrations is assumed in each phase. The composition of the outgoing flow is always identical to the composition of the fluid phase in the contactor, no matter the state of the system, monophasic or biphasic;
- temperature and pressure are maintained constant.

#### 3.1.1. Description of the dynamics of the contactor (Conventional Dynamic Model, CDM)

In this work, variables like  $\hat{X}$  represent mol quantities, while  $F$  represents flow rates, and superscripts L and G indicate the high density 'liquid' phase and the low density 'fluid' phase, respectively;  $x$  and  $y$  are mol fractions. The global and partial mass balances in the contactor can be written as follows:

$$F^{IN} - F^{OUT} = \frac{d\hat{H}^L}{dt} + \frac{d\hat{H}^G}{dt} \quad (1)$$

$$F^{IN} \cdot y_i^{IN} - F^{OUT} \cdot y_i = \frac{d}{dt}(\hat{H}^L \cdot x_i) + \frac{d}{dt}(\hat{H}^G \cdot y_i) \quad (2)$$

$i = 1, \dots, 4$

Let  $\Psi$  be the volume fraction occupied by the liquid phase in the contactor, we can define the hold-up in each phase by:

$$\hat{H}^L = \Psi \cdot \frac{V_{\text{cont}}}{v^L(T, P, x_i)} \quad (3)$$

$$\hat{H}^G = (1 - \Psi) \cdot \frac{V_{\text{cont}}}{v^G(T, P, y_i)} \quad (4)$$

with  $V_{\text{cont}}$  being the effective volume of the contactor (200 ml) and  $v^L$  and  $v^G$ , respectively, the liquid phase and the fluid phase molar volumes.

The equilibrium condition is then expressed by the equality of fugacities of each component in the liquid and fluid phase:

$$x_i \cdot \phi_i^L(T, P, x_i) = y_i \cdot \phi_i^G(T, P, y_i) \quad i = 1, \dots, 4 \quad (5)$$

Fugacity coefficients  $\phi_i$  are obtained using the cubic equation of state proposed by Redlich and Kwong [11] and modified by Soave [12]:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (6)$$

where the mixture parameters  $b$  and  $a(T)$  are calculated using the MHV2 mixing rules proposed by Michelsen [13]. Equations of state such as SRK equation gives satisfying results at high pressure but have to be used only when dealing with apolar or poorly polar compounds. Conversely, activity coefficient models (differently named  $\gamma$ - $\phi$  approach) cannot be used at high

pressure but are particularly appropriate for thermodynamic calculations involving polar compounds. The MHV2 approach conciliates these two application domains, involving an activity coefficient model into mixing rules of an equation of state. This approach is now commonly recognized as a good choice for high pressure phase equilibrium calculations involving polar compounds, as is the case here. Moreover, binary activity parameters needed for the activity coefficient model can be issued from low pressure experimental data. The UNIQUAC [14] activity coefficient model has been chosen to determine the value of the free excess Gibbs energy needed in the calculation of the mixture parameters. As binary interaction parameters between DMC and methanol, DMC and water and DMC and CO<sub>2</sub> were partially or not available at all in the literature, they had to be experimentally determined in a preliminary study. This part of our work is not described here. For other binaries, coefficients were obtained by fitting literature data [15–19]. All parameters used in this work are presented in Table 1, where experimentally determined parameters are written in bold. Agreement between calculated and experimental binary equilibria involved was found satisfactory.

The sum of mole fraction values in each phase must be equal to 1, leading to the last equation of the system written in accordance with the Rachford–Rice formulation [20]:

$$\sum_{i=1}^4 x_i - \sum_{i=1}^4 y_i = 0 \quad (7)$$

The resolution of this system of 2NC + 4 equations, comprising differential and algebraic equations, enables the calculation of the 2NC + 4 variables:  $\hat{H}^G$ ,  $\hat{H}^L$ ,  $F^{\text{OUT}}$ ,  $\Psi$ ,  $x_i$  ( $i = 1, \dots, 4$ ) and  $y_i$  ( $i = 1, \dots, 4$ ) as a function of time. This calculation has been carried out using the Fortran routine RBLSD [21] available in the ProSim™ software package (PROSIM S.A., France). This program implements the Gear’s numerical method [22].

Initially, the amount of each component introduced into the contactor, as well as the temperature and pressure, are known, and the system is considered at equilibrium. Thus, each variable can be initialised. In addition to the variables, the numerical method needs values of derivatives at the initial instant. This initialisation can be sometimes sensitive, because it is impor-

tant for the residual functions to be close to zero, and for the variables to remain physically consistent.

### 3.1.2. Description of the dynamic behaviour of the contactor based on a Simplified Approach Model (SAM)

As we mentioned in the introduction, we have tested a simplified approach that might set us free from numerical problems. Its results are compared to those of the CDM.

In SAM, mass balances are made at each time increment, and, except for calculation of compositions of phases under thermodynamic equilibrium, no numerical algorithm is necessary. The system is considered as steady state between two time increments.

Initially, the total amount of each component,  $\hat{M}_{i,t=0}$ , introduced into the contactor is known, as well as temperature, pressure and CO<sub>2</sub> inlet flow rate. The overall composition of the mixture in the contactor is obtained by:

$$z_{i,t} = \frac{\hat{M}_{i,t}}{\sum_{i=1}^4 \hat{M}_{i,t}} \quad i = 1, \dots, 4 \quad (8)$$

Solving the equality of fugacities (Eq. (5)), gives the composition of each phase, as well as molar vaporization ratio  $\omega$ , and then molar volumes of each phase. Molar vaporization ratio  $\omega$  is defined as the ratio of the number of moles of the generated fluid phase after the equilibration to the total number of moles involved in the equilibration. Volumes  $V^L$  and  $V^G$  occupied by each phase can then be calculated:

$$V_t^L = v_t^L \cdot (1 - \omega_t) \cdot \sum_{i=1}^4 \hat{M}_{i,t} \quad (9)$$

$$V_t^G = v_t^G \cdot \omega_t \cdot \sum_{i=1}^4 \hat{M}_{i,t} \quad (10)$$

$$V_t^{\text{tot}} = V_t^L + V_t^G \quad (11)$$

With a time increment, the outgoing quantity and hold-up of each phase between  $t$  and  $t + \Delta t$  are expressed by:

$$F_{i,t+\Delta t}^{\text{OUT}} = \left( (V_t^{\text{tot}} - V_{\text{cont}}) \cdot \frac{y_{i,t}}{v_t^G} \right) \cdot \frac{1}{\Delta t} \quad i = 1, \dots, 4 \quad (12)$$

$$\hat{H}_{i,t+\Delta t}^L = V_t^L \cdot \frac{x_{i,t}}{v_t^L} \quad i = 1, \dots, 4 \quad (13)$$

Table 1  
Binary interaction parameters for the CO<sub>2</sub>–methanol–DMC–water system<sup>a</sup>

	CO <sub>2</sub> –methanol	CO <sub>2</sub> –water	CO <sub>2</sub> –DMC	DMC–methanol	DMC–water	Methanol–water
$A_{ij}$ (cal mol <sup>-1</sup> )	515.974	1621.77	<b>-33.041</b>	<b>637.88</b>	<b>-435.901</b>	781.604
$A_{ji}$ (cal mol <sup>-1</sup> )	108.737	1016.50	<b>-35.011</b>	<b>38.69</b>	<b>2476.66</b>	-664.981

<sup>a</sup> Experimentally determined parameters shown in bold.

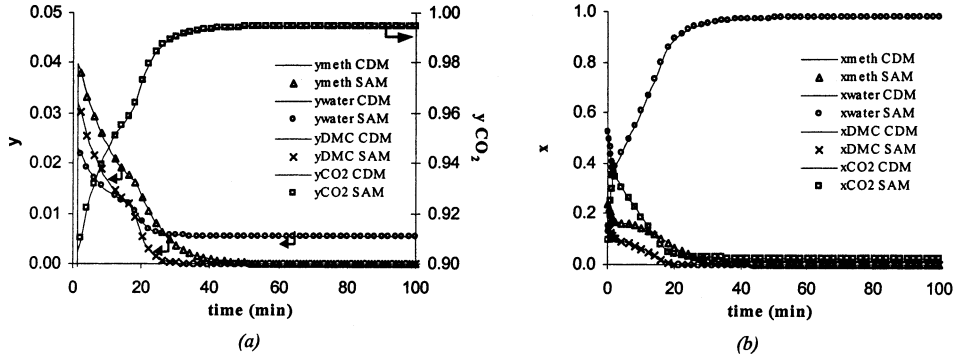


Fig. 3. Fluid phase (a) and liquid phase (b) composition in the contactor (symbols refer to SA model and lines to CD model).

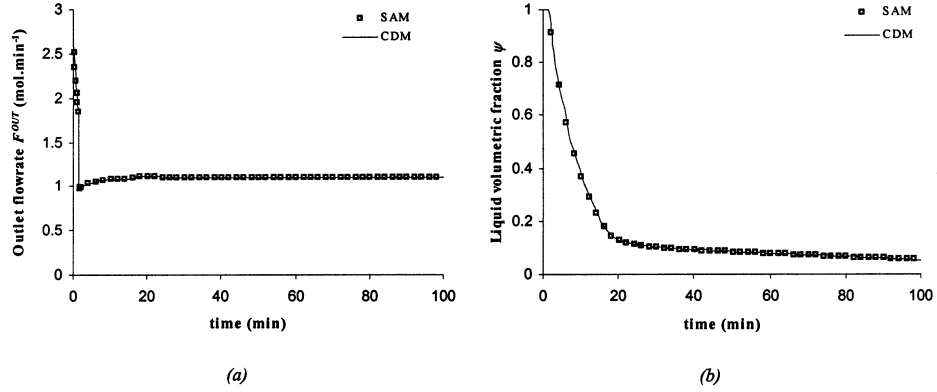


Fig. 4. Outlet flow rate  $F^{OUT}$  (a) and liquid volume fraction  $\psi$  (b) in the contactor (symbols refer to SA model and lines to CD model).

$$\hat{H}_{i,t+\Delta t}^G = (V_{cont} - V_t^L) \cdot \frac{y_{i,t}}{v_t^G} \quad i = 1, \dots, 4 \quad (14)$$

The amount of component  $i$  involved in the equilibration and in the mass balance at time  $t + \Delta t$  is calculated as follows:

$$\hat{M}_{i,t+\Delta t} = \Delta t \cdot F_i^{IN} + \hat{H}_{i,t+\Delta t}^G + \hat{H}_{i,t+\Delta t}^L \quad i = 1, \dots, 4 \quad (15)$$

Global composition of the mixture is obtained using Eq. (8) and a new computation, corresponding to an other increment of time, is started.

### 3.1.3. Comparison of results obtained with the two models, CDM and SAM

Figs. 3–5 present the comparison between results obtained with the CDM and SAM, and it can be seen that these results are very similar. We can observe on Fig. 3a Fig. 4b Fig. 5 from the values of fluid phase molar fraction, fluid phase hold-up and liquid volume fraction, that at the initial moment and during a short time of about 1.5 min, the mixture remains as a monophasic liquid. Even during this period, the two models propose identical values of the variables  $x_i$ ,  $\hat{H}^L$  and  $F^{OUT}$ .

Indeed, when using CDM, we have found cases where the convergence of the resolution was highly dependent upon the initialisation values. In contrast, resolution of SAM is stable, easy to implement and gives the same results as long as the time increment is sufficiently small. In this example the time increment is equal to 0.01 min but less satisfactory results are ob-

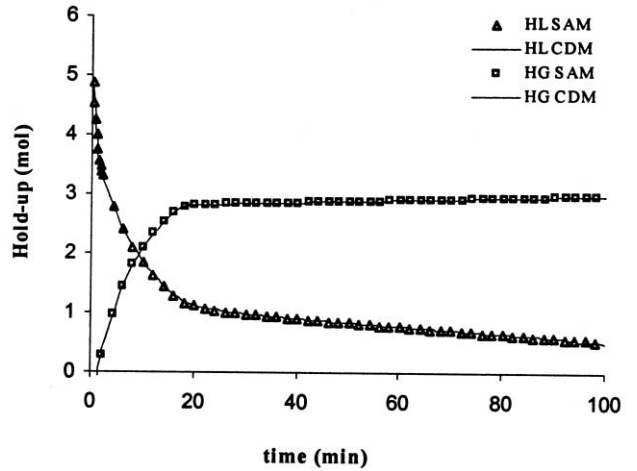


Fig. 5. Liquid  $\hat{H}^L$  (a) and fluid  $\hat{H}^G$  (b) hold-ups in the contactor (symbols refer to SA model and lines to CD model).

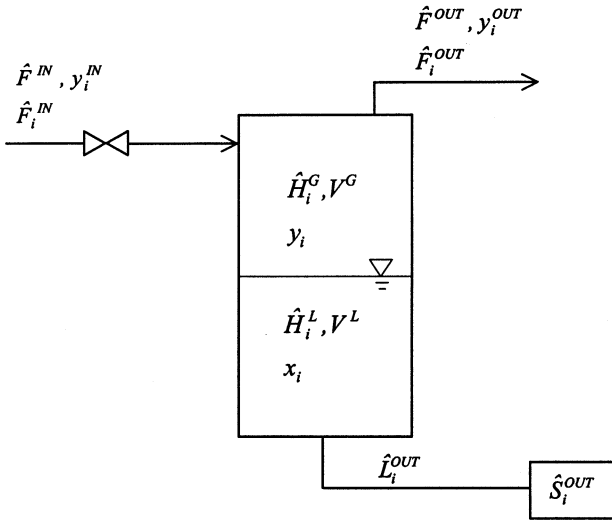


Fig. 6. Schematic representation of the separator.

tained when we choose a time increment greater than 0.5 min. This adjustable parameter may be fixed to a large value and then decreased until no further improvement is observed.

As a consequence, we have chosen to adopt this convenient simplified approach for the rest of this study.

### 3.2. The separator

The separator is schematically represented on Fig. 6. The separation is achieved by a depressurisation valve and a cyclonic separator. Thereby, the modelling of this step is more complex than for the contactor. Liquid generated in the separator can be withdrawn, and the externally accumulated withdrawal is noted  $\hat{S}_i$ . Temperature and pressure are considered as constant.

Two descriptions of the separation step have been investigated. In the first one, the separator is regarded as a theoretical stage in which fluid outgoing quantity  $\hat{F}_i^{OUT}$  and liquid hold-up are at equilibrium. In the second case, the equilibrium is assumed directly after the valve and the fluid and the liquid phases undergo perfect segregation in the separator.

In the following, the first description is termed TSM (Theoretical Stage Model) and the second EPSM (Equilibrium and Perfect Segregation Model).

#### 3.2.1. Description of the TS model

At time  $t$ , the total amount of component  $i$  submitted to equilibration is calculated as follows:

$$\hat{M}_{i,t} = \hat{F}_{i,t}^{IN} + \hat{H}_{i,t}^L + \hat{H}_{i,t}^G \quad i = 1, \dots, 4 \quad (16)$$

The overall composition of the mixture is then obtained by Eq. (8), and, resolving equality of fugacities, we can calculate composition of each phase at equi-

librium, as well as vaporization ratio and molar volumes of phases. In the same way as for the contactor, volumes occupied by each phase are obtained using Eqs. (9)–(11). Hold-up of each phase, as well as outgoing quantities, are calculated in a similar way as for the contactor. These variables are obtained by comparing volumes necessary for phases with volume available in the separator  $V_{sep}$ . In the separator, liquid hold-up can be withdrawn continuously, or only when the separator is full of liquid, or never withdrawn, in which case a part of the liquid may overflow towards the next separator. For example, if the liquid formed is continuously removed from the separator, hold-up between  $t$  and  $t + \Delta t$  are calculated by:

$$\hat{H}_{i,t+\Delta t}^G = V_{sep} \cdot \frac{y_{i,t}}{v_i^G} \quad i = 1, \dots, 4 \quad (17)$$

$$\hat{H}_{i,t+\Delta t}^L = 0 \quad i = 1, \dots, 4 \quad (18)$$

Then, fluid and liquid outgoing quantities are deduced from:

$$\hat{F}_{i,t+\Delta t}^{OUT} = (V_t^G - V_{sep}) \cdot \frac{y_{i,t}}{v_i^G} \quad i = 1, \dots, 4 \quad (19)$$

$$\hat{L}_{i,t+\Delta t}^{OUT} = V_t^L \cdot \frac{x_{i,t}}{v_i^L} \quad i = 1, \dots, 4 \quad (20)$$

Thus, the accumulated collected withdrawal is obtained by:

$$\hat{S}_{i,t+\Delta t}^{OUT} = \hat{S}_{i,t}^{OUT} + \hat{L}_{i,t+\Delta t}^{OUT} \quad i = 1, \dots, 4 \quad (21)$$

Total amount of component  $i$  at time  $t + \Delta t$  can then be calculated from Eq. (16) and a new computation is started. At initial time, the separator is full of  $\text{CO}_2$ .

#### 3.2.2. Description of the EPS model

In this case, if two phases have been generated (the depressurization may not always yield a biphasic system), equilibrium is assumed directly after the depressurization valve. The resulting mixture enters the separator where the liquid phase mixes with the already present liquid phase, and the same for the fluid phase. This description is proposed because there is no intimate mixing of phases in the separator since the inlet stream enters the separator at the top of it. Each phase is considered as homogeneous in the separator but interphasic mass exchange is not effective (perfect segregation), so that a new equilibrium cannot be achieved. In this description, the thermodynamic equilibrium is regarded as slow, compared to the transport phenomena. Thus total amount of component  $i$  involved in the flash is calculated from the entering flow rate:

$$\hat{M}_{i,t} = \hat{F}_{i,t}^{IN} \quad i = 1, \dots, 4 \quad (22)$$

The equilibrium is calculated from the overall mixture composition obtained with Eq. (8). In the case of

Table 2  
Characteristic data for the simulation of the contactor

$T$ (K)	$P$ (MPa)	CO <sub>2</sub> inlet flow rate (mol min <sup>-1</sup> )	$\hat{M}_{\text{CO}_2,0}$ (mol)	$\hat{M}_{\text{meth},0}$ (mol)	$\hat{M}_{\text{water},0}$ (mol)	$\hat{M}_{\text{DMC},0}$ (mol)
324.5	20	1.091	0.361	1.236	2.751	0.747

Table 3  
Experimental conditions for the run, with initial mixture presented in Table 2

CO <sub>2</sub> inlet flow rate (mol min <sup>-1</sup> )	Contactor		Separator 1		Separator 2		Separator 3	
	$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
1.091	324.5	20	308	7.5	306	6.2	295	2.0

continuous withdrawal of the liquid phase of the separator, the volume corresponding to the fluid phase  $Vh^G$  can be obtained from:

$$Vh_t^G = Vh_{t-\Delta t}^G + V_t^G \quad (23)$$

From the fact that the total volume of the separator is fixed, we can deduce the outgoing quantities between  $t$  and  $t + \Delta t$  from the set of equations:

$$\hat{F}_{i,t+\Delta t}^{\text{OUT}} = \frac{(Vh_t^G - V_{\text{sep}})}{Vh_t^G} \cdot \left( \hat{H}_{i,t}^G + V_t^G \cdot \frac{y_{i,t}}{v_i^G} \right) \quad i = 1, \dots, 4 \quad (24)$$

$$\hat{L}_{i,t+\Delta t}^{\text{OUT}} = V_t^L \cdot \frac{x_{i,t}}{v_i^L} \quad i = 1, \dots, 4 \quad (25)$$

and the fluid hold-up between  $t$  and  $t + \Delta t$  and the accumulated withdrawal from:

$$\hat{H}_{i,t+\Delta t}^G = \frac{V_{\text{sep}}}{Vh_t^G} \cdot \left( \hat{H}_{i,t}^G + V_t^G \cdot \frac{y_{i,t}}{v_i^G} \right) \quad i = 1, \dots, 4 \quad (26)$$

$$\hat{S}_{i,t+\Delta t}^{\text{OUT}} = \hat{S}_{i,t}^{\text{OUT}} + \hat{L}_{i,t+\Delta t}^{\text{OUT}} \quad i = 1, \dots, 4 \quad (27)$$

## 4. Results and discussion

### 4.1. The contactor

According to bibliographic results on DMC synthesis, the reaction has to take place under high pressure (around 20 MPa) and temperature higher than 423 K, in order to activate the catalyst. The present technical constraints of our experimental device do not allow operating at temperatures higher than 333 K. Anyway, as the main purpose of this work was to validate a thermodynamic and a modelling approach, it is more demonstrative to choose operating conditions (temperature, pressure and concentrations) where a biphasic system is present during the main part of the run. The composition of the initial mixture introduced into the contactor is the same as that presented in Table 2. Conditions of temperature and pressure for each unit of the process are presented in Table 3.

Fig. 7 reports the evolution of the composition of the liquid phase in the contactor as a function of time. The composition of the liquid phase on a CO<sub>2</sub> free basis is the only experimental accessible variable from the pilot, so comparison of experimental and calculated results can only be made on this variable.

Every 10 min, a sample is removed from the bottom of the contactor, while the flask receiving the sample is immersed in ice in order to avoid loss of methanol, water or DMC. CO<sub>2</sub> is supposed to leave the mixture without carrying other products away. When opening the valve to collect the sample, no drop of pressure is observed on the pressure gauge.

As can be seen from Fig. 7, a good agreement is shown between experiments and results of the SA model. The small deviations may be the consequence of various factors: from a modelling point of view, the model does not take into account energy balance, and even if no significant pressure variation is observed on the 5 bar accuracy pressure gauge, weak temperature

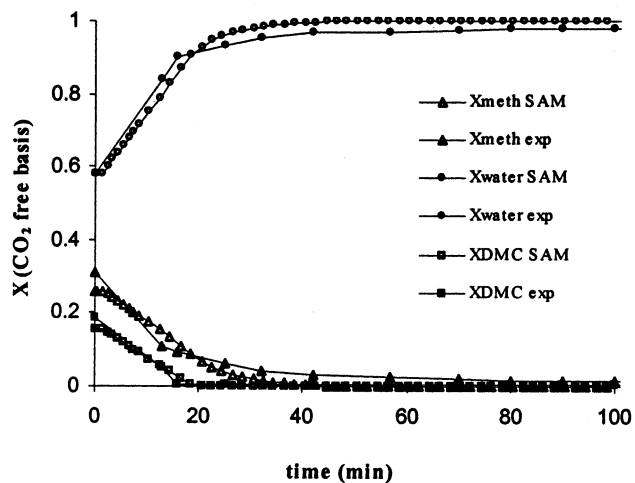


Fig. 7. Liquid phase CO<sub>2</sub> free basis composition in the contactor (open symbols refer to experimental data and filled symbols to modelling results).

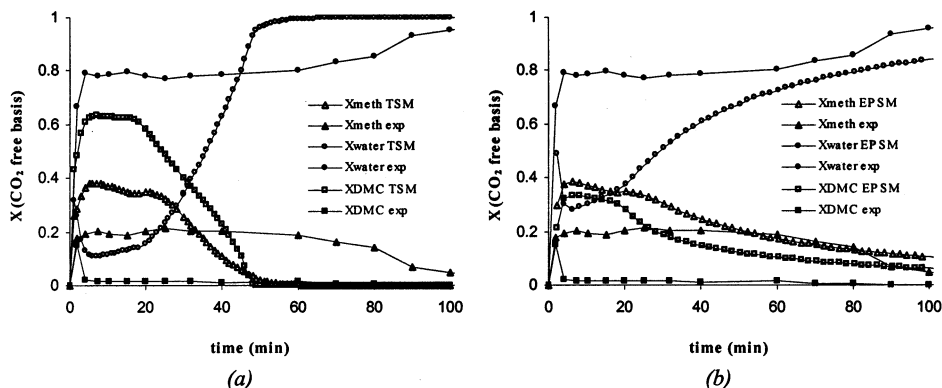


Fig. 8. Liquid phase composition in the first separator (a) TS model; (b) EPS model (open symbols refer to experimental data and filled symbols to modelling results).

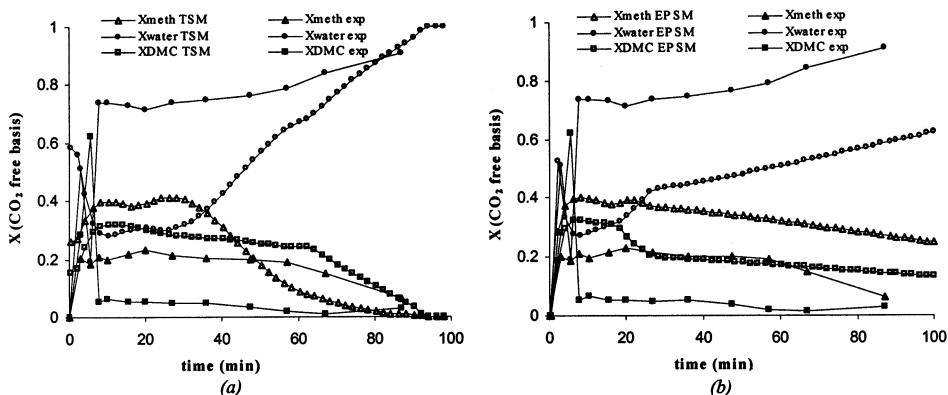


Fig. 9. Liquid phase composition in the second separator (a) TS model; (b) EPS model (open symbols refer to experimental data and filled symbols to modelling results).

variations (max. 1°C) have been detected during the run. This may have an influence on such a system that is very sensitive to pressure and temperature. Finally, it is important to notice that the use of concentrations to compare the results greatly amplifies experimental errors on the curves, since the three concentrations are highly dependent.

Considering the fact that these results are obtained with a model including no adjustable parameter, we believe that these results are very satisfactory and allow us to validate three aspects of our work:

- the thermodynamic model used to calculate the thermodynamic equilibrium of the quaternary mixture, and principally the binary interaction coefficients determined experimentally;
- the approximate numerical approach (SAM) used to describe the behaviour of this mixture in the contactor;
- the experimental procedure and the method of collection of samples from the bottom of the contactor.

Some comments on the behaviour of the process may be given from Fig. 7: water tends to remain in the liquid phase even if DMC and methanol are rapidly

removed. The rates of decrease of DMC and methanol mole fractions are comparable. The slower extraction of water, compared to methanol, could have been expected, but DMC, whose volatility is close to that of water, does not follow the same trend. In fact, water is removed from the liquid phase but much more slowly than DMC and methanol. As a remark concerning the operation of DMC synthesis, it would not be interesting to perform it when a liquid phase is present because water would tend to remain in it. Moreover, in order to avoid mass transfer limitations, it is always preferable to operate in a single supercritical phase.

Starting from the model presented here, it will be easy to implement a module in which equations for the reactions will be written, when sufficient information about kinetics is available. The model will be useful to find favourable thermodynamic conditions in order to run the reaction under supercritical conditions.

#### 4.2. The separators

Results for separator 1, 2 and 3 are presented in Figs. 8–10, respectively and provide a comparison between



experimental and calculated results, the latter given by the two kinds of modelling we mentioned, TSM or EPSM. As in the case of the contactor, the only experimentally measurable variable, composition of the liquid phase, is reported. In these experiments the liquid phase is not continuously removed from the separator, so that liquid is accumulated in the separators and only samples are taken for measurements. The experimental procedure is the same as that described for the contactor.

It appears from Figs. 8–10, that poor agreement exists between experimental and calculated results, whatever the model used. In the initial phase of the run, experimental and calculated results do not match at all, whatever the separator and the model considered. Experimentally, this starting phase is not easy, because the tuning of depressurisation valves is not immediate, and, as seen on Fig. 4, modelling shows that the inlet flow rate of the first separator drastically varies during the first minutes of the run, disturbing the stability of pressures and temperatures of the separators. Our simulation cannot account for this disturbed phase and considers that the system is constantly under the specified conditions of temperature and pressure. This can be very cumbersome, because, according to results of the simulation, all variables undertake very large variations during this initial phase. Closer examination of these curves shows that, even if the agreement is not very good with the EPSM, this latter seems to give better tendencies for the behaviour of the mixture inside the three separators. The TSM gives some inconsistent results, especially in the case of the second separator. Indeed, the overall description of the liquid mixture, i.e. the occurrence of a main component, is better represented by the EPSM, although not so convincing for the third separator. This can be explained because the results in this last stage are dramatically dependent on all the preceding results.

As we mentioned, the initial phase is not well predicted, but, even if this part of the run is not considered, one must wonder why discrepancies between experimental and calculated results are so important, while we obtained very satisfactory results in modelling of contactor, allowing validation of the thermodynamic modelling, as well as the experimental procedure of removal of sample. We have therefore to consider all possible differences existing between the contactor and the separators.

From an experimental point of view, it has to be noticed that pressure is much more difficult to maintain at a constant value in the separators. Indeed, the inlet flow rate into the contactor has been set constant by the volumetric pump, and besides, contains only  $\text{CO}_2$ , while for the separators, inlet streams vary in terms of compositions and flow rates. Moreover, every pressure variation is likely to induce a temperature variation because our separator regulation temperature device has a slow dynamic (slower than the contactor's one because the heating water flows successively in the three separator jackets). All these perturbations may have a strong influence on this very sensitive system.

Although the sample collection procedure is the same as for the contactor, it may have a greater influence because the volume of a separator is 20 ml compared to the 200 ml of the contactor. Thus, removing for example 0.5 ml of liquid may induce a great disturbance of the state of the mixture in the separator, and this has been sometimes detected on the pressure measurement.

Moreover, mixing of the phases inside the separators is not done mechanically, as it is in the contactor. Thereby, gradients of concentrations may exist in the phases, and the homogeneity hypothesis may not be justified.

All these arguments may explain discrepancies existing between experimental and calculated composition of the liquid phase in the separators, and we believe that they are mainly due to experimental limitations

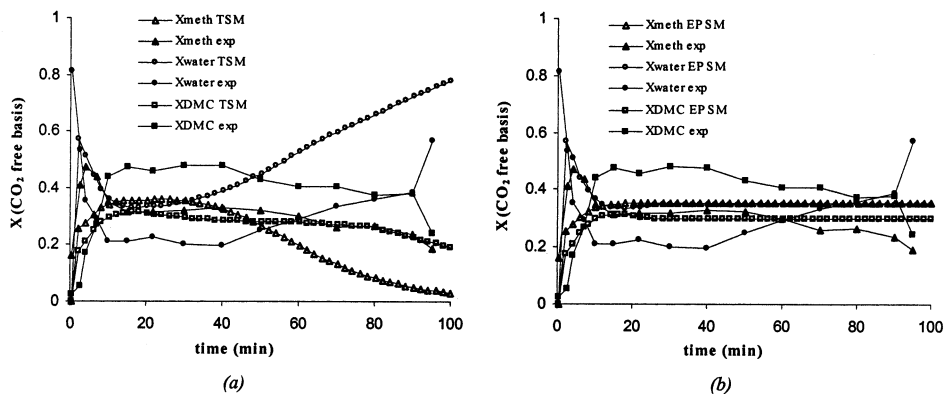


Fig. 10. Liquid phase composition in the third separator (a) TS model; (b) EPS model (open symbols refer to experimental data and filled symbols to modelling results).

relative to the pilot configuration. Indeed, we have chosen to study a small actual commercial pilot, where technology is designed to be simple and efficient, and not to demonstrate the validity of modelling descriptions. Another explanation might be found in the fact that the cyclonic separators, efficiently designed for ‘heavy’ extracted compound (oils, solids, etc.), could be questioned when used with mixtures of ‘light’ compounds, as considered here. In particular, possible mechanical entrainment of a fraction of microdroplets generated in the depressurization, is not taken into account by the model and may be one cause of the observed discrepancy. Although it is difficult, regarding all these remarks, to conclude strictly to the validity of one of the two models for the separators, the EPS modelling approach seems to give a better estimation of tendencies of the quaternary mixture behaviour in the separators of the pilot.

## 5. Conclusion

This paper has presented a simple dynamic modelling of a process of separation of a quaternary mixture, but where thermodynamic description was done using efficient available models (SRK equation of state with MHV2 mixing rules). A simplified model was compared to the rigorous resolution of the system of algebro-differential equations, and was shown to enable a correct description of the dynamic behaviour. The modelling was compared to experiments and gave good results for the contactor, while it was not very satisfactory for the description of the separation, done with a cascade of cyclonic separators. Even if discrepancies between experimental and calculated results probably originate from experimental procedure, and because we think that thermodynamic modelling is correct, the hydrodynamic description of the separators here is likely to be oversimplified. The cyclonic separators cannot be regarded as simple theoretical stages (TSM) as is often done in the literature [9], and we proposed an other description (EPSM), that, although more suitable, needs still to be improved, taking into account, for instance, the imperfect collection of droplets.

Even if it seems possible to isolate water with the help of a cascade of several cyclonic type separators, as available here, it is not realistic to envisage the separation of the resulting methanol–DMC binary mixture with this type of separator, these two components having too strong affinities. Moreover, according to simulation results obtained from EPSM, the amount of water present after 100 min operation is about 0.4 mol in the contactor, 0.3 mol in the first separator, 0.13 in the second one and 0.11 in the last one (from the 2.751 mol initially present in the contactor), which means that a great part of the water has left the process, together with

CO<sub>2</sub>, DMC and methanol as an effluent (we operated here in the open-loop mode).

The use of simple separators in order to separate a liquid mixture when volatility of components, as well as their solubility into CO<sub>2</sub>, are comparable, is therefore likely to be very inefficient. Thus, in this case, modelling could provide a great help in order to investigate the feasibility of this separation, either using a greater number of separators, or by implementing a more complex strategy of separation. For instance a suitable way would be to consider the operation of one or several columns of countercurrent extraction. This could be done according to the approach proposed by Chrischoou and Schaber [23] and Chrischoou and Stephan [24] who presented a systemic method to investigate the separation of mixtures incurred in enzyme-catalyzed reactions. Research on modelling of this separation is in progress in our laboratory. Most of the conclusions presented here concerning the dynamic modelling or the hydrodynamic description of the separators, have been drawn from the study of a specific mixture (DMC, water, methanol and CO<sub>2</sub>), but we are confident that they will remain valid in essence for the fractionation of many other liquid mixtures with supercritical CO<sub>2</sub>.

## Appendix A. Nomenclature

$a$	mixture parameter in the SRK equation of state ( $\text{m}^6 \text{bar mol}^{-1}$ )
$A_{ij}$	binary interaction parameter in the UNIQUAC model ( $\text{cal. mol}^{-1}$ )
$b$	mixture parameter in the SRK equation of state ( $\text{m}^3 \text{mol}^{-1}$ )
$F$	fluid flow rate ( $\text{mol min}^{-1}$ )
$\hat{F}$	fluid quantity (mol)
$\hat{H}$	molar hold-up (mol)
$\hat{L}$	liquid quantity (mol)
$\hat{M}$	molar quantity submitted to the flash (mol)
$P$	pressure (MPa)
$R$	universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$\hat{S}$	externally collected withdrawal (mol)
$T$	temperature (K)
$t$	time (min)
$V$	volume ( $\text{m}^3$ )
$Vh$	hold-up volume for EPS description ( $\text{m}^3$ )
$v$	molar volume ( $\text{m}^3 \text{mol}^{-1}$ )
$X$	liquid mol fraction on a CO <sub>2</sub> -free basis
$x$	liquid mol fraction
$Y$	fluid mol fraction on a CO <sub>2</sub> -free basis
$y$	fluid mol fraction
$z$	overall mol fraction

### Subscripts

cont	contactor
$i$	component $i$
$j$	component $j$
sep	separator
$t$	time $t$

### Superscripts

G	fluid phase
IN	inlet
L	liquid phase
OUT	outlet
tot	total

### Greek letters

$\Delta t$	time increment (min)
$\phi$	fugacity coefficient
$\omega$	molar vaporization ratio
$\Psi$	liquid volume fraction

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