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Influence of the vapor–liquid equilibria (VLE) on the kinetics in gas–liquid and gas–liquid–solid systems

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Abstract

Gas–liquid and gas–liquid–solid reactors are frequently characterized by the presence of components, reagents or products, that are partitioned between liquid and vapor phase. In this case we have a difficulty in describing the kinetic behaviour of such type of reactors when it occurs that: (i) the amount of partitioned component in the two phases is never negligible in both phases; (ii) the vapor–liquid equilibrium could have a non-ideal behaviour. We need therefore, to introduce in the kinetic model the mass balance equations for describing the partition of the components affecting their concentration in liquid phase also considering, when necessary, the non-ideal behaviour of the involved phases. Vapor–liquid equilibria (VLE) in reactive systems are poorly treated in the literature, especially for reactions occurring at high pressures. In the present work we will examine the different possibilities occurring in practice and the methods to solve them. Some practical examples are reported for better explaining both the theoretical and practical approach.

Keywords: Vapor–liquid equilibria; Gas–liquid system; Gas–liquid–solid system

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1. Introduction

Kinetic studies in gas–liquid and gas–liquid–solid systems are often complicated by the non-ideal behaviour of reagents and/or products that are partitioned between the liquid and vapor phase. This occurs especially when both the solubility of a reagent or a product and the volatility are relatively high. In this case the concentration of the components in the liquid phase can strongly be affected by the amount of the same component in the vapor phase. Besides, as often kinetic data are collected in batch conditions for the liquid phase, activity coefficients of the partitioned components can consistently change during the time as a consequence of changing the composition of the reaction mixture. Therefore, it is necessary, in these cases, to study the vapor–liquid equilibria (VLE) before the kinetics, possibly by adopting an independent approach.

We can define, first of all, two different possible situations, respectively, characterized by high or low pressure. At low pressure, in the simplest ideal cases, Henry's law can be used to describe the partition of gases and Raoult's law for the components below the critical conditions. For non-ideal systems a classical γ–ϕ method can be adopted determining for a component the activity coefficient in the liquid phase (γ) and the fugacity coefficient in the vapor one (ϕ). Many models give the dependence of the activity coefficient on the composition such as the ones suggested by Van Laar, Margules, Wilson, NRTL, etc. However all these models requires vapor–liquid partition experimental data for evaluating all the binary interaction parameters. For n components we need to examine $n(n+1)/2$ binary systems. Predictive models, based on the group

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Nomenclature

a_L, a_S	gas–liquid and liquid–solid mass transfer area
C_i, C_i^*	concentration of component *i* in the liquid bulk and at the gas–liquid interface
$C_{i\mathrm{L}}$, $C_{i\mathrm{S}}$	concentration of component *i* in liquid bulk and solid, respectively
D_i	diffusion coefficient of component *i*
F	gas volumetric flow rate
F_G^o, F_G	inlet and outlet molar flow rates
F_L^o, F_L	inlet and outlet molar flow rates
$H_{i,\mathrm{M}}$	Henry's constant for component *i* in the mixture
k_j, k_{ej}	kinetic and equilibrium constants
k_L, k_S	gas–liquid and liquid–solid mass transfer coefficients
K_i	vapor–liquid partition coefficient
M_i	molecular weight of component *i*
M_S	solvent molecular weight
n	reaction order
n_L, n_V	total moles in the liquid and vapor phase, respectively
$n_{i\mathrm{L}}$, $n_{i\mathrm{V}}$	moles of component *i* in liquid and vapor phase, respectively
$n_{i\mathrm{T}}$	total moles of component *i*
N	moles of solvent
N_C	number of components
N_R	number of reactions
p_i, p_i^*	partial pressure of component *i* in the gas bulk and at the gas–liquid interface
p_i^0	vapor pressure of pure component *i*
p_w	vapor pressure of water
r_j	reaction rate for the reaction *j*
R	gas constant
S, S_0	area of chromatographic signals
t	time
t_R	corrected retention time
T, P	absolute temperature and total pressure, respectively
V_L, V_V	liquid and vapor phase volume, respectively
V_R	reactor volume
w_S	weight of solvent
x_i^o, x_i	liquid phase mole fraction in inlet and outlet streams
y_i^o, y_i	liquid phase mole fraction in inlet and outlet streams
z	direction of diffusion
z_i	compressibility factor

Greek letters

$\alpha_{i,j}$	stoichiometric coefficient of component *i* in the reaction *j*
β_i	correction term for non-ideal behaviour
γ_i	activity coefficient of component *i*
γ_i^*	normalized activity coefficient of component *i*
γ_i^∞	infinite dilution activity coefficient of component *i*
η_j	effectiveness factor for reaction *j*
ρ_i	liquid density of component *i*
ρ_M	molar density of the mixture
ϕ_i^V, ϕ_i^L	fugacity coefficient of component *i* in the vapor and liquid phase

contributions, such as UNIFAC or ASOG, are very useful avoiding the described experimental approach. However, when the partitioned component is only one a simpler experimental approach based on the determination of the activity coefficient, at infinite dilution, can be used. At low pressure vapor phase is very often considered ideal. Alternatively, fugacity coefficients are normally calculated with the virial equation. γ–ϕ methods can hardly be used for high pressure conditions because the difficulty of describing the non-ideal gas phase behaviour and also for the frequently occurring simultaneous presence of subcritical and supercritical components. In these conditions the use of an equation of state (EOS) to describe both phases is preferred. However, also in this case many experimental data are necessary in order to evaluate all the binary interaction parameters. In order to avoid the heavy experimental approach before mentioned, the authors have developed a very simple method using UNIFAC for generating reliable equilibrium data of all binaries involved at pressures at which UNIFAC works well (5–10 atm). From these generated data, binary interaction parameters for RKS (Redlick–Kwong–Soave)

EOS can be determined by mathematical regression analysis. These parameters can then be used, after extrapolation, to describe multicomponent systems at higher pressures.

In this work, examples of the different proposed strategies, adopted by the authors in different kinetic studies for gas–liquid and gas–liquid–solid systems, will be discussed. In particular we observed in our previous works, that VLE strongly affects the kinetics of the following reactions: (1) ethoxylation and propoxylation of fatty alcohols: an example of low pressure reaction characterized by liquid-phase non-ideal behaviour [1,2]; (2) chloroform fluorination: an example of low pressure reaction characterized by high non-ideality of the reagents and with products that are more volatile than the reagents [3]; (3) *p*-cresol alkylation with isobutene: a low pressure gas–liquid–solid system studied in semibatch conditions by using an acid ion-exchange solid resin as a catalyst [4]; (4) methanol homologation to acetaldehyde with hydrogen and carbon monoxide: an example of a high pressure (150–250 atm) gas–liquid reaction [5,6]. The adopted strategy for describing the VLE, in each of the mentioned reactions, has been different and the reasons of the choice of any single strategy will be discussed in this work, while some of the mentioned examples (3 and 4) will be treated in a more detailed way.

2. Mass balance equations for partitioned systems in chemical regime

The most general partitioned system can be represented as reported in the scheme of Fig. 1, that is related to a well mixed gas–liquid or gas–liquid–solid reactor. By referring to a single component i, the following general mass balance equation can be written:

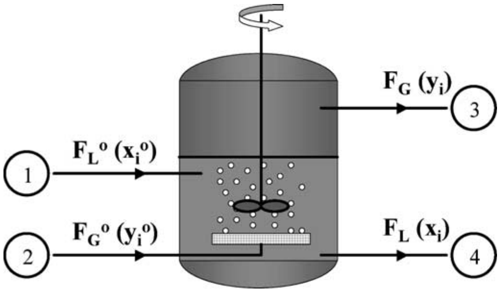


Fig. 1. General scheme of a reactor with vapor–liquid partition.

$$(F_L^o x_i^o + F_G^o y_i^o) = (F_L x_i + F_G y_i) + V_L \sum_{j=1}^{N_R} \alpha_{i,j} r_j + \frac{dn_{iT}}{dt}, \quad i = 1, N_C \qquad (1)$$

By considering the scheme of Fig. 1, in the most common situation we can have that streams 1, 3 and 4 are null (semibatch G–L or G–L–S reactors). In other cases we can have a reactive flash with stream 2 null. When the products are more volatile than the reagents (example 2) it is possible to have streams 2 and 4 null. Eq. (1), written in a general form, must be adapted to the description of the mentioned particular cases, therefore, for a semibatch operation we can write, for example:

$$F_G^o y_i^o = V_L \sum_{j=1}^{N_R} \alpha_{i,j} r_j + \frac{dn_{iT}}{dt}, \quad i = 1, N_C \qquad (2)$$

while, for a continuous reactor, in steady state conditions, we have

$$F_L^o x_i^o = F_G y_i + V_L \sum_{j=1}^{N_R} \alpha_{i,j} r_j, \quad i = 1, N_C \qquad (3)$$

It is clear that, in all the mentioned cases, the reaction rates can be affected by both the interphase mass transfer phenomena and the occurring partition altering the composition of the liquid phase. The chemical reaction rate can be written as a generic relation in the following way:

$$r_k = f(C_i, T), \quad i = 1, N_C, \ k = 1, N_R \qquad (4)$$

where one or more C_i terms can be affected by the vapor–liquid partition. In the simplest case, partition can be considered ideal and interpreted by means of the Henry's law for supercritical components and the Raoult's law for components below their critical temperature. However very often this is a rough approximation that has the only consequence of increasing the uncertainty of the involved kinetic parameters. The range of approximation can be strongly narrowed by an independent evaluation of the non-ideal behaviour characterizing the system.

This non-ideal behaviour intervenes, as mentioned, in altering the reacting composition and we can write, at this purpose, for any instant, the following equations system describing the vapor–liquid partition:

$$x_i = \frac{n_{i\mathrm{L}}}{n_{t\mathrm{L}}} = \frac{n_{i\mathrm{V}}}{n_{t\mathrm{V}}}\frac{1}{K_i},\quad n_{i\mathrm{T}} = n_{i\mathrm{V}} + n_{i\mathrm{L}},\quad i = 1, N_\mathrm{C},$$
$$n_\mathrm{L} = \sum_{i=1}^{N_\mathrm{C}} n_{i\mathrm{L}},\qquad n_\mathrm{V} = \sum_{i=1}^{N_\mathrm{C}} n_{i\mathrm{V}},\qquad V_\mathrm{L} = \sum_{i=1}^{N_\mathrm{C}} \frac{n_{i\mathrm{L}} M_i}{\rho_i},$$
$$f(P, V_\mathrm{V}, n_\mathrm{V}) = 0$$
$$\left(\text{equation of state; for ideal case}: P\frac{RTn_\mathrm{V}}{V_\mathrm{R} - V_\mathrm{L}}\right) \tag{5}$$

As it can be seen, the effects of non-ideal behaviour are all concentrated in the K_i term and in the EOS. K_i can assume different forms for the different possible cases that are:

Low or moderate pressure:

$$\text{Sub-critical conditions}: \quad K_i = \frac{p_i^0}{P}\beta_i \tag{6}$$

$$\text{Super-critical conditions}: \quad K_i = \frac{H_{i,\mathrm{M}}}{P}\beta_i \tag{7}$$

where β_i corresponds to a Raoult's law deviation term containing the contribution to non-ideal behaviour of both vapor and liquid phases, p_i^0 is the vapor pressure for subcritical components, $H_{i,\mathrm{M}}$ is the Henry's constant for supercritical components in the mixture.

The determination of the evolution of the reacting composition can be performed by solving simultaneously Eqs. (1) and (5) while the non-ideal behaviour of each compound has been confined to the evaluation of the β_i values. These values can be determined in different ways by distinguishing, as before, between the sub or supercritical condition of any single component, being different the approaches in the two cases. As a matter of fact, β_i for a component in sub-critical conditions can be considered $\beta_i = \gamma_i/\phi_i^\mathrm{V}$, while for a supercritical component $\beta_i = \gamma_i^*/\phi_i^\mathrm{V}$.

A different approach must be followed if the reaction occurs at high pressure employing, in this case, an EOS describing both phases in equilibrium, obtaining a partition coefficient that is the ratio of the fugacity coefficients for the component i in the two phases:

$$\text{High pressure}: \quad K_i = \frac{\phi_i^\mathrm{L}}{\phi_i^\mathrm{V}} \tag{8}$$

3. Mass balance equations for partitioned systems with mass transfer limitation

When mass transfer limitations are operative, the influence of VLE in the reaction rate is confined to the determination of the equilibrium solubility of the partitioned component in the liquid phase, because, we need to define the gas–liquid interface concentration affecting both gas and liquid side gradients. Normally, this interface concentration is assumed to be correspondent to the solubility equilibrium value. A non-ideal behaviour of the solubility affects, therefore, both mass transfer and reaction rates. Independent experiments would be made, therefore, to evaluate the equilibrium solubilities values, in order to avoid mistakes in the determination of both kinetic and mass transfer parameters. For dealing with this subject it is opportune to distinguish two different possible cases, that are, respectively, gas–liquid (G–L) and gas–liquid–solid (G–L–S) systems, being different the mass balance equations to be considered. In the first case we have to take into account for the possibility that mass transfer rates can be affected by the chemical reaction, when chemical rate is very high and the reaction occurs mainly in the liquid boundary layer, enhancing the mass transfer rates. It is necessary, in this case, to evaluate the concentration profile, inside the boundary layer, and the mass balance, in steady state conditions, for a reacting component becomes:

$$D_i\left(\frac{\mathrm{d}^2 C_i}{\mathrm{d}z^2}\right) - \sum_{j=1}^{N_\mathrm{R}} \alpha_{i,j} r_j = 0,\quad i = 1, N_\mathrm{C} \tag{9}$$

with the opportune boundary conditions containing the interface concentration C_i^* that can be affected by non-ideality (see [7]).

More simple is the approach for GLS systems, because, in this case the gas–liquid profile inside the liquid boundary layer, normally, is not affected by the reaction occurring inside the solid catalytic particle and is assumed to be linear. Therefore, by considering all the possible steps occurring before the reaction, with the exception of the gas side mass transfer rate, that is normally very fast, and introducing the steady state assumption, we can write:

$$r_j = k_\mathrm{L} a_\mathrm{L}\left(\frac{p_i^* \rho_\mathrm{M}}{H_{i,\mathrm{M}}\beta_i} - C_{i\mathrm{L}}\right) = k_\mathrm{S} a_\mathrm{S}(C_{i\mathrm{L}} - C_{i\mathrm{S}})$$
$$= \eta_j k_j a_\mathrm{S} C_{i\mathrm{S}}^n \tag{10}$$

Again we have a term $p_i^*/H_{i,\mathrm{M}}$ that can be strongly affected by the non-ideal behaviour which deviation is expressed by β_i.

4. Methods for evaluating non-ideal behaviour in liquid phase at low pressure

Several experimental methods and correlation models have been proposed in the literature with the scope of determining the non-ideal behaviour of the liquid phase at low pressure conditions [8,9]. Among the experimental methods, one of the most commonly employed technique, is the evaluation of infinite dilution activity coefficients that can be performed with two alternative methods: the inert gas stripping method [10] and gas-chromatographic retention time method [11]. Inert gas stripping consist in dissolving a small amount of volatile compound in the chosen solvent and then stripping it with an helium stream that is directly sent to an on-line gas-chromatograph equipped with a sampling valve and analyzing the time decay of the compound concentration in the stream. The experimental data can be interpreted by means of an expression like the following:

$$\ln\left(\frac{S}{S_0}\right) = -\left(\frac{Fp_i^0}{RTN}\right)\gamma_i^\infty t \qquad (11)$$

By plotting $\ln(S/S_0)$ versus time, the value of γ_i^∞ can be evaluated from the slope.

The gas-chromatographic retention time method [11] consists in impregnating a solid with the solvent and using it as a stationary phase in a packed chromatographic column; the analysis of the net retention time of the injected volatile component allows the direct evaluation of the activity coefficient, at infinite dilution, by the expression:

$$\gamma_i^\infty = \frac{w_\mathrm{S} R}{M_\mathrm{S} z_i}\left[\frac{T}{p_\mathrm{S}^0 t_\mathrm{R} F}\right]\left(\frac{P}{P - p_\mathrm{W}}\right) \qquad (12)$$

Starting from the γ_i^∞ values, a dependence of the activity coefficient from the composition can easily be evaluated [8,9].

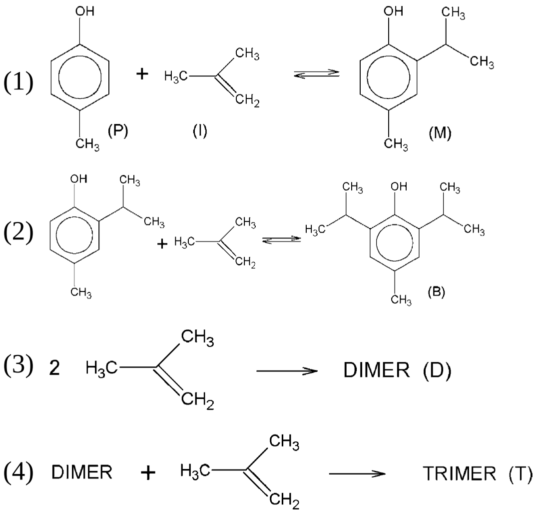
At low pressure conditions, the correlation of VLE data is commonly performed using a γ–ϕ approach that consists in the evaluation of liquid non-ideal behaviour with an excess Gibbs energy model (Van Laar, Margules, NRTL, UNIQUAC, etc.) while gas deviation are taken into account using virial EOS. All these models require an extensive experimental work, especially for multicomponent mixtures, that have the scope of the evaluation of the binary interaction parameters. A useful alternative approach is represented by the use of a group contribution method such as, UNIFAC and ASOG [8,9] which allow a quite accurate prediction of VLE behaviour in binary and multicomponent mixtures without the necessity of experimental determinations.

5. Methods for evaluating non-ideal behaviour in both gas and liquid phase at high pressure

The description of phase equilibria at high pressures, is usually performed by means of an EOS allowing the calculation of fugacity coefficients, for each component, in both the phases determining the partition coefficients, as defined by Eq. (8). The EOS approach involves the experimental determination of the interaction parameters for all the possible binary system of the mixture. Some group contribution methods (GC-EOS and UNIWAALS) have been developed but the group contribution data are not, at now, sufficiently extended [12]. The authors [13,14] have suggested the possibility to combine the use of UNIFAC with RKS EOS by using the first one to generate equilibrium data in the range of T and P where UNIFAC gives reliable results (below 10 atm). By interpreting these data sets with RKS EOS the related interaction parameters for the binaries can be determined by regression analysis. These binary interaction parameters can then be extrapolated to higher T and P, allowing, in this way, predictive description of multicomponent VLE. The proposed method has been tested with different binary system and has shown performances similar to other predictive methods such GC-EOS and UNIWAALS, but is more simple to be used and can be more widely applied considering the large groups list of UNIFAC.

6. Example 1—GLS system at low pressure: alkylation of *p*-cresol with isobutene

The alkylation of *p*-cresol with isobutene is a reaction catalyzed by cation-exchange resins and consists in a first alkylation followed by successive dialkylation and olygomerization of isobutene. The kinetics of this reaction have been studied in a completely mixed slurry reactor operated in batch conditions for the liquid phase and in continuous for the gas phase. The reactions scheme is the following:



For this reactive system the differential mass balance equations can be written in compact form in the following way, assuming that the reactions occurs in the liquid phase:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \sum_{j=1}^{N_\mathrm{R}} \alpha_{i,j} r_j \quad \text{or} \quad \frac{\mathrm{d}n_{i\mathrm{L}}}{\mathrm{d}t} = V_\mathrm{L} \sum_{j=1}^{N_\mathrm{R}} \alpha_{i,j} r_j \qquad (13)$$

with a stoichiometric coefficients matrix ($\alpha_{i,j}$), i.e.:

j	*i*					
	P	*I*	*M*	*B*	*D*	*T*
1	−1	−1	1	0	0	0
2	0	−1	−1	1	0	0
3	0	−2	0	0	1	0
4	0	−1	0	0	−1	1

Coupled with Eq. (13), we have to introduce two additional mass transfer relations that expresses pseudo-steady-state condition with respect to the gaseous reagent (isobutene) both in the bulk liquid and on the solid external surface:

$$\frac{\mathrm{d}C_\mathrm{lb}}{\mathrm{d}t} = k_\mathrm{L} a_\mathrm{L}(C_\mathrm{l} - C_\mathrm{lb}) - k_\mathrm{S} a_\mathrm{S}(C_\mathrm{lb} - C_\mathrm{ls}) \simeq 0,$$
$$\frac{\mathrm{d}C_\mathrm{ls}}{\mathrm{d}t} = k_\mathrm{S} a_\mathrm{S}(C_\mathrm{lb} - C_\mathrm{ls}) - (r_1 + r_2 + 2r_3 + r_4) \simeq 0 \qquad (14)$$

In order to integrate the ordinary differential equation (13) we need to define the expressions for reaction rates r_j as a function of both the kinetics parameters and the concentrations:

$$r_1 = \eta_1 k_1 \left(C_{P\mathrm{s}} C_\mathrm{ls} - \frac{C_{M\mathrm{s}}}{k_\mathrm{e1}} \right),$$
$$r_2 = \eta_2 k_2 \left(C_{M\mathrm{s}} C_\mathrm{ls} - \frac{C_{B\mathrm{s}}}{k_\mathrm{e2}} \right), \qquad r_3 = \eta_3 k_3 C_\mathrm{ls}^2,$$
$$r_4 = \eta_4 k_4 C_\mathrm{ls} C_{D\mathrm{s}} \qquad (15)$$

The evaluation of the kinetics and equilibrium parameters must be independently pursued. The only partitioned component is assumed to be isobutene and its deviation from ideality have been taken into account measuring infinite dilution activity coefficients, in binary mixture with *P*, *M* and *B*, with the stripping method [10]. Knowing the values of infinite dilution activity coefficients, it is possible to evaluate the activity coefficient as a function of the composition with the following expression [8,9]:

$$\gamma_i = \exp(1 - x_i)^2 \ln \gamma_i^\infty \qquad (16)$$

The values obtained for infinite dilution activity coefficients are, respectively, 3.0–3.5 for *I*/*P*, 1.18–1.34 for *I*/*M* and 0.86–0.87 for *I*/*B*.

Adopting the model represented by Eqs. (13)–(16) the experimental semibatch runs have been used for the determination of kinetic parameters of the system and in Fig. 2 is reported an example of the agreement obtained between experimental and calculated evolution with time of the moles of reagents and products.

7. Example 2—GL system at high pressures: methanol homologation

Methanol homologation is a promising alternative route to the industrial production of acetaldehyde or ethanol [15]. The reaction occurs according to the

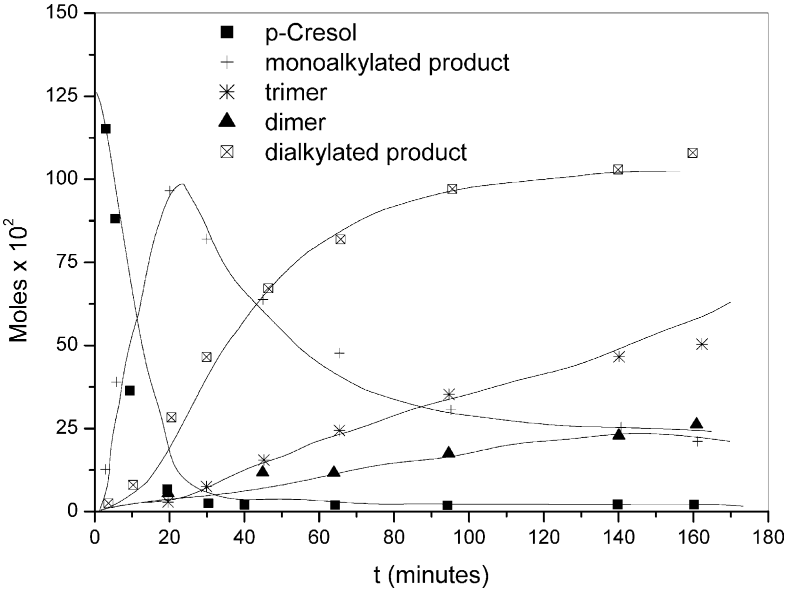


Fig. 2. Alkylation of *p*-cresol with isobutene: kinetic run performed at 50 °C, with 1100 rpm stirrer speed in the presence of 40 g of catalyst. Points are experimental; curves are calculated.

Table 1

Partition analysis on a run performed at 185 °C and 190 atm using a catalyst with composition 2 mmol $Co(Ac)_2$, 11.15 mmol CH_3I, 6.7 mmol $P(Ph)_3$[a]

Component	Liquid composition (mol.%)		Vapor composition (mol.%)	
	Calculated	Experimental	Calculated	Experimental
$t = 75$ min				
CH_3OH	52.00	50.35	6.21	6.48
C_2H_5OH	0.17	0.50	0.03	0.05
H_2O	21.30	20.50	1.49	0.77
CH_3CHO	13.90	13.00	1.86	1.65
Dioxan	8.40	8.66	1.21	0.61
Acetal	3.00	4.23	0.17	0.20
Methyl acetate	0.70	2.29	0.16	0.17
$t = 120$ min				
CH_3OH	48.00	47.60	5.63	5.69
C_2H_5OH	0.37	0.49	0.07	0.07
H_2O	23.20	22.70	2.07	1.88
CH_3CHO	15.80	15.87	2.13	2.55
Dioxan	8.20	8.37	1.19	0.55
Acetal	2.80	2.60	0.15	0.19
Methyl acetate	1.10	1.45	0.24	0.29

[a] Reactants: 7.4 mol CH_3OH, 0.82 mol dioxane; autoclave volume: 1.1.

following scheme regarding the main reactions:

$$CH_3OH + CO + H_2 \rightarrow CH_3CHO + H_2O \tag{17}$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \tag{18}$$

In parallel with the reactions (17) and (18), others reactions can take place, the main ones being the following:

$$CH_3CHO + 2CH_3OH \rightleftarrows CH_3CH(OCH_3)_2 + H_2O \tag{19}$$

$$2CH_3OH + CO \rightarrow CH_3COOCH_3 + H_2O \tag{20}$$

A good selectivity to acetaldehyde is obtained with cobalt based catalysts, whereas ruthenium catalyst favor the formation of ethanol. In this reactive system both reagents and products are partitioned between the liquid and the vapor phases, then the kinetic behaviour of the reaction can correctly be determined by considering VLE of all the components at the reaction pressure that is between 190 and 250 atm.

Kinetic runs performed in a semi-batch reactor can be interpreted with the mass balance differential equations system represented by relations (13), while, the expressions for the reaction rates resulted:

$$r_1 = k_1 C_1 p_7 \left(1 - \sigma \frac{C_2 C_6}{C_1 p_7 p_8}\right), \qquad r_2 = k_2 C_2 p_8,$$
$$r_3 = k_3 C_1^2 C_2 \left(1 - \frac{1}{K_{e3}} \frac{C_4 C_6}{C_1^2 C_2}\right), \qquad r_4 = k_4 C_1 p_7 \tag{21}$$

In these expressions σ represents a catalyst deactivation parameter and the subscripts identify the components with the following meaning: 1—methanol, 2—acetaldehyde, 3—ethanol, 4—acetal, 5—acetate, 6—water, 7—carbon monoxide, 8—hydrogen. For the solution of the differential equations system (13), we have to calculate, at each integration step, the vapor–liquid partition, by solving the algebraic system (5).

For the description of vapor–liquid equilibrium, at the high pressure conditions used in this reaction, UNIFAC-RKS predictive approach has been used [13,14]. With the scope to ascertain the reliability of the suggested UNIFAC-RKS method in methanol homologation, the kinetic parameters have been determined from batch runs by analyzing the composition of both vapor and liquid phases, at different times. The described kinetic model and the UNIFAC-RKS method were then used to describe vapor–liquid partition of all the components. The obtained agreement between the experimental and calculated equilibrium phases composition can be appreciated, for a batch run, in Table 1. The obtained results are satisfactory considering that larger errors observed are related only to the components that are present in small amount and are, therefore, greatly affected by analytical errors.

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