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LGCB

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RTD analysis of fixed bed columns

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0	0	November 2001	Draft version
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CONTENT

I Introduction

The aim of the present work is to analyse the liquid hydrodynamic in the fixed bed part of the nitrifying columns. Liquid residence time distribution experiments were performed on the C50 and C150 LGCB columns for various gas and liquid flow rates.

The RTD experiments were performed using a salt as liquid tracer and a conductivity analyser for salt concentration measurements.

The RTD experiments are analysed using the theoretical approach for the N-tanks-in-series model and the N-tanks-in-series with liquid back-mixing NitriSim model.

The two approaches are compared and relation between models parameters (N, the number of tanks-in-series and fback, the liquid back-mixing fraction). The models parameters are correlated to the operating variables corresponding to the condition in which the columns are operated (gas and liquid flow rates) will be studied.

II RTD and fixed bed columns

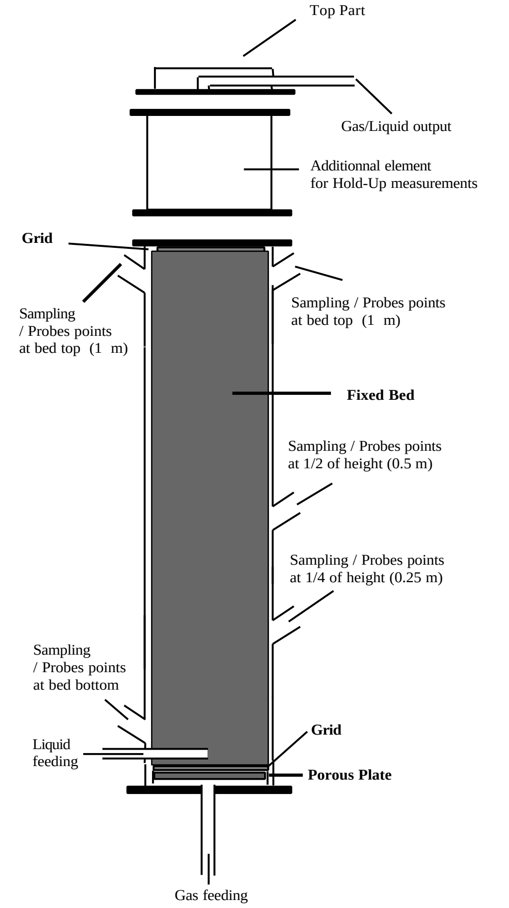
II.1 Objectives

The objectives of the present work are to analyse the liquid flow behaviour inside a fixed bed comparable to this of the UAB nitrifying column (bench columns and pilot nitrifying reactor).
The current work will be focused :

- on the method used for the RTD experiments,
- on the influence of gas and liquid flow rates on the hydrodynamic behaviour of the column
- on the comparisons between two columns (C50 and C150).

II.2 LGCB columns C50 and C150

The two fixed bed column built at LGCB were designed in order to be as comparable as possible to the UAB nitrifying column, excepting that they don't have the top and the bottom parts. Studies on the LGCB column are restricted to the fixed bed part. The main difference between the two columns is their diameter, which is respectively 50 mm and 150mm, and then the columns were respectively called C50 and C150. Details of the design of the two columns are given in table 1.



	Column C50	**Column C150**
Height :	1.015m	1.010m
Diameter :	53 mm	150 mm
Total volume :	2.26 L	17.85 L
Section :	20.21 10^{-4} m^2	176.7 10^{-4} m^2
Glass beads diameter :	4mm	4mm
Minimal voidage (theoretical):	0.34	0.34
Characteristic dimensions : D/d :	13.25	37.5
Liquid flows:	0 –10 L/h	0-10 L/h
Gas flows :	0.05 – 1 L/min	0.05 – 30 L/min

Table 1 : Details of the design and characteristics of the LGCB fixed bed columns

II.3 RTD experiments: the conductivity method

II.3.1 Preliminary studies

Several methods and tracers have been tested with the C50 column to perform RTD experiments (Lebouil, 2001).
The tracers tested were :

- H^+ ions, using a pH meter as RTD recorder.
- oxygen (O_2), using P_{O2} probe as RTD recorder. Such experiments can be performed only in absence of oxygen gas flow.
- a salt (NaCl), using a conductivity meter probe as RTD recorder.

The methods tested were step and pulse input of tracer at the bottom of the bed.

These preliminary studies have led to conclude that the most reliable method, from the tested ones, is the step-up input of salt. It was also checked that there was no interaction between salts and column by comparison of RTD curves obtained with salts and O_2 as tracers, and that the salt chosen (NaCl) gives the same RTD curve response as that obtained using another salt ($(NH_4)_2SO_3$).

II.3.2 RTD experiments : method used and theory

II.3.2.1 Principle of the step response RTD experiments

For the step-up method, two liquid solutions with different tracer (salt) concentrations are used. One is free of salt, the second is a solution of 100 mg/l of NaCl.

- at t<0 the solution 1 (C=0 mg/l) is used to feed the column ;
- from t=0 the solution 2 (C=100 mg/l) is used to feed the column

The concentration of salt in the liquid output of the fixed bed column is measured with a conductivity meter probe (probe (CDC745-9, Radiometer analytical, Copenhagen). The concentrations measured are recorded online with a step of 1s to 5s (figure 1).

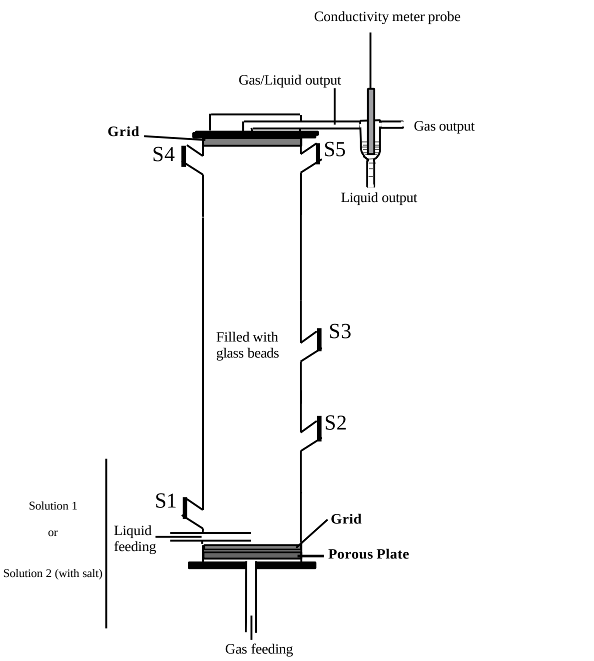


Figure 1 : Scheme of the experimental apparatus for RTD experiments

II.3.2.2 Theory

The theoretical residence time (t) of liquid is calculated by : $t = \frac{V_L}{F}$

The experimental residence time (t_{RT}) can be calculated from the RTD experiments as :

$$t_{RT} = \int (1 - F(t)).dt \text{ with } F(t) = \frac{C(t)}{C_{\max}}$$

C(t) being the salt concentration at the output of the column, C_{max} the maximum salt concentration at the output of the column

For a N-tanks in series model, analytical solutions exist for the function F_q (i.e. $F(q) = \frac{C(q)}{C_{\max}}$,

q being the reduced time defined as $q = \frac{t}{t}$) ,:

$$F_q = \frac{N(Nq)^{N-1}}{(N-1)!} e^{-Nq}$$ for pulse injection of tracer

$$1 - F_q = e^{-Nq} \sum_{k=1}^{N} \frac{(Nq)^{k-1}}{(k-1)!}$$ for a step-up of tracer , which corresponding theoretical (1-F_q) curves are reported in figure 2.

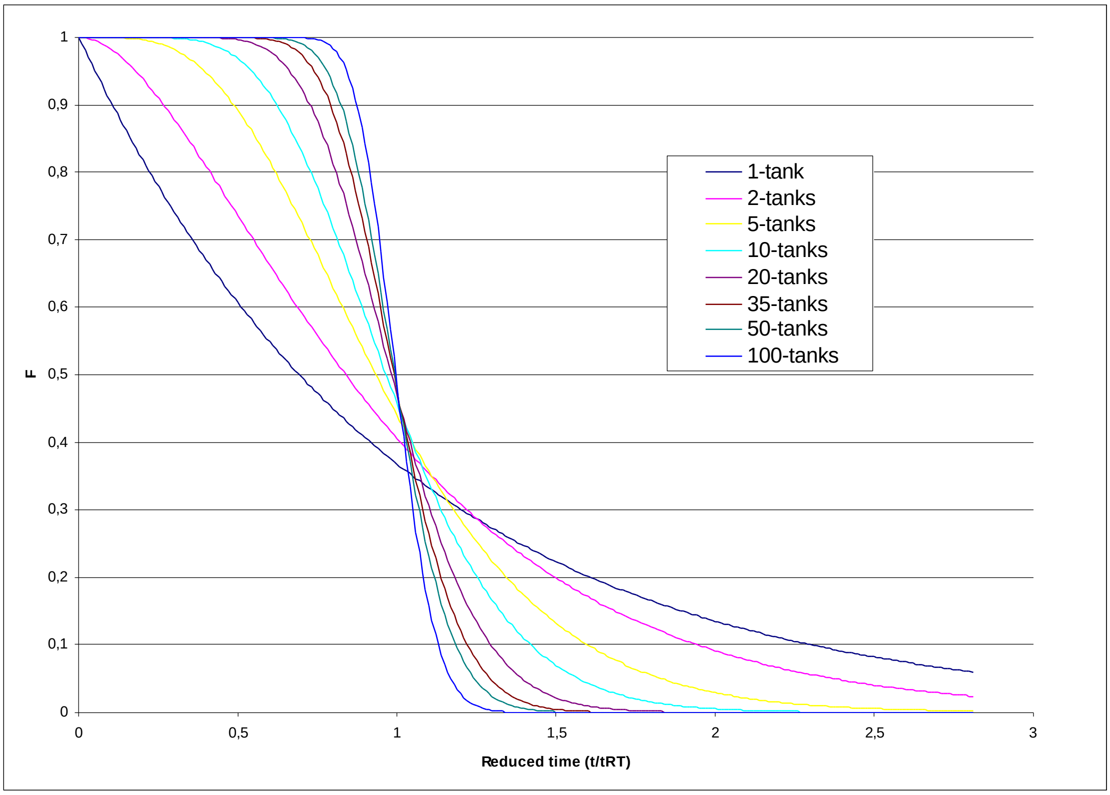


Figure 2 : The step response F curves for tanks-in-series model (Levenspiel, 1999)

II.4 RTD experiments : analysis of experiments

The $F(t)$ RTD curves obtained for different operating conditions (various gas and liquid flow rates) and for the two columns (C50 and C150) are analysed in order to determine:

- The voidage of the fixed bed
- The liquid and the gas fraction in the fixed bed
- The number of tanks required to fit the liquid RTD curve with the N-tanks-in-series model developed in TN27.1; 27.2 and 27.3
- The relations between liquid back-mixing parameter and number of tanks-in-series in the liquid flow model
- The relations between the number of tanks-in-series in the liquid flow model, the operating conditions and the column design

Two approaches can be used to analyse the RTD experiments.
The first one is based on the theory of $F(t)$ curves for the N-tanks-in-series model. By this approach, residence time (t_{RD}), voidage of the column and number of tanks-in-series can be calculated. But this direct approach cannot be used for the more complex N-tanks-in-series with back-mixing model developed for the nitrifying columns (NitriSim model)
The second approach involves the model parameters identification (TN 55.2).

The number of tanks being an integer value, it is not possible to identify directly this parameter. Two methods can be used to calculate this parameter, one involving the direct analysis of the $F(t)$ RTD curve (report to II.4.1.3), the second involving parameters identification of the NitriSim model (report to II.4.2)

II.4.1 Direct calculation from the experimental $F(t)$ RTD curves

According to the theoretical equations describing the $F(t)$ RTD curves (report to the theory section above), some calculations can be made.

II.4.1.1 Voidage of the fixed bed calculated from $F(t)$ RTD curves

The voidage of the fixed bed is calculated using RTD experiments with liquid flow but without gas flow. The theoretical full volume of the column can be calculated knowing the dimension of the columns (table 1). These volumes are respectively 2.239 Litre for the C50 column and 17.848 Litre for the C150 column.

The free volume occupied by the liquid V_{free} is deduced from the calculation of the residence time by : $V_{free} = t_{RD}.F$

Then the voidage of the bed is : $e = \frac{V_{free}}{V_{tot}}$

II.4.1.2 Fraction of gas (e_G) and liquid (e_L) in the fixed bed calculated from $F(t)$ RTD curves.

The gas fraction can be determined by two ways :

1 – by the measurement of the hold-up, H_G, (TN 55.2) : $e_G = \dfrac{H_G}{V_{tot}}$

2 – by the measurement of the liquid fraction (e_L), as e_L can be calculated from the RTD experiments by : $e_L = \dfrac{t_{RD}.F}{V_{tot}}$, and $e_G = e - e_L$.

II.4.1.3 Number of tanks calculated from $F(t)$ RTD curves.

As previously presented, the theoretical F_q curves (figure 2) depend on the number of tanks. Then a theoretical correlation (figure 3) can be built linking the number of tanks-in-series a function representative of F_q curves. This function is called Int_F_q and is the area of F_q curves between $q = 0$ and $q = 1$:

$$Int\_F_q = 1 - \int_0^1 F_q(q).dq \qquad , \qquad q = \frac{t}{t_{RT}}$$ being the reduced time.

For each experimental F_q curve, the experimental value of Int_F_q can be calculated and then a number of tanks can be deduced. It must be noted that :

- this correlation supposes that the F_q curve can be represented by a N-tanks-in-series models;
- this correlation is applicable whatever is the design of the column;
- the correlation is implicitly based on the analysis of only the first part of the F_q curve (between $q = 0$ and $q = 1$).

For these reasons, this correlation must be used carefully.

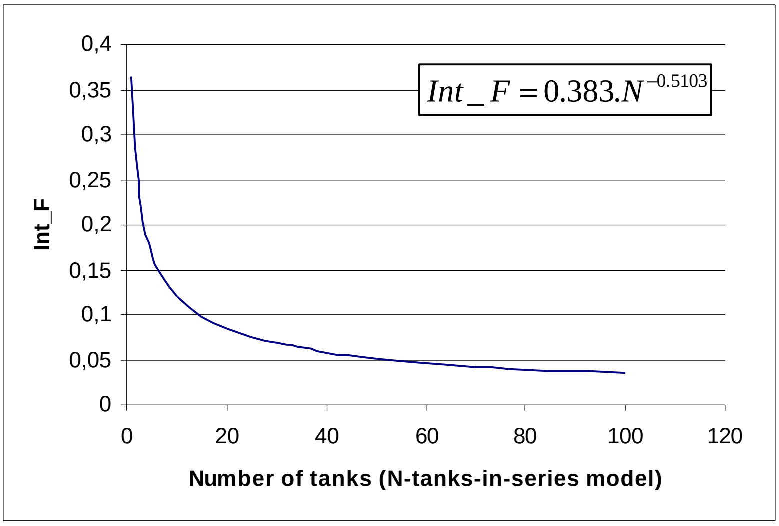


Figure 3 : Correlation between Int_F and the number of tanks

II.4.2 Parameters identification of the N-tanks-in-series model from $F(t)$ RTD curves

In order to study the relations between the number of tanks (N) and the liquid back-mixing (f_{back}) parameters of the N-tanks-in-series model (TN 27.1; 27.2 ; 27.3) with the column design and the gas and liquid flow rates, these parameters must be identified for each experiments.
With the NitriSim- model (N-tanks-in-series with back-mixing) computed using the Simlab Matlab toolbox(TN 55.2) all parameters of the model can be identified (excepting N, the number of tanks).

II.4.2.1 NitriSim, Simlab toolbox and parameters identification

Matlab is an intuitive language and a technical computing environment. It provides core mathematics and advanced graphical tools for data analysis, visualisation and algorithm and application development. Matlab can be associated to companion toolboxes developed for specific applications (signal and image processing ; Data analysis ; Financial and economics analysis ; control systems design….). As this language is used within the MELiSSA team as well by ADERSA for the development of algorithms for the processes control and UAB for modelling and identification, it was decided to develops also at LGCB models and applications with this language in order to facilitate exchanges in the MELiSSA team.

A Matlab toolbox for laboratory scale chemical and biological processing was initiated at LGCB. The toolbox called **SimLab** solves processes involving several reactions (chemical/biological), gas/liquid equilibria and acid/base equilibria for various hydrodynamic behaviour. The hydrodynamic model developed for the nitrifying columns (the NitriSim N-tanks-in-series model with back-mixing), was integrated in the SimLab toolbox, and the parameters can be given through a user-friendly interface (Figure 4).

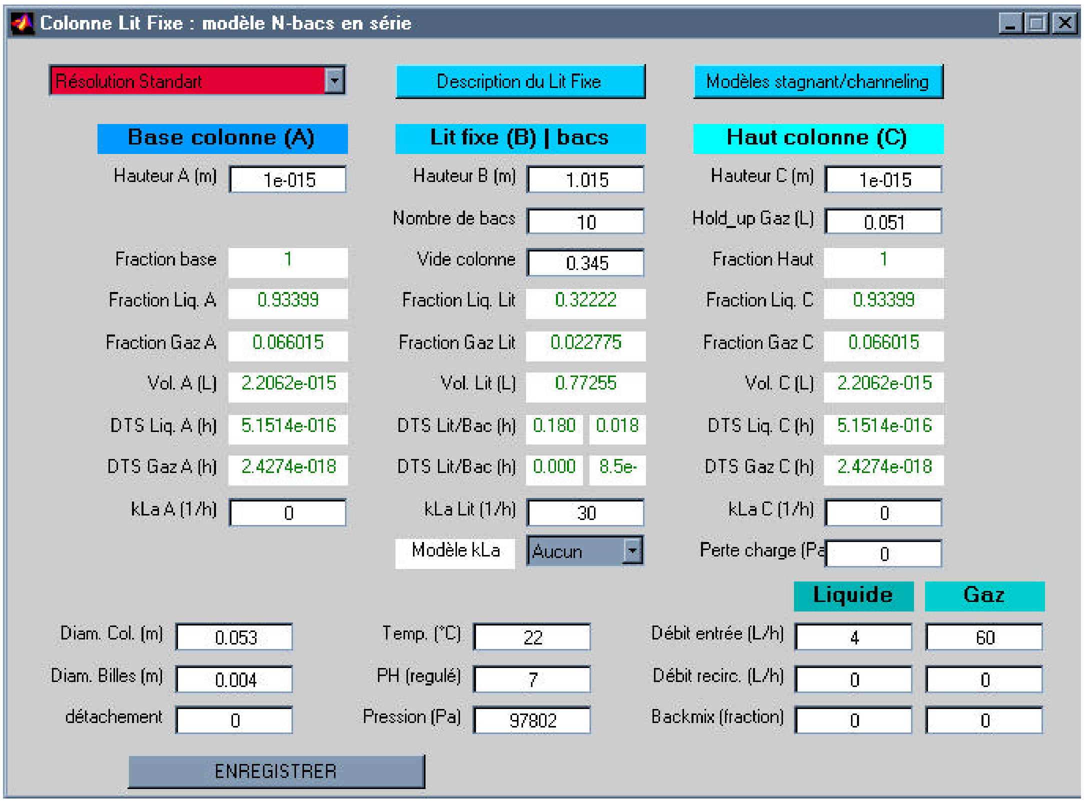


Figure 4 : interface of the SimLab toolbox for the N-tanks in series model of the nitrifying columns.

As detailed in TN 27.1,27.2, 27.3 an 39.2, the model for the nitrifying column is a set of n ordinary differential equations (ODE) for each phase (liquid, gas, solid) of the form :

$$\frac{dx_j}{dt} = f(x_{i(i=1,n)}, t)$$ for each x_j of the n compound

The system of 3n ODE, is solved with the ODE toolboxes of Matlab. ODE15S, a variable order method, was chosen, being able to solve stiff and non stiff differential equations, and being also able to detect and solve Differential Algebraic Equation.

For parameters identification, a Gauss-Newton algorithm was developed in the Matlab language and integrated in the SimLab toolbox. The scripts developed for parameter identification have been designed in order to make the identification procedure easily manageable and to enable identification of any kind of parameter (hydrodynamic, kinetic, physical parameters). The principle of the procedure is presented in figure 5.

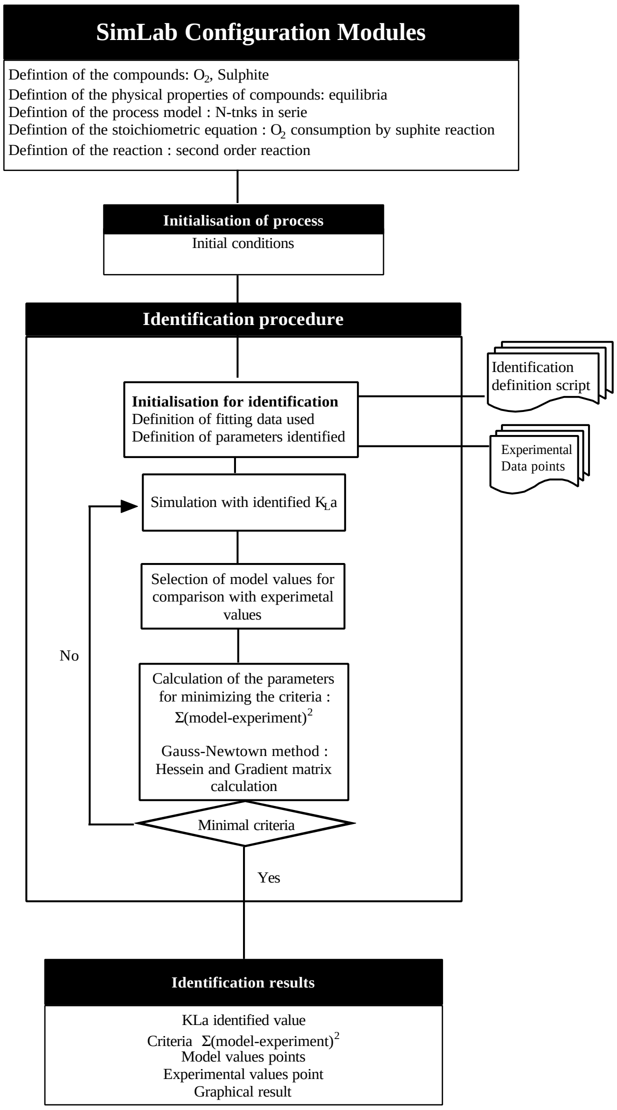


Figure 5 : Overview of identification procedure

The identifications are performed by minimising the criteria : $\sum(\text{exp value} - \text{model value})^2$.

II.4.2.2 Parameters identified

We have restricted the identification on RTD curves to the gas hold-up (H_G) to the liquid back-mixing (f_{back}). These dentifications were performed fixing

- the voidage of the bed e to the mean value calculated from RTD experiment (see above)
- the number of tanks-in-series to an arbitrary value
- the gas and the liquid flow rate to the values measured.

II.4.2.3 Calculation of the number of tanks for the description of the liquid flow behaviour from parameters identification of the N-tanks-in-series model.

The method consists in the use of the linear relation which exists between N and fback (figure 4a) and to define the theoretical number of tank as this for which the both following condition are respected:

- The fback value is minimal, but positive
- The criteria is minimal

An example of the determination of N by this method is given in figure 6a for an experiment on the C50 column with a gas flow rate of 1 l/min and a liquid flow rate of 2.9 l/h. The figure 6a illustrates the linearity of the interrelation between the identified value of the liquid back-mixing fraction and the fixed number of tanks used for the identification. The criteria calculated is presented in figure 6b. From the linear relation (figure 6a), the number of tanks and the liquid-back-mixing are deduced. It can be observed the very good fitting of the model and of the experimental curve (figure 6c), suggesting that, in this experimental case, more complicated hydrodynamic models (TN55.2) are not necessary.

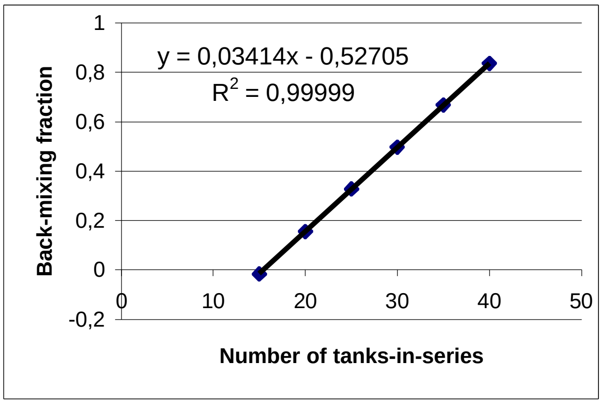
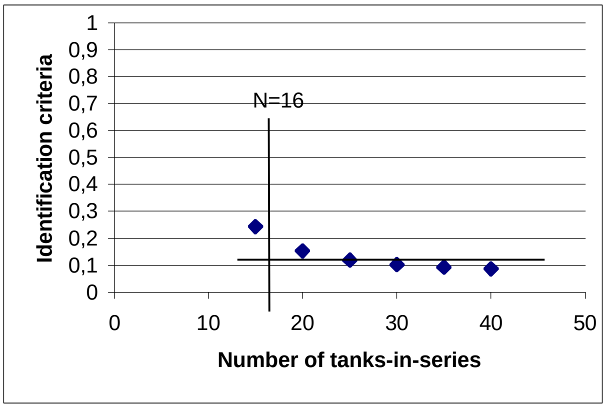
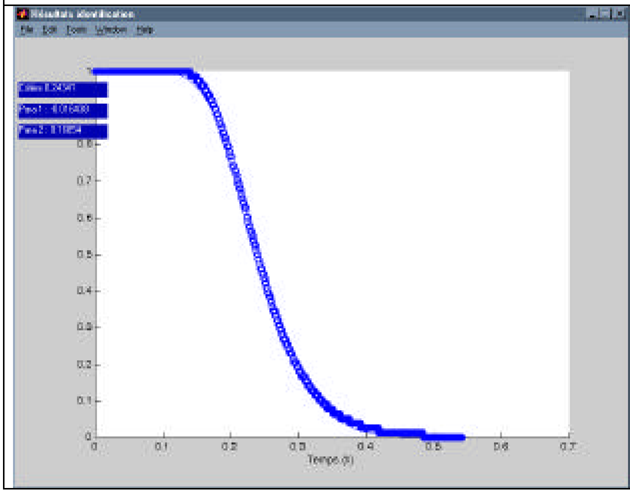


Figure 6a : Relation between the number of tanks and the liquid back-mixing fraction in the N-tanks-in-series model. Liquid back-mixing fraction is identified using RTD curve of C50 column operated with 1L/min of gas and 2.9 l/h of liquid.

	Figure 6b : Criteria for the identification of the liquid back-mixing fraction, as function of the number of tanks, using RTD curve of C50 column operated with 1L/min of gas and 2.9 l/h of liquid.
	Figure 6c : Identification of the liquid back-mixing fraction, for N=15, using RTD curve of C50 column operated with 1L/min of gas and 2.9 l/h of liquid

III RTD experiments with C50 and C150 columns

Before detailing the results obtained with C50 and C150 column it must be kept in mind that the UAB nitrifying columns are operated with the following conditions.

	Liquid RT	Gas superficial velocity (m/s)
8 Liters pilot column	1.5 h – 2 h 90 min – 120 min	0.011 – 0.02
Bench columns (including recycling flows rates)	0.29 h – 0.32 h 17.4 min – 19.2 min	0.0002 (low flow rates) 0.0002 – 0.0015 (nitrifying flow rates) 0.013 (highest flow rates)

Flow characteristic of UAB nitrifying columns (concern the fixed bed part – also called part B of columns)

The experiments presented below were performed for larger ranges of operating conditions, but include the conditions in which are operated the nitrifying columns.

III.1 C50 experiments

III.1.1 F_q RTD curves

The F_q RTD curves obtained are reported in figures 7. The correspondences between flows rates (for gas and liquid) and superficial velocities according to the voidage of the column calculated from RTD experiments without gas flow (table 3) are reported in table 2. Details of the experiments including the operating conditions (flow rates, superficial velocities) and the results obtained from calculation and identification from RTD curves are compiled in table 2.

The shapes of the F_q RTD curves are comparable for the different gas flow rates, when it exist both gas and liquid flows. The liquid hydrodynamic behaviour tends to plug flow for the highest liquid flow rate and to perfectly mixed for the lowest liquid flow rate. But when there is no gas flow, the liquid in the column has a plug-flow behaviour whatever is the liquid flow rate (figure 7f).

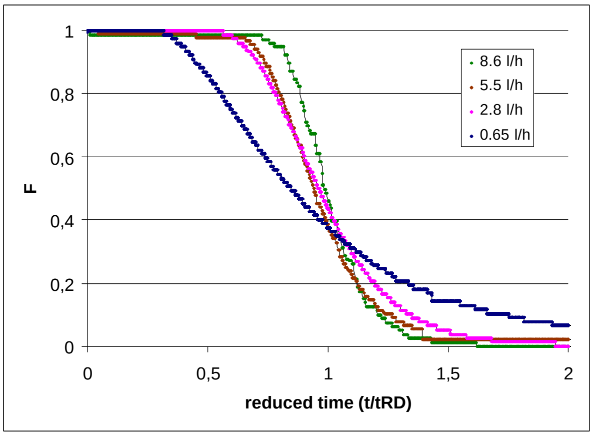


Figure 7a : F_q RTD curve of C50 column for a gas flow rate of 1L/min

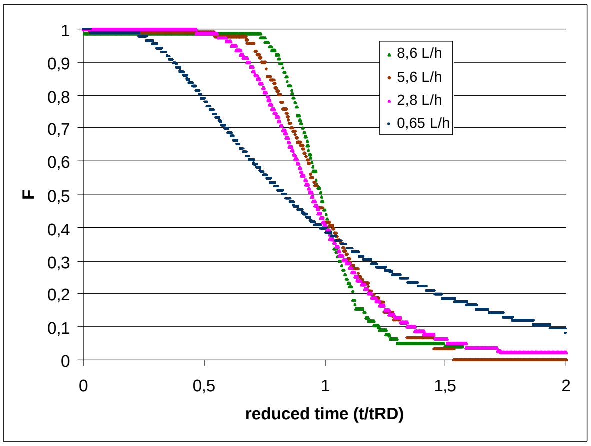


Figure 7b : F_q RTD curve of C50 column for a gas flow rate of 0.8L/min

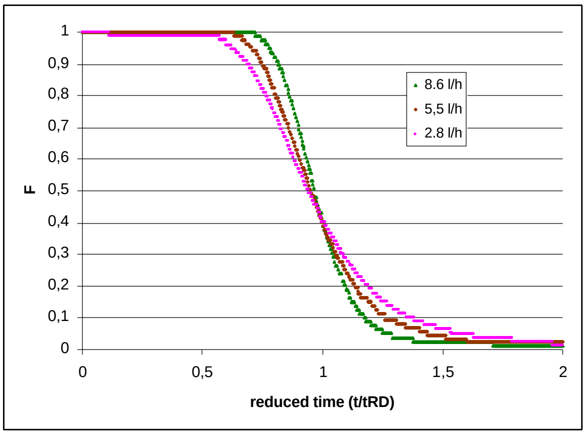


Figure 7c : F_q RTD curve of C50 column for a gas flow rate of 0.6L/min

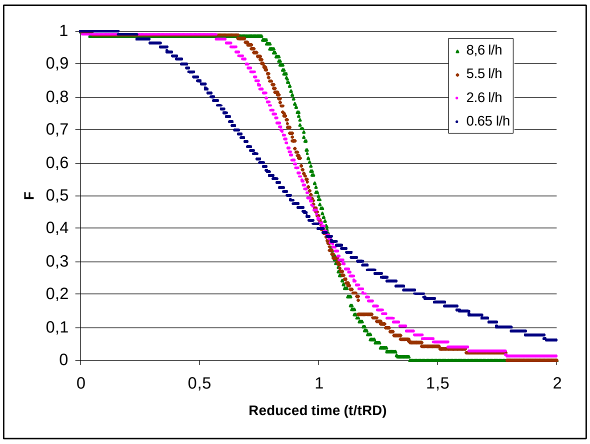


Figure 7d : F_q RTD curve of C50 column for a gas flow rate of 0.4L/min

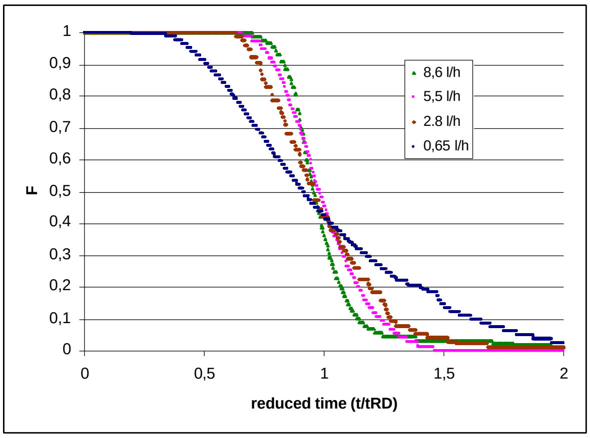


Figure 7e : F_q RTD curve of C50 column for a gas flow rate of 0.2L/min

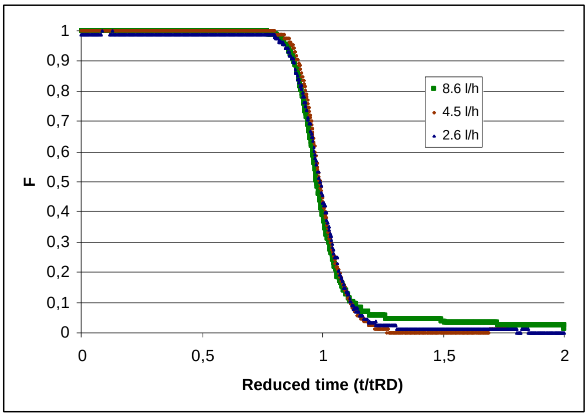


Figure 7f : F_q RTD curve of C50 column without a gas flow rate

					Theoretical calculation from RTD curves					Identification with NitriSim model				
Liquid flow rate (L/h)	**Gas flow rate (L/min)**	**liquid t_{RT} (min)**	**Liquid m/s**	**Gas m/s**	**voidage**	**Liquid fraction**	**Gas fraction**	**Gas volume (l)**	**Number of tanks-in-series**	**Liquid fraction**	**Gas fraction**	**Gas volume (l)**	**Number of tanks-in-series**	**Liquid back-mixing fraction**
8.93	0	6.12	0.00281	0	0.407	0.407	0	0	74	-	-	-	-	-
8.93**	0	6.04	0.00281	0	0.401	0.401	0	0	-	-	-	-	-	-
4.37	0	10.66	0.00138	0	0.347	0.347	0	0	112	0.3441	0	0	71	0.0036
4.37**	0	10.74	0.00138	0	0.349	0.349	0	0	-	-	-	-	-	
2.34	0	17.39	0.00074	0	0.302	0.302	0	0	57	-	-	-	-	-
2.34**	0	17.29	0.00074	0	0.301	0.301	0	0	-	-	-	-	-	-
8.72	1	5.36	0.00275	0.01889	0.4	0.348	0.052	0.116	34	0.379	0.021	0.046	47	0.0011
8.72	0.8	5.72	0.00275	0.01511	0.4	0.371	0.029	0.064	28	0.370	0.030	0.067	40	0.0011
8.72	0.6	6.13	0.002747	0.01133	0.4	0.398	0.002	0.004	36	0.392	0.008	0.017	49	0.0068
8.72	0.4	5.41	0.002747	0.00755	0.4	0.351	0.049	0.109	40	0.366	0.034	0.076	55	0.0055
8.72	0.2	5.60	0.002747	0.00378	0.4	0.363	0.036	0.082	33					
5.07	1	8.93	0.00159	0.01889	0.4	0.337	0.063	0.142	14	0.364	0.036	0.080	23	0.0021
5.07	0.8	9.43	0.00159	0.01511	0.4	0.356	0.044	0.100	16	0.357	0.043	0.096	20	0.0275
5.07	0.6	9.48	0.00159	0.01133	0.4	0.357	0.043	0.095	17	0.370	0.030	0.068	22	0.0037
5.07	0.4	9.85	0.00159	0.00755	0.4	0.371	0.029	0.064	18	0.380	0.020	0.044	25	0.0121
5.07	0.2	9.51	0.00159	0.00378	0.4	0.358	0.042	0.093	29	0.359	0.041	0.091	33	0.0107
2.94	1	14.95	0.00092	0.01889	0.4	0.327	0.073	0.164	12	0.348	0.052	0.117	16	0.0018
2.94	0.8	16.01	0.00092	0.01511	0.4	0.350	0.050	0.112	11	0.367	0.033	0.073	15	0.0380
2.94	0.6	16.17	0.00092	0.01133	0.4	0.354	0.046	0.104	10	0.344	0.056	0.124	14	0.0388
2.94	0.4	16.22	0.00092	0.00755	0.4	0.355	0.045	0.101	12	0.355	0.045	0.100	15	0.0186
2.94	0.2	17.94	0.00092	0.00378	0.4	0.392	0.008	0.017	15	0.388	0.012	0.027	18	0.0144
0.679	1	70.85	0.00021	0.01889	0.4	0.358	0.042	0.095	3	0.361	0.039	0.088	4	0.1767
0.679	0.8	50.45	0.00021	0.01511	0.4	0.255	0.145	0.325	2	0.259	0.141	0.316	3	0.3111
0.679	0.4	76.51	0.00021	0.00755	0.4	0.386	0.014	0.031	3	0.390	0.010	0.023	4	0.1976
0.679	0.2	69.30	0.00021	0.00378	0.4	0.350	0.050	0.112	5	0.350	0.050	0.111	5	0.0178

Table 2 : Results of RTD experiments with the C50 fixed bed column. ** step down tracer experiment

III.1.2 Voidage of the fixed bed

As it can be seen in table 3, the determination of the voidage is more difficult than it was attempted. From RTD experiments, if the hydrodynamic flow behaviour is the same (figure 7f), the voidage calculated varies from 0.3 to 0.4.

Using a theoretical glass bead density of 2.4 g/cm^3, a voidage of 0.42 can be calculated considering the mass of the beads used to fulfil the column.

The measurement of the liquid contained in the fixed bed column give a voidage of 0.36, what can be considered as the lowest value for the voidage (due to retention forces all the liquid contained in the fixed bed cannot be measured). This suppose that the values of 0.35 and 0.3 obtained from RTD are false. It appears then that for low liquid superficial velocities, without gas flow, a dead volume appears in the fixed bed. It is probable that the liquid velocity is insufficient to contra-balance retention of liquid by the beads, inducing the dead volume.

The theoretical voidage of **0.4** is taken for the C50 column as it is in accordance with the voidage calculated for the highest liquid flow rate used.

Voidage calculated from gas free RTD experiments with different liquid flow rate. RTD experiments were performed for step-up and step down responses		
Liquid flow rate (L/h)	Residence time (t_{RD}) (min)	Fixed bed voidage
8.9 (step-up response)	6.12	0.407
8.9 (step-down response)	6.04	0.401
4.4 (step-up response)	10.66	0.347
4.4 (step-down response)	10.74	0.349
2.3 (step-up response)	17.38	0.302
2.3 (step-down response)	17.28	0.301
Voidage calculated from the mass of beads used to fulfil the column (bead density: 2.4 g/cm^3)		0.423
Voidage calculated from the volume of liquid measured in the fixed bed		0.363

Table 3 : Voidage of the C50 fixed bed column.

III.1.3 Gas and liquid fraction and hold-up

Gas fraction, liquid fraction and hold-up are linked together (report to II.1.4.2). The gas volume calculated directly from RTD curves are reported in figure8a and those identified from the NitriSim model are reported in figure8b. It must be outlined that the value identified are independent of the number of tanks and of the back-mixing parameters. Both in figure8a and 8b, the volume of gas can be compared to the volumes measured from hold-up in a column without liquid flow.

The results obtained are disappointing as it appears that, except for the hold-up measurement, the volumes of gas are widely distributed whatever is the method used to determined this volume (direct calculation or identification). It must be outlined that as the gas volume is deduced from the liquid RTD, an experimental error of only 5% on the liquid volume, on the flow rate or on the residence time is sufficient to induce an error of more than 50% on the gas volume.

In Figure 8c it can be seen that the values of gas volume (i.e. gas fraction) that can be calculated directly from RTD experiments (II.4.1.2), are often the same as those identified, but some of the identified gas volumes are lower.

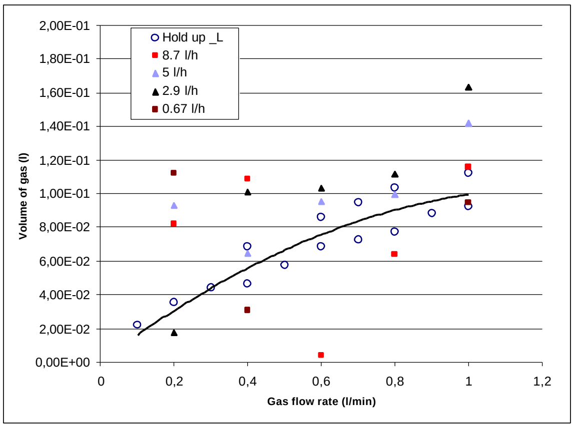


Figure 8a : Gas volume in the fixed bed, calculated from RTD curves

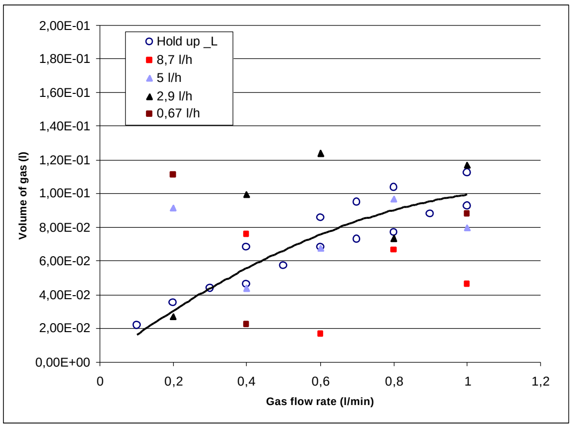


Figure 8b : Gas volume in the fixed bed, identified with the NitriSim model

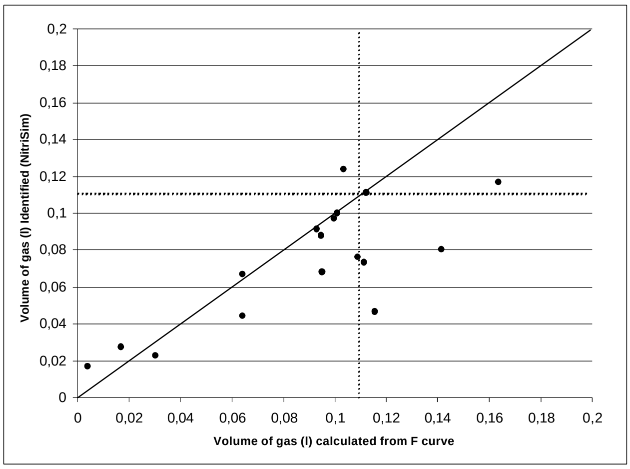


Figure 8c : Gas volume : comparison between direct calculation and identification

III.1.4 Number of tanks and back-mixing

The number of tanks-in-series and the back-mixing identified with the NitriSim model (as detailed in section II.4.2.3) are reported in table 2.

The back-mixing is linked to the number of tanks used to model an experiment (report to II.4.2.3). A relation seem also exist between the minimal back-mixing value and the minimal number of tanks-in-series characterising a liquid flow behaviour (figure 9). For small number of tanks-in-series the back-mixing is higher, what implies a more important perfectly mixed behaviour of the liquid flow. For more than 15 tanks in series, the back-mixing can be interpreted as a representation of the axial dispersion.

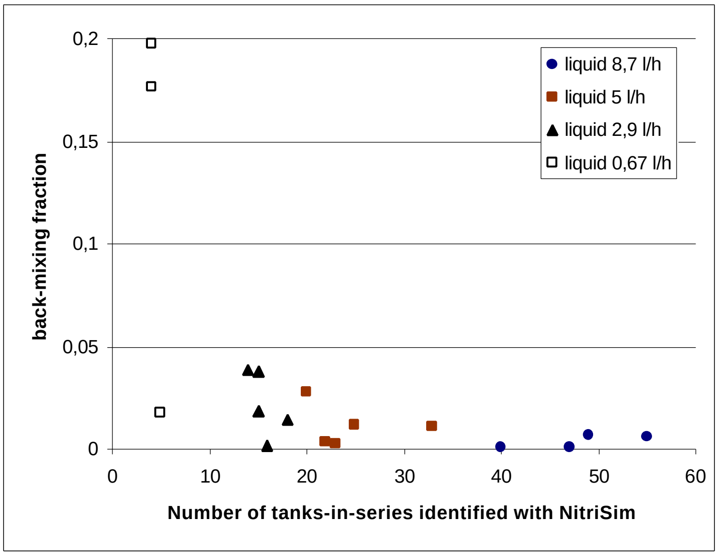


Figure 9 : Minimal values of back-mixing and of number of tanks-in-series for the representation of the liquid flow.

III.1.5 Number of tanks-in-series and operating conditions

In figures 10a and 10b are reported respectively the number of tanks calculated using the Int_F function and identified from the NitriSim model. The number of tanks vary respectively from 2 to 40 and from 5 to 55 for Inf_F calculation and parameter identification. More generally, the number of tanks is about 35% higher when the parameter is identified than when it is calculated by the Int_F function (figure 10e) and there is a better fitting of F curves with the identified values.

Without gas flow, the liquid hydrodynamic behaviour is a plug-flow (N>50, table 2) whatever is the liquid flow rate. With gas, the liquid hydrodynamic change quite immediately and depends in these conditions mainly of the liquid superficial velocity (figures 10).

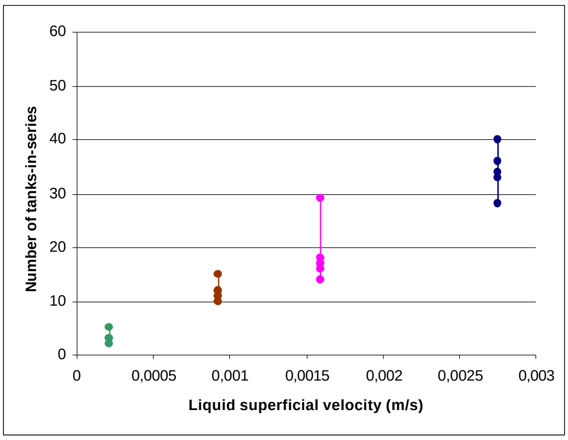


Figure 10a: Number of tanks-in-series calculated from Int_F function.

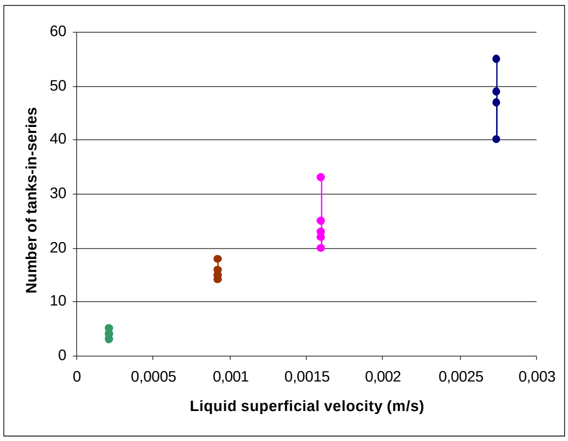


Figure 10b: Number of tanks-in-series identified with the NitriSim model

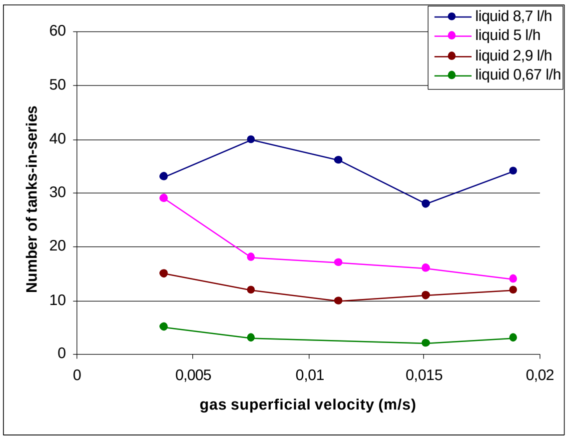


Figure 10c: Number of tanks-in-series calculated from Int_F function.

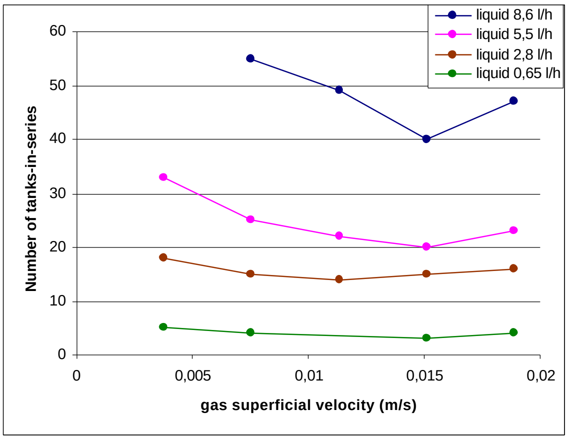


Figure 10d: Number of tanks-in-series identified with the NitriSim model

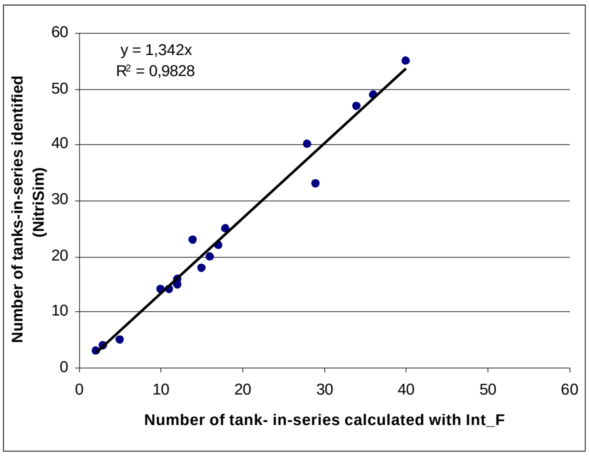


Figure 10e: Number of tanks-in-series : comparison between NitriSim identification and Int_F calculation

III.2 C150 experiments

III.2.1 F_q *RTD curves*

The F_q RTD curves obtained are reported in figures 11. Details of the experiments including the operating conditions (flow rates, superficial velocities) and the results obtained from calculation and identification from RTD curves are compiled in table 4.

As previously with the C50 column, the shapes of the F_q RTD curves are comparable for the different gas flow rates, when it exist both gas and liquid flows. For the flow rates used (i.e. the superficial liquid velocities) the liquid hydrodynamic behaviour is rather near a perfectly mixed behaviour than a plug-flow behaviour. This is coherent with the previous observation on the C50 column which indicates that for low liquid superficial velocities the number of tanks-in-series is reduced.

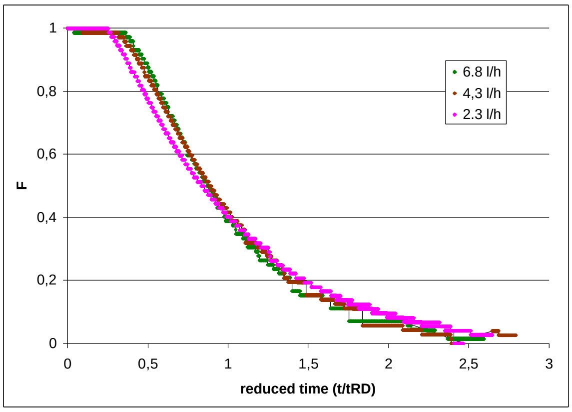


Figure 11a : F_q RTD curve of C150 column for a gas flow rate of 30L/min

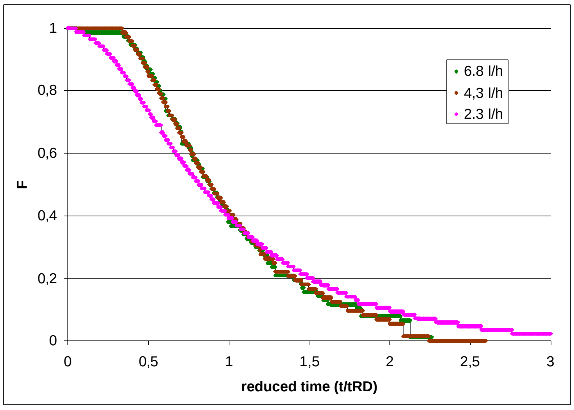


Figure 11b : F_q RTD curve of C150 column for a gas flow rate of 15L/min

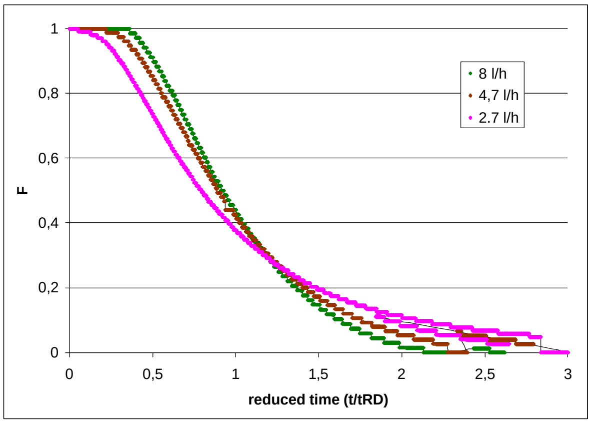


Figure 11c : F_q RTD curve of C150 column for a gas flow rate of 5L/min

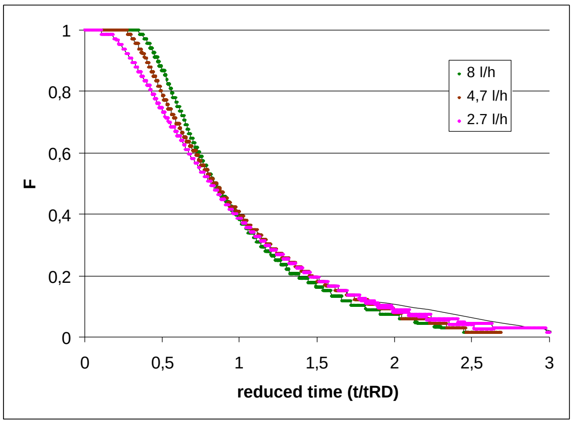


Figure 11d : F_q RTD curve of C150 column for a gas flow rate of 1L/min

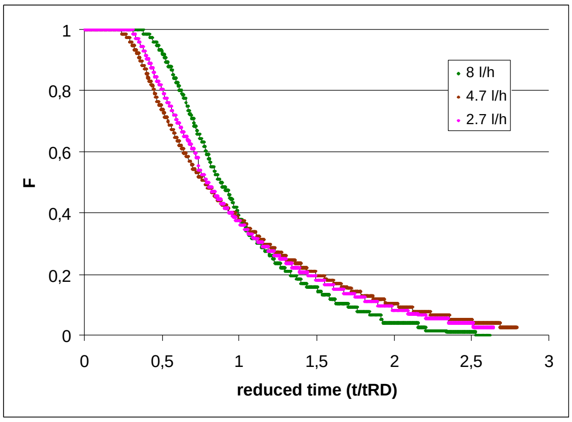


Figure 11e : F_q RTD curve of C150 column for a gas flow rate of 0.5L/min

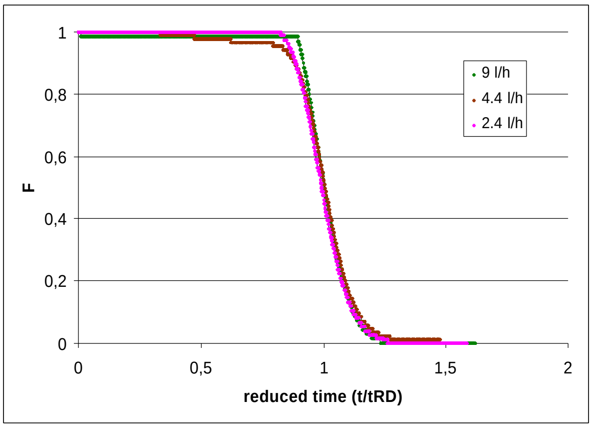


Figure 11f : F_q RTD curve of C150 column without a gas flow rate

III.2.2 Voidage of the fixed bed

As for the C50 column, the voidage calculated is sensitive to the liquid flow rate (table 5). The voidage calculated varies from 0.30 to 0.38. The voidage calculated from the liquid recovered from the column is only of 0.34, but a non negligible fraction of liquid is retained in the column. A high liquid flow rate (33 l/h) gives a voidage of **0.38**. This value will be taken as the voidage of the C150 column for the further calculations and simulations.

Voidage calculated from gas free RTD experiments with different liquid flow rate.		
Liquid flow rate (L/h)	Residence time (t_{RD}) (min)	Fixed bed voidage
33.34	12.32	0.383
9.04	43.30	0.365
4.42	78.10	0.322
2.36	137.98	0.305
Voidage calculated from the mass of beads used to fulfil the column (bead density: 2.4 g/cm^3)		0.428
Voidage calculated from the volume of liquid measured in the fixed bed		0.337

Table 5 : Voidage of the C150 fixed bed column.

						Theoretical calculation from RTD curves				Identification with NitriSim model				
Liquid flow rate (L/h)	**Gas flow rate (L/min)**	**Liquid t_{RT} (min)**	**Liquid m/s**	**Gas m/s**	**voidage**	**Liquid fraction**	**Gas fraction**	**Gas volume (l)**	**Number of tanks-in-series**	**Liquid fraction**	**Gas fraction**	**Gas volume (l)**	**Number of tanks-in-series**	**Liquid back-mixing fraction**
9,04	0	43,29	0,00037	0	0,365	0,365	0	0	98	-	0	0	-	-
4,42	0	78,10	0,00018	0	0,322	0,322	0	0	42	-	0	0	-	-
2,36	0	137,98	0.000097	0	0,305	0,305	0	0	99	-	0	0	-	-
33,34	0	12,32	0,00138	0	0,383	0,383	0	0	99	-	0	0	-	-
6,79	30	48,17	0,000281	0,0744	0,38	0,306	0,074	1,326	3	0,304	0,076	1,356	4	0,10846
6,79	15	44,26	0,000281	0,0372	0,38	0,281	0,099	1,770	4	0,281	0,099	1,766	4	0,11432
8,05	5	40,82	0,000333	0,0124	0,38	0,307	0,073	1,307	5	0,307	0,073	1,304	5	0,00552
8,05	1	39,43	0,000333	0,00248	0,38	0,296	0,084	1,493	3	0,293	0,087	1,552	4	0,17963
8,05	0,5	38,17	0,000333	0,00124	0,38	0,287	0,093	1,663	4	0,282	0,098	1,741	5	0,07309
4,3	30	69,84	0,000178	0,0744	0,38	0,280	0,100	1,777	3	0,284	0,096	1,718	4	0,18187
4,3	15	67,95	0,000178	0,0372	0,38	0,273	0,107	1,913	4	0,274	0,106	1,897	4	0,09643
4,67	5	61,46	0,000193	0,0124	0,38	0,268	0,112	1,997	3	0,271	0,109	1,943	4	0,13503
4,67	1	65,64	0,000193	0,00248	0,38	0,286	0,094	1,670	3	0,306	0,074	1,316	3	0,21627
4,67	0,5	63,16	0,000193	0,00124	0,38	0,276	0,104	1,864	2	0,306	0,074	1,316	3	0,21627
2,29	30	125,96	0.000094	0,0744	0,38	0,269	0,111	1,977	2	0,249	0,131	2,342	2	0,34486
2,29	15	125,52	0.000094	0,0372	0,38	0,268	0,112	1,994	2	0,212	0,168	2,993	2	0,2595
2,71	5	114,52	0,000112	0,0124	0,38	0,290	0,090	1,609	2	0,294	0,086	1,526	2	0,34624
2,71	1	108,63	0,000112	0,00248	0,38	0,275	0,105	1,874	2	0,276	0,104	1,851	2	0,17354
2,71	0,5	97,21	0,000112	0,00124	0,38	0,246	0,134	2,390	3	0,316	0,064	1,148	3	0,24107

Table 4 : RTD results obtained with the C150 column.

III.2.3 Gas and liquid fraction and hold-up

The gas volume calculated directly from RTD curves are reported in figure 12a and those identified from the NitriSim model are reported in figure 12b. As for the C50 column, the gas volume is widely distributed and no correlation can be determined.

A good correlation exists between the gas volumes identified and the volumes calculated directly from the RTD curves (figure 12c).

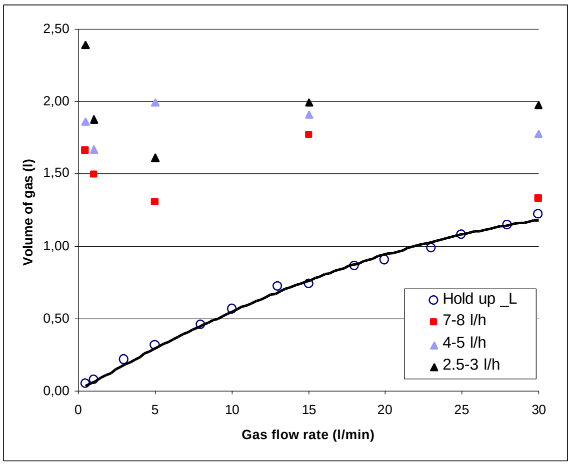


Figure 12a : Gas volume in the fixed bed, calculated from RTD curves

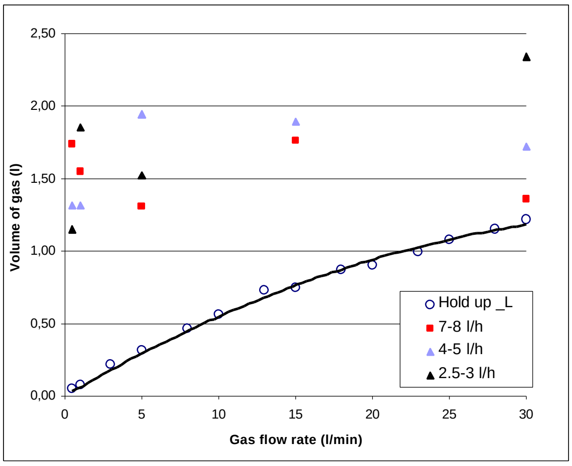


Figure 12b : Gas volume in the fixed bed, identified with the NitriSim model

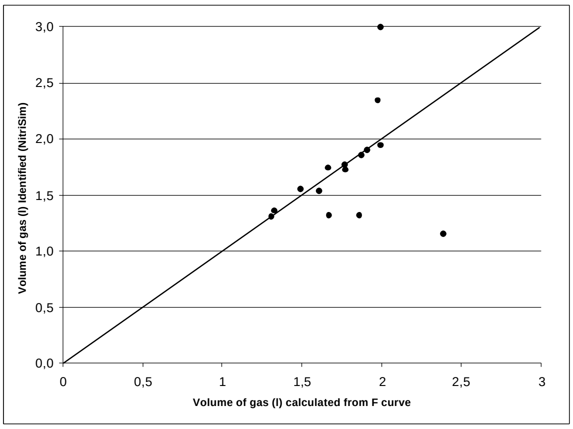


Figure 12c : Comparison between identified and calculated gas volumes

III.2.4 Number of tanks and back-mixing

The minimal number of tanks-in-series associated to the minimal liquid back-mixing value are reported in table 4. The value were identified accordingly to the method detailed in section II.4.3.

A small number of tanks-in-series, between 2 and 5, are necessary to represent the liquid hydrodynamic. As for the C50 column, this small number of tanks-in-series are correlated to a relatively high value of the liquid back-mixing. The back-mixing value decreases when the number of tanks-in-series increases what is in accordance with the previous observations made on the C50 column for higher liquid superficial velocities.

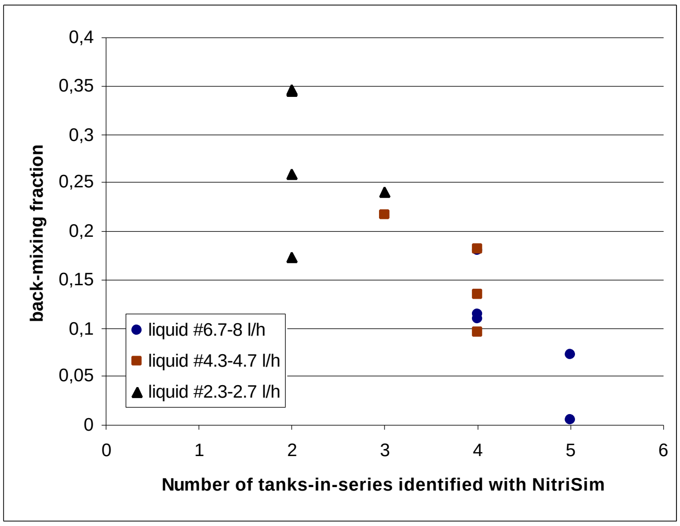


Figure 13 : Minimal values of back-mixing and of number of tanks-in-series for the representation of the liquid flow.

III.2.5 Number of tanks-in-series and operating conditions

The number of tanks-in-series calculated with Int_F correlation and identified from NitriSim are reported in figures 14 as functions of gas and liquid superficial velocities. In the operating conditions range tested, the number of tanks-in-series is rather dependent of the liquid superficial velocity rather than of the gas superficial velocity. This is coherent with the previous results obtained with the C50 column.

As observed with the C50 column, the identified values are generally higher than the calculated values (figure 14e). If the value of tanks-in-series identified are closer for the C150 column than for the C50 column, this is due to the fact that the number of tanks is lower (lower variability possible for the integer value). It can be outlined that the tanks-in-series values identified have a more homogenous distribution (figure 14b) than the calculated ones.

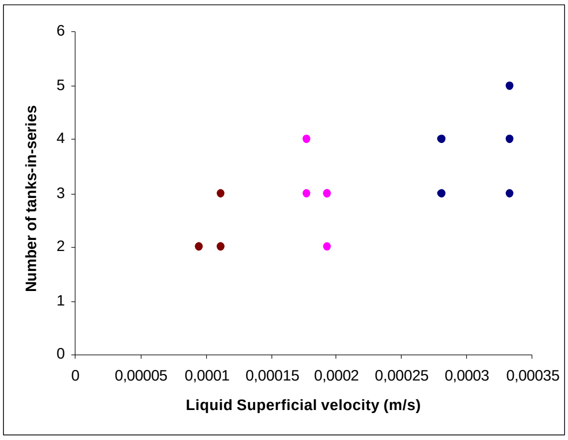


Figure 14a: Number of tanks-in-series calculated from Int_F function.

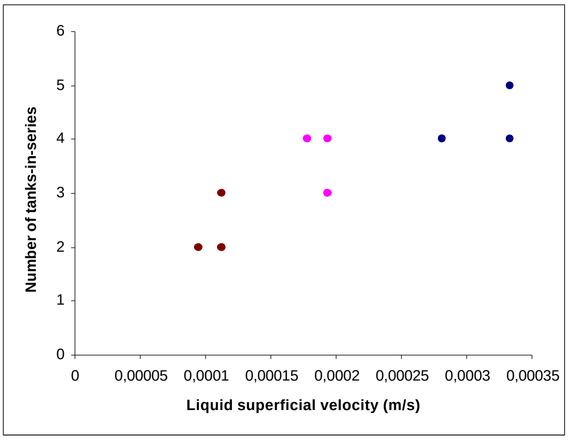


Figure 14b: Number of tanks-in-series identified with the NitriSim model

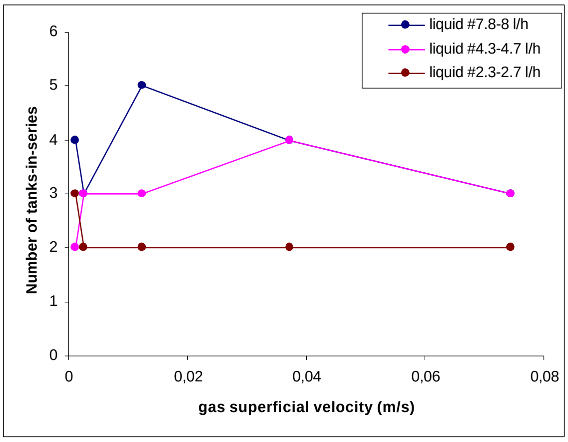


Figure 14c: Number of tanks-in-series calculated from Int_F function.

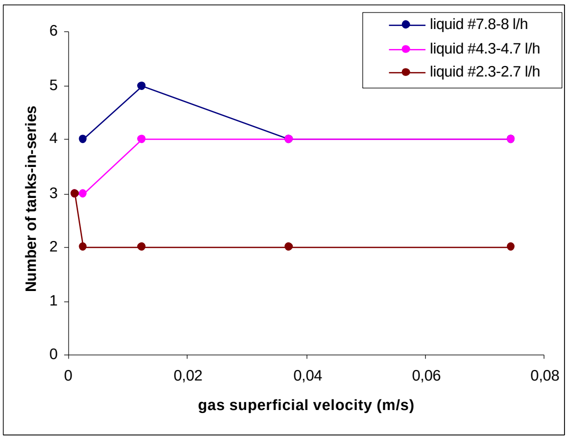


Figure 14d: Number of tanks-in-series identified with the NitriSim model

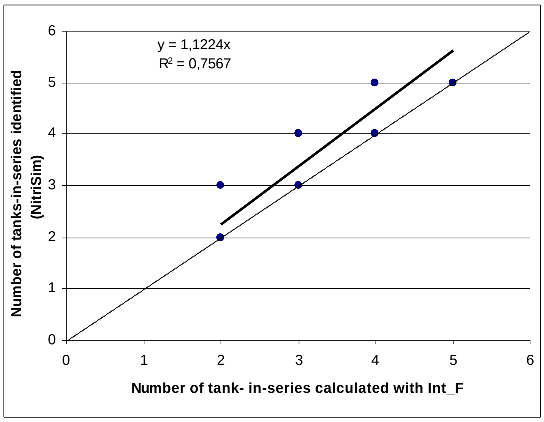


Figure 14e: Number of tanks-in-series : comparison between NitriSim identification and Int_F calculation

III.3 Comparison and compilation of some results obtained on the two columns

III.3.1 Measurement of the voidage of the fixed bed by RTD experiments

As previously noticed (report to section II.1.2 and II.2.2) the voidage of the fixed bed calculated from RTD experiments without gas flow vary with the liquid flow rate. This phenomenon is interpreted as insufficient superficial velocities to contra-balance retention forces induced by the beads arrangement what leads to form dead volumes in the fixed bed. The fact that a linear relation between the voidage calculated and the adimensional factor $\frac{d}{D}$, d being the beads diameter and D the column diameter, can be established (figure 15) is in favour of this interpretation. This also suggests that a minimal liquid flow rate must be used if we want to determine the voidage by RTD measurement.

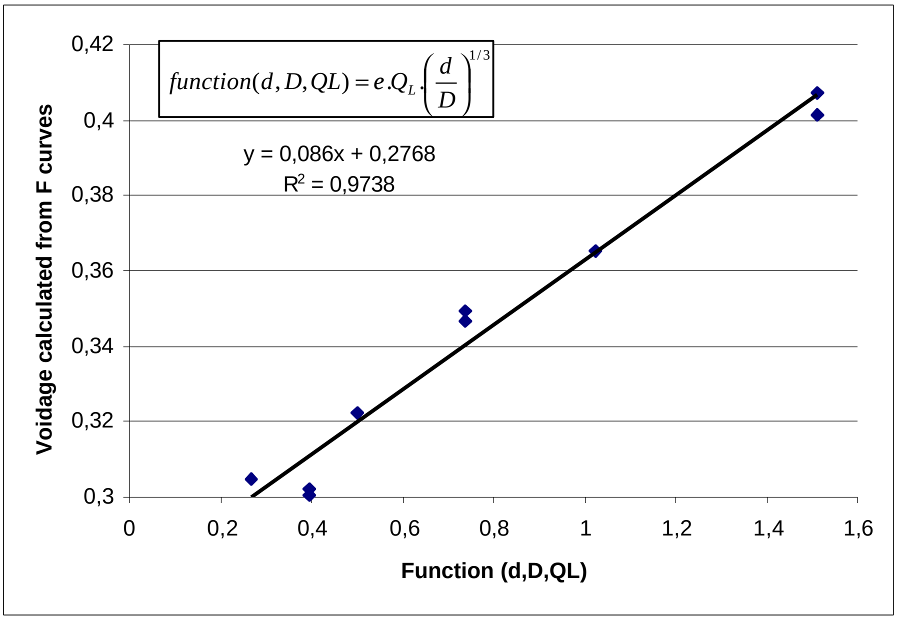


Figure 15: voidage calculated in the C50 and C150 column as a function of d, the bead diameter, D the column diameter, the voidage of the column (i.e. respectively 0.4 and 0.38 for C50 and C150) and Q_L the liquid flow rate (in l/h).

III.3.2 Number of tanks and superficial velocities

A relation was searched between the number of tanks-in-series (identified values) and the operating condition. The simplest relation found has the form :

$$N = a.\frac{(v_L)^b}{(v_G)^c} \qquad \text{(C1)}$$

The parameters of the correlation C1 were identified taking into account results obtained with only C50 column and with the two column C50 and C150. The parameters identified are reported in table 5 and in figures 16. The parameters are quite the same in the two cases, suggesting that the column design by itself has few influence.

	C50 column data		C50 and C150 columns data	
Parameter	Value	Standard Error	Value	Standard Error
a	200868,77	49,5%	318155,8	58,6%
c	0,2161	21,8%	0,2283	23,0%
b	1,0989	5,4%	1,1583	6,1%

Table 5 : Parameters identified for the correlation C1

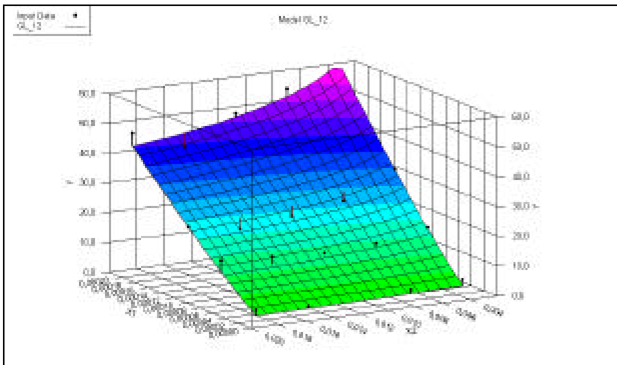


Figure 16a : Correlation C1 use to fit the number of tanks-in-series identified for the C50 column.

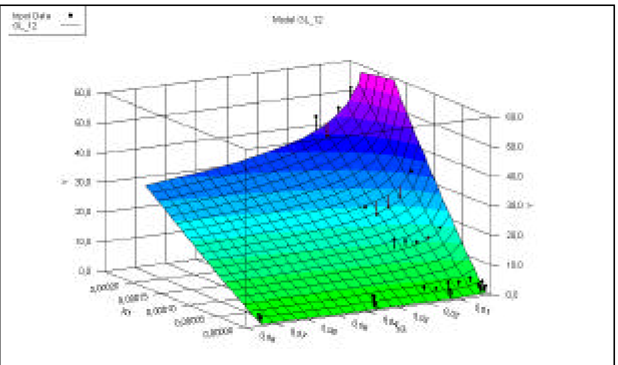


Figure 16b : Correlation C1 use to fit the number of tanks-in-series identified for the C50 and the C150 columns.

The design parameter $\frac{d}{D}$ characterising the two columns can also be associated to correlation C1, giving :

$$N = a.\frac{(v_L)^b}{(v_G)^c}\left(\frac{d}{D}\right)^f \qquad \text{(C2)}$$

The results of the parameters identification for this correlation for the C50 and C150 columns are reported in table 6 and in figures 17. As previously remarked the $\frac{d}{D}$ parameter don't have an important effect (f=-0.138 +/- 0.231, and then can be f=0).

	C50 and C150 columns data	
Parameter	Value	Standard Error
a	22897,11	53,5%
b	1,1410	4,9%
c	0,2040	20,3%
f	-0,1382	167,2%

Table 6 : Parameters identified for the correlation C1

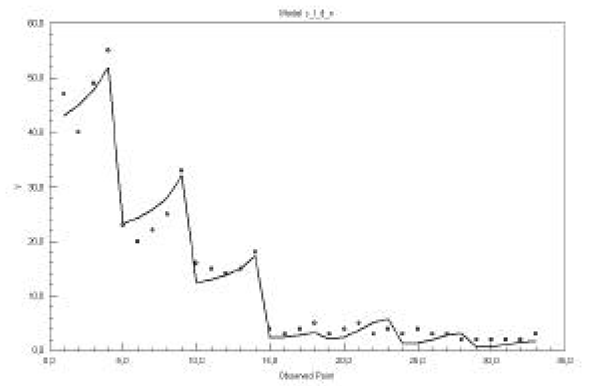


Figure 17a : Correlation C2 use to fit the number of tanks-in-series identified for the C50 and the C150 columns.

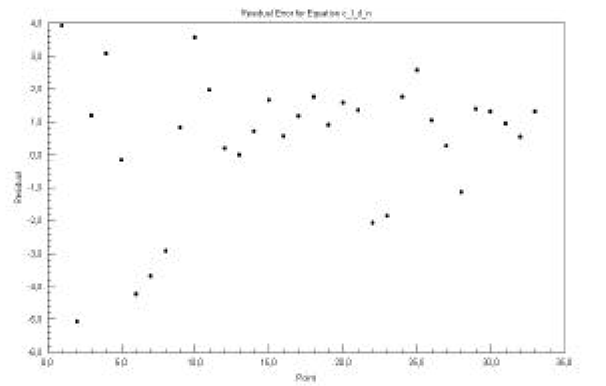
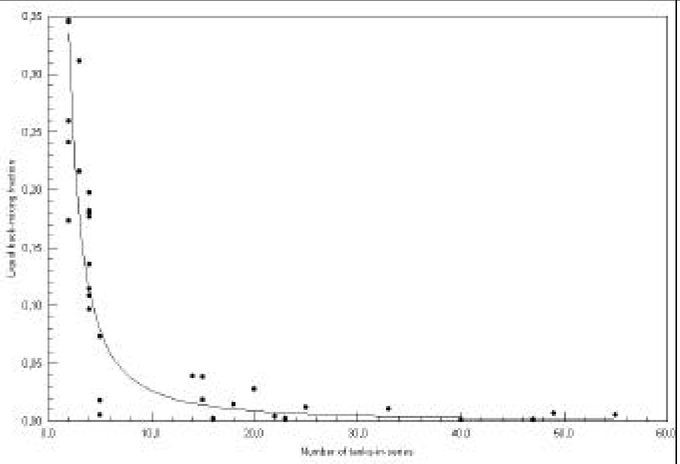


Figure 17b : Residual error obtained with correlation C2 for the C50 and C150 columns.

III.3.3 Number of tanks-in-series and liquid back-mixing fraction

The number of tanks-in-series and the liquid back-mixing fraction are compiled in figure 18. The back-mixing fraction quickly increases for small number of tanks-in series. The correlation used to fit the data is : $fback = N^{a}$, a=-1.571 +/- 0.068

	Figure 18 : Number of tanks in series and liquid back-mixing fraction identified on C50 and C150 columns.

IV Conclusions

Residence time distribution experiments were performed for the two column C50 and C150, equivalent in their design ($\frac{d}{D}$ factor) respectively to the bench and the pilot nitrifying columns. Analyses of the RTD curves were performed both using the theory of N-tanks-in-series model and the N-tanks-in-series with liquid back-mixing NitriSim model.

Concerning the comparison of the two methods used for the analysis of the RTD experiments it can be concluded that :

- The number of tanks calculated directly from RTD experiments are about 35% lower than this identified with the NitriSim model. This may be a consequence of the presence of a liquid back-mixing in the NitriSim model.
- The residence time, the liquid and gas volumes (or fraction) are comparable with the two methods.

The direct calculations from RTD curves can then be used to have a first estimation of the parameters to used in the NitriSim model.

It was difficult to determine **the voidage of the fixed** by RTD mesurement as it “apparently” decreases with the liquid superficial velocity. A minimal superficial velocity must be used to contra-balance the formation of liquid layer around the beads.

The determination of the **gas volume** (i.e. gas fraction or hold-up) from RTD experiments is also difficult as experimental errors (on liquid flow rate or residence time), even if they are small, are sufficient to induced important variation in the calculation of this variable. The values calculated are of the same order of magnitude as those measured directly from hold-up on the columns but are widely distributed. Then it is better to use the values calculated from the hold-up than the values calculated from RTD experiments.

The **number of tanks-in-series** are mainly dependent on the liquid superficial velocity and the design of the column ($\frac{d}{D}$ factor) seems not to play a role. For the experiments performed in this works, the following relation can be used to estimate the number of tanks both in the C50 and the C150 column:

$$N = 318155.\frac{(v_L)^{1.158}}{(v_G)^{0.228}} \quad (v_L \text{ and } v_G \text{ in m.s}^{-1})$$

Nevertheless, experiments are required to confirm this relation for high liquid superficial velocity on the C150 column.
In the range of superficial velocities used actually in the nitrifying columns, the number of tanks for the liquid phase in the fixed bed part would be of about 5 tanks-in-series.m^{-1} (C150-pilot column) and of about 15 tanks-in-series.m^{-1} (C50-bench columns).

The **liquid back-mixing** value identified is low for number of tanks-in series greater than 15, corresponding to an axial dispersion in a plug-flow hydrodynamic. When the hydrodynamic of the liquid is more perfectly mixed, the back-mixing fraction is higher (0.1-0.4) what is a characteristic of the predominance of a perfectly mixed behaviour.

It is important to keep in mind that the results presented in this work for the number of tanks in series and the back-mixing fraction concern only the liquid phase. As previously noticed, in the NitriSim model, the number of tanks-in-series enables the representation of the distribution of the biomass on the beads. If a number of tanks-in-series higher than this required to represent the liquid flow is required, the back-mixing parameter must be increased, accordingly to the linear relation linking number of tanks and back-mixing. A rough estimation of the liquid back-mixing fraction for a number of tanks in series higher than this required to represent the liquid flow can be obtained using the relation : $fback(N) = fback(N_{Liq}).(1.5(N - N_{Liq}) + 1)$, N_{Liq} and $fback(N_{Liq})$ being respectively the number of tanks-in-series required to represent the liquid hydrodynamic and the liquid back-mixing fraction associated to this number of tanks.

References

Lebouil D. , 2001 , Mesures de DTS dans des colonnes à lit fixe par une méthode conductimétrique. – ENSCCF training report.

Levenspiel O., 1999, Chemical reaction engineering 3rd Edition, Wiley & Sons ed.