MELiSSA

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TECHNICAL NOTE 63.2

$k_L a$ in fixed bed columns :
flow rates and columns design effects

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Content

I Introduction

The gas balance sulphite method for $k_L a$ measurement was developed and successfully applied for a fixed bed reactor (TN 55.2). As concluded in TN 55.2 some complementary studies were required.

In technical note 63.1 the hydrodynamic parameters (number of tanks-in-series and liquid back-mixing) were studied.
Additional experiments were also performed in order to check the reliability of the gas balance sulphite method by comparing the $k_L a$ measured by different techniques. It was demonstrated that using a sulphite solution of 10g/l reduces sufficiently the non-coalescent effect of the sulphite in fixed bed column, enabling the measurement of a $k_L a$ value comparable to that of the physical method (i.e operating with a coalescent behaviour)

In this technical note the following points will be investigated :
- the repeatability of the measurements. This is important in order to calculate the standard deviation of experimental measurements. This is a critical point as it was also observed an instability of the gas oxygen fraction (i.e. of $k_L a$) during experiments (TN 55.2).
- the variation of $k_L a$ with both gas and liquid superficial velocity changes
- the influence of the column design (here the difference of diameter between C50 and C150).

The main objective of this work is to establish a reliable correlation for the estimation of $k_L a$ in the fixed bed column used in the MELiSSA loop.

II k_La and fixed bed columns

II.1 Previous works and current objectives

The work presented in this technical note completes the studies started in TN 55.2 (k_La measurement in fixed bed columns) and in TN 63.1 (RTD analysis).
In these preliminary studies :

- the design of the experimental C50 and C150 fixed bed columns was fixed.
- the method and the protocol for the k_La measurement (gas mass balance method - Poughon et al., 2002) was validated.
- The liquid hydrodynamic (parameters of the NitriSim model) of the two fixed bed columns C50 and C150 was analysed and correlations for comparable columns (i.e. UAB columns) were established.

The main results obtained in these preliminary studies are briefly summarised in the next section.

II.2 LGCB column

II.2.1 Characteristics of LGCB C50 and C150 columns
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 in order to actually measure a representative gas-liquid mass transfer in the fixed bed. Studies on the LGCB column are therefore **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. This design was chosen in order to be consistent with the UAB columns.

It may be important to keep in mind the current operating characteristics of the column operated in UAB (Table 1a). The characteristics of the columns assembled in LGCB are summarised in Table 1b.

	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)

Table 1a :Flow characteristic of UAB nitrifying columns (concern the fixed bed part – also called part B of columns)

		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
	Voidage measured	0.40	0.38
Characteristic dimensions :	D/d :	13.25	37.5
Liquid flow rates:		0 –10 L/h	0-10 L/h
		$0 – 3.1 \ 10^{-3}$ m.s^{-1}	0-4.1 10-4 m.s^{-1}
Gas flow rates :		0.05 – 1 L/min	0.05 – 30 L/min
		$9.4 \ 10^{-4} – 1.9 \ 10^{-2}$ m.s^{-1}	$1.2 \ 10^{-4} – 7.4 \ 10^{-2}$ m.s^{-1}

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

II.2.2 Columns and NitriSim model

The liquid RTD experiments have led to conclude, for the two columns, operated with both gas and liquid, that the number of tanks (N_{liq}) and the liquid back-mixing ($fback(N_{Liq})$) required to represent the liquid hydrodynamic can estimated by the following correlations.

$$N_{Liq} = 318155.\frac{(v_L)^{1.158}}{(v_G)^{0.228}}$$ (v_L and v_G the liquid and gas superficial velocities in m.s^{-1})

$$fback(N_{Liq}) = N_{Liq}^{1.571}$$

However it is possible to use a higher number of tanks-in-series than the value N_{Liq} calculated by the previous expression, by correcting the liquid back-mixing parameter. This could be useful for suitably discretise the fixed bed solid part. The correction of fback is :

$$fback(N) = fback(N_{Liq}).(1.5(N - N_{Liq}) + 1)$$

It must be outlined that in absence of gas flow, the liquid phase has a plug-flow behaviour in the two columns.

The same columns as those used in TN 63.1 are used in the present work which voidage were calculated to 0.4 and 0.38 for the C50 column and the C150 column respectively.

II.3 $k_L a$ measurement by the gas mass balance method coupled with sulphite oxidation in the liquid phase

II.3.1 Principles

The principles of the $k_L a$ measurement by the gas mass balance method were detailed in TN 55.2 and by Poughon et al. (2002).

The method is based on the measurement of the difference between the molar oxygen gas fraction at the input (y^E) and at the output (y^S) of the column. The oxygen transferred from the gas to the liquid is immediately consumed for the oxidation of the sulphite to sulphate in the liquid phase, maintaining a dissolved oxygen concentration to zero. $k_L a$ is then directly calculated from the mass balance on the gas phase (Table 2). The scheme of the principle of the experimental apparatus for this method is presented in Figure 1.

The main advantages of this method are as follows :

- the calculation of $k_L a$ from the oxygen gas fraction measurements (y^S and y^E, respectively for the output and for the input of the reactor) are independent of the liquid hydrodynamic (Table 2);
- the method is faster and more accurate than the other classical methods involving a chemical reaction in the liquid phase.

If the method presents the drawback of the use of sulphite, which classically decreases the coalescence of the liquid and then can affect the $k_L a$ measured, it was demonstrated that at least for the C50 column, for a sulphite solution of 10g.l^{-1} the $k_L a$ measured is comparable to this measured by a physical method (Poughon et al. ,2002).

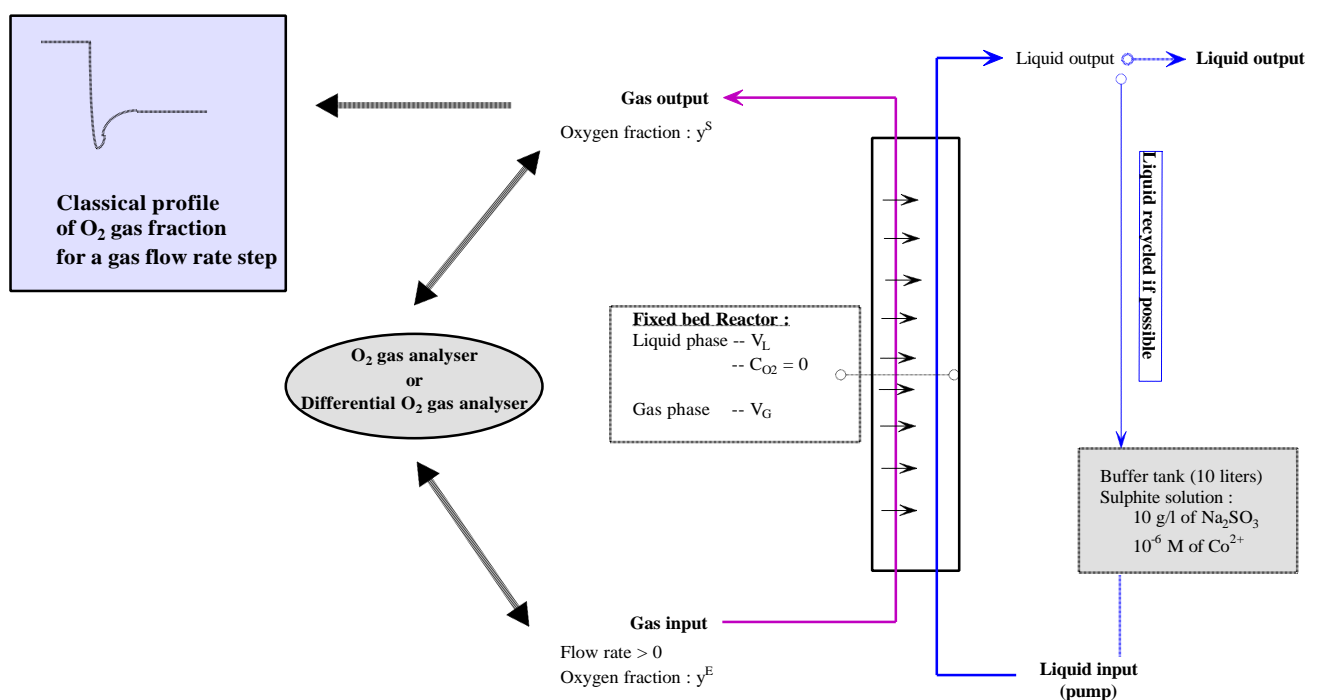Figure 1 : Principle of the sulphite gas balance method for $k_L a$ measurement

Gas phase with constant molar flow rate hypothesis	
Gas phase perfectly mixed	Gas phase plug flow
$$k_L a = \frac{G^E.He(T)}{P.V_L}.\left(\frac{y^E - y^S}{y^S}\right)$$	$$k_L a = \frac{G^E.He(T)}{P.V_L}.\ln\left(\frac{y^E}{y^S}\right)$$
Gas phase with variable molar flow rate hypothesis With $G_0 = G^E.(1-y^E) = G^S(1-y^S)$	
Gas phase perfectly mixed	Gas phase plug flow
$$k_L a = \frac{\dfrac{y^E}{y^S.(1-y^E)} - \dfrac{1}{1-y^S}}{\left(\dfrac{V_L.P}{G_0.He(T)}\right)}$$	$$k_L a = \frac{\dfrac{1}{1-y^E} - \dfrac{1}{1-y^S} + \ln\left[\dfrac{y^E.(1-y^S)}{y^S.(1-y^E)}\right]}{\left(\dfrac{V_L.P}{G_0.He(T)}\right)}$$

Table 2 : Analytical solutions for the determination of k_La with a steady-state gas mass balance method associated to chemical reaction in the liquid phase to maintain $C_{O2}\big|_L = 0$.

When the output oxygen fraction decreases under 0.15 the total molar flow rate is significantly changed. Then in all subsequent calculation for the k_La, the relation used is the plug flow hydrodynamic for the gas taking into account the variation of the molar flow rate.

II.3.2 Oxygen saturation concentration and Henry's coefficient

As can be seen in Table 2, the saturation concentration (or the corresponding Henry's constant He(T) for dilute solutions) is always involved and has a non negligible impact in the calculations. The fraction of dissolved oxygen is linked to the Henry's constant by the relation $x_{O2} = \dfrac{y_{O2}.P}{m(T)}$, m(T) being the Henry's constant expressed in Pa (if the total pressure P is also in Pa).

Notice that He(T) in Table 2 is the Henry's constant expressed in l.Pa.mol^{-1} while m(T) is the Henry's constant expressed in Pa. The relation ship between He(T) and m(T) is therefore expressed by : $He(T) = \dfrac{M_L}{\rho_L.1.013.10^{-5}} m(T)$

In order to take into account the effect of temperature we used a correlation for the solubility of oxygen in pure water $\left(x_{O2}^{\circ}(T)\right)$ as function of temperature given in Handbook of Chemistry and Physics (1996) :

$$\ln\left(x_{O2}^{\circ}(T)\right) = -66.7354 + \frac{8747.55}{T} + 24.4526\ln\left(\frac{T}{100}\right) \quad (273.15 < T < 348.15 \ ; \ +/- \ 0.36\%)$$

Then the Henry's constant of oxygen in pure water is calculated as $m^{\circ}(T) = \dfrac{y_{O2}.P}{x_{O2}^{\circ}(T)}$

The salts in the solution affect the oxygen transfer by decreasing the solubility of the gas compared to the pure solution (salting out effect) (Schumpe, 1993). In this study, for methods involving sulphite, the correlation proposed by Schumpe (1993) was used, with the parameters reported in Table 3:

$$\log\left(\frac{m°(T)}{m(T)}\right) = \sum (h_i + h_G).C_i\big|_L$$

This enables to calculate m(T) from ions concentrations and m°(T) which leads to the value of He(T) as function of temperature and liquid phase composition.

Na^+	SO_3^{2-}	SO_4^{2-}	O_2
0.1171	0.1537	0.1185	0

Table 3 : Salting out parameter hi (in l.mol⁻¹) for the compounds used in this study (Schumpe, 1993)

II.3.3 Effect of the temperature on the calculation of k_La

The temperature is not controlled as the columns used are not jacketed columns. The temperature is measured and is taken into account in the calculations (see above for the calculation of Henry's constant).

The experiments are rapid enough to consider that the temperature is constant during each experiments. Nevertheless it must be kept in mind that the k_La values calculated are dependent of the temperature at which the measurements were made. Experiments at LGCB were performed around 20°C (room temperature) while nitrifying columns operate at 30°C.

As an example, Ory et al. (1999) have established the following relation between k_La and temperature for a 450 ml reactor supplied in gas by a glass porous diffuser (pore size 100μm): $k_La(T) = 0.92288.T(°C) + 6.444$, temperature varying between 15 and 35 °C and k_La varying between 20 h⁻¹ and 39 h⁻¹. In the example of Ory et al. (1999), a variation of 28% is observed for the k_La value measured at 20°C and at 30°C. This variation must **only be considered as indicative** as we have not studied the influence of temperature in LGCB fixed bed columns.

More theoretically, the following relation can be used (Danckwerts, 1970) :

$$\frac{k_La\big|_{T=30°C}}{k_La\big|_{T=20°C}} = \sqrt{\frac{D_{O2}\big|_{T=30°C}}{D_{O2}\big|_{T=20°C}}}$$

$D_{O2}\big|_T$ being the diffusivity of O₂ in water at temperature T.

Knowing that $D_{O2}\big|_{T=20°C} = 1.85 \, 10^{-9}$ m².s⁻¹ and $D_{O2}\big|_{T=30°C} = 2.3 \, 10^{-9}$ m².s⁻¹, it can be assumed that $k_La\big|_{T=30°C} = 1.12 \, k_La\big|_{T=20°C}$

II.3.4 Other remarks

Some other points concerning the $k_L a$ measurement at LGCB must be outlined.

First, in the previous work, the correlations taken from the literature have failed, even this of Deront et al. (1999) which was established with a column similar to the C50 and C150 columns. This relation of Deront et al. (1999) takes into account the pressure drop inside the column, what is at the present time a non measured parameter.

The lack of the measurement of pressure drop is the second point to outlined in this work. The installation of a system for pressure drop measurement is under study.

The third point concerns the stability of the outlet oxygen gas fraction during the experiments (TN 55.2). The explanations for this observation were :

> i) a possible variation of the volumes (gas/liquid) during the experiments. It was not possible to verify or to reject this first assumption with the he hydrodynamic (RTD analysis) study (TN 63.1), as this method was insufficiently accurate to determine the volumes variations.

> ii) a variation of pressure. This second assumption could be verified only with the pressure drop system which is planned.

> iii) a variation of the solution composition This assumption can only explain a part of the variation (influence on the Henry's constant of the oxidation of sulphite to sulphate).

It will be checked in this work if the variations observed are within the range of the accuracy of the measurements (repeatability of the experiments).

III Experiments and results

III.1 C50 and C150 experiments

The details of the experiments performed on C50 and C150 columns are reported in annexe I and II.

For the both columns gas and liquid flow rates (i.e. superficial velocities) are varied in the largest range that can be obtained by the mass flow-controllers (gas) and by the pump (liquid).

Temperature is measured and is taken into account in the calculation of the Henry's constant and in the calculation of the gas molar flow rate (by the perfect gas relation).

The pressure is measured at the output of the column and in lack of other measurements, the pressure drop is estimated only by considering the hydrostatic pressure ($r.g.h$) : at the bottom of the column we consider $P_{bottom} = P_{top} + r_L.g.h$, what corresponds in fact to a first order estimation of pressure profile into columns.

The k_La is calculated considering a plug-flow behaviour for the gas phase and taking into account the gas molar flow rate variation due to the consumption of oxygen.

The liquid volume V_L (required for k_La calculation – see Table 2) is calculated assuming that the gas volume V_G is equal to the hold-up measured without liquid flow as it was not possible to determined the variation of gas volume from RTD experiments (TN 55.2; TN 63.1), then : $V_L = V_{Total} - V_{beads} - V_{Hold-up}$. The range of the values obtained in TN 63.1 are reported in the following Table :

	C50	C150
Vtotal (l)	2.24	17.85
Vbeads (l)	1.34	11.07
$V_L°$ (l) or free column volume	0.9	6.78
V_L (% $V_L°$)	86%-98%	71%-83%
Hold-up (% $V_L°$)	2%-14%	17%-29%

In order to observe the influence of the volume, and then the possible consequences of the inaccuracy of the determination of the liquid volume (V_L), a k_La° is also calculated assuming that the liquid volume is constant and equal to the voidage volume of the column. k_La° is in principle the lowest possible value of k_La that can be calculated as be reducing the liquid volume involved in the calculation, the k_La calculated increases.

Each k_La measurement is repeated by 4 series of experiments. One series consists for a fixed liquid flow rate to increase or to decreased gradually the gas flow rate. For a series the sulphite solution used is not changed. In the 4 series of experiments, 2 are performed by increasing the gas flow rate and 2 by decreasing the gas flow rate.

It is important to keep in mind that all correlations are given for:
- **k_La value in h⁻¹.**
- **Superficial velocities in m.s⁻¹**
- **Pressure in atm.**

III.2 C50 results analysis : $k_L a$ and flow rates (superficial velocities)

Experiments were performed for 4 different liquid flow rates (8.7 l.h^{-1} ; 5 l.h^{-1}, 3 l.h^{-1} and 0.7 l.h^{-1}) and for 10 gas flow rates (from 0.1 to 1 l.min^{-1}). Details of the results of the 160 experiments are presented in annexe I, and a summary with the averaged $k_L a$ values (40 different operating conditions) is reported in Table 4.
The liquid flow rates used correspond to a range of residence times of 6 to 18 min.

It can be observed that for given operating conditions, the 4 values of $k_L a$ are very closed (about +/- 3% to +/- 8%), indicating a good repeatability and then a good accuracy of the measurements, whatever is the history of the operating conditions on the column. Then the averaged $k_L a$ value calculated is representative of the measurements performed for in the different series. This averaged value and the standard deviation are reported in Table 4.

The correlations found in the literature have usually the form (TN 55.2):

$$k_L a = a.\left(u_G\right)^b.\left(u_L\right)^c$$

(u_G and u_L being respectively the gas and the liquid superficial velocities)

Other parameters such as pressure drop and column characteristic (particule diameter, d_P; column diameter D_c….) can be introduced in the correlations. Whatever is the form under which these parameters are introduced, the overall form of the correlation can be expressed by:

$$k_L a = a.\left(u_G\right)^b.\left(u_L\right)^c.\left(\frac{dP}{dZ}\right)^d \left(d_p\right)^e \left(D_c\right)^f ....$$

UG (m/s)	UL (m/s)	Calculation assumming Vl=Vtot-Hold-up			Calculation assumming Vl=Vtot	
		mean $k_L a$ (h^{-1})	Absolute deviation	%deviation	mean $k_L a°$ (h^{-1})	%deviation
1,89E-02	2,75E-03	185	10,84	5,86%	157	5,86%
1,70E-02	2,75E-03	174	9,52	5,47%	150	5,47%
1,51E-02	2,75E-03	161	8,65	5,37%	140	5,37%
1,32E-02	2,75E-03	148	7,66	5,19%	130	5,19%
1,13E-02	2,75E-03	134	5,07	3,78%	122	3,78%
9,44E-03	2,75E-03	120	3,72	3,10%	113	3,10%
7,55E-03	2,75E-03	104	4,46	4,30%	101	4,30%
5,67E-03	2,75E-03	89	2,46	2,77%	88	2,77%
3,78E-03	2,75E-03	67	5,80	8,63%	72	8,63%
1,89E-03	2,75E-03	44	1,49	3,35%		3,35%
1,89E-02	1,59E-03	186	5,79	3,11%	175	3,11%
1,70E-02	1,59E-03	178	4,96	2,78%	167	2,78%
1,51E-02	1,59E-03	167	4,92	2,95%	158	2,95%
1,32E-02	1,59E-03	155	4,95	3,20%	148	3,20%
1,13E-02	1,59E-03	139	4,18	3,00%	134	3,00%
9,44E-03	1,59E-03	125	4,97	3,97%	121	3,97%
7,55E-03	1,59E-03	110	5,32	4,84%	107	4,84%
5,67E-03	1,59E-03	92	4,49	4,88%	90	4,88%
3,78E-03	1,59E-03	64	4,80	7,47%	56	7,47%
1,89E-03	1,59E-03	41	10,33	24,92%	26	24,92%
1,89E-02	9,25E-04	186	10,68	5,74%	175	5,74%
1,70E-02	9,25E-04	175	9,57	5,47%	166	5,47%
1,51E-02	9,25E-04	164	8,27	5,06%	155	5,06%
1,32E-02	9,25E-04	151	8,70	5,77%	146	5,77%
1,13E-02	9,25E-04	138	8,72	6,34%	135	6,34%
9,44E-03	9,25E-04	123	7,87	6,38%	124	6,38%
7,55E-03	9,25E-04	105	5,63	5,38%	97	5,38%
5,67E-03	9,25E-04	83	7,48	8,97%	83	8,97%
3,78E-03	9,25E-04	64	5,95	9,31%	65	9,31%
1,89E-03	9,25E-04	44	4,33	9,75%	45	9,75%
1,89E-02	2,14E-04	185	7,04	3,80%	163	3,80%
1,70E-02	2,14E-04	176	8,88	5,05%	154	5,05%
1,51E-02	2,14E-04	169	11,68	6,93%	146	6,93%
1,32E-02	2,14E-04	156	12,80	8,20%	134	8,20%
1,13E-02	2,14E-04	142	12,13	8,53%	122	8,53%
9,44E-03	2,14E-04	123	4,57	3,72%	111	3,72%
7,55E-03	2,14E-04	103	3,87	3,74%	98	3,74%
5,67E-03	2,14E-04	87	3,10	3,58%	83	3,58%
3,78E-03	2,14E-04	66	2,45	3,71%	65	3,71%
1,89E-03	2,14E-04	42	3,00	7,06%	42	7,06%

Table 4 : Summary of $k_L a$ measurements on C50 column for different gas and liquid flow rates

III.2.1 Correlation for $k_L a$ calculation from superficial velocities

The parameters for the correlation $k_L a = a.(u_G)^b.(u_L)^c$ were identified from our experiments using mean $k_L a$ values calculated (including the standard deviation for each value) (Figure 2-1) and using all the value measured (Figure 2-2). The results of the parameters identification are reported in Table 5. The identification using all the $k_L a$ values calculated is comparable to these performed using the averaged $k_L a$ (4 values for each condition).

It clearly appears that in the range of operating conditions tested, the gas flow is the more important parameter. The liquid flow has quite no effect (high probability that the parameter c is equal to 0). This result is surprising as in correlation found in the literature (TN 55.2), the liquid flow has always a non negligible influence. This can explain the important discrepancies observed when correlation of the literature were used (TN 55.2). However it must be understood that in the reported experiments the liquid superficial velocity was rather low ($< 2.75 \ 10^{-3}$ m.s^{-1}) which explains that the influence on $k_L a$ is weak.
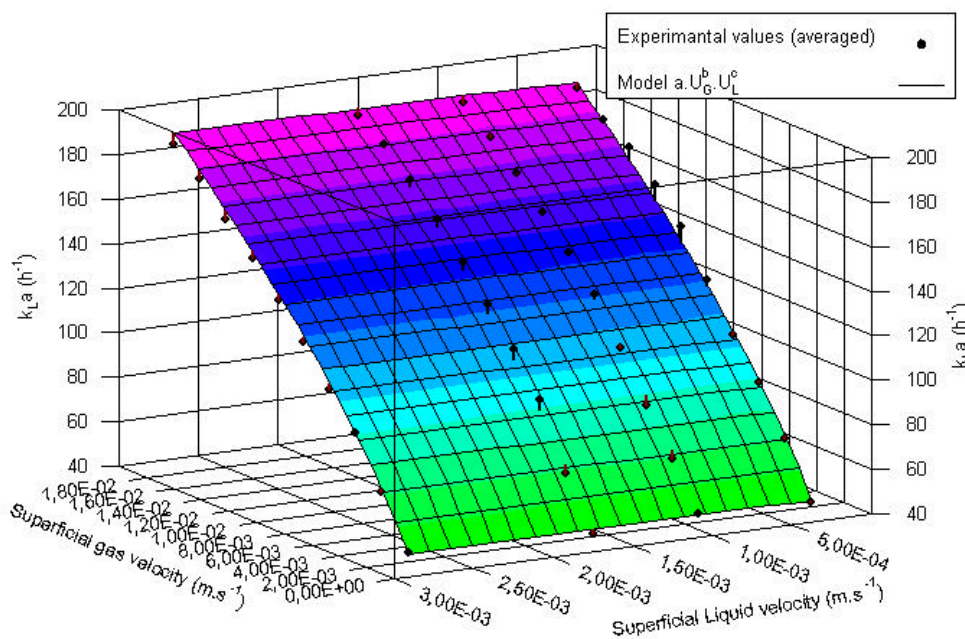

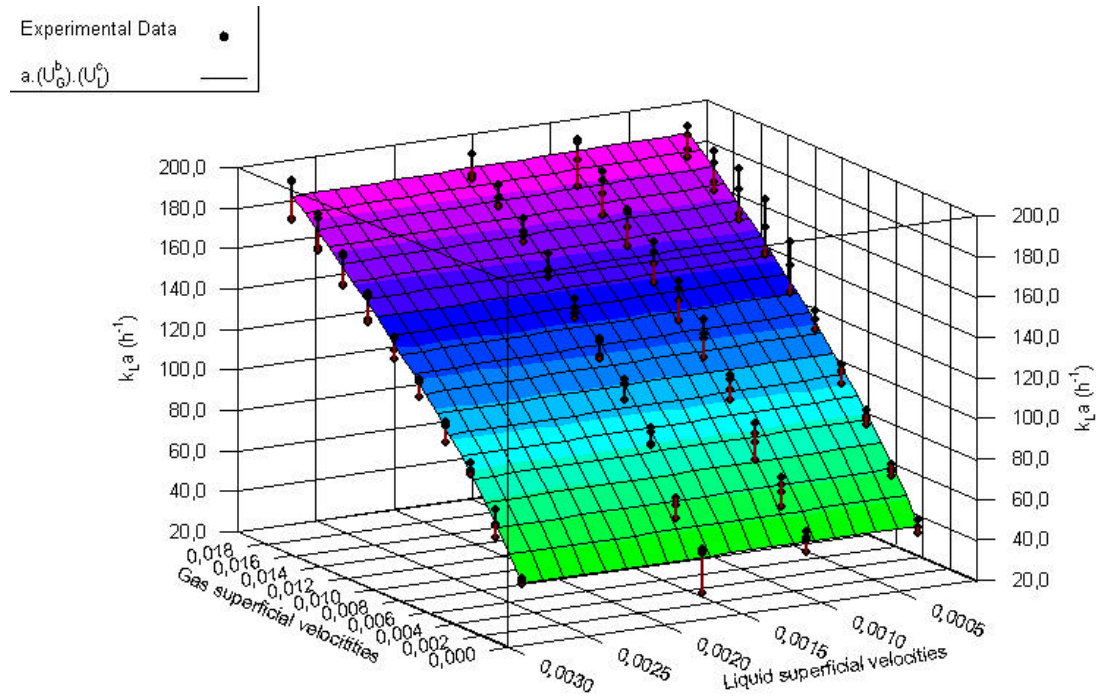Figure 2.1 : Parameters correlation identification for the averaged $k_L a$ values calculated (dots). ($r^2 = 0.99$)

Figure 2.2 : Parameters correlation identification for all k_La values calculated (dots). (r^2= 0.978)

Parameters identification for averaged k_La values (r^2=0.998)			
	Value	Standard Error	t-ratio	Prob(t)
a	2440,57	3,51%	28,45	0,0
b	0,63686	0,88%	113,14	0,0
c	0,004375	81,67%	1,22	0,23
Parameters identification for all calculated k_La values (r^2=0.978)			
	Value	Standard Error	t-ratio	Prob(t)
a	2359,62	4,23%	23,63	0,0
b	0,63415	1,51%	66,35	0,0
c	0,000894	439,39%	0,23	0,82

Table 5 : $k_La = a.\left(u_G\right)^b.\left(u_L\right)^c$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.

III.2.2 Correlation for k_La calculation from superficial velocities and pressure

As previously noticed, the pressure drop is not measured, and only the hydrostatic pressure is considered (i.e. Pressure at the bottom = Pressure at the top + ρgh). The pressure at the top of the column is measured. It is interesting to determined the influence of this pressure. The logarithmic pressure $P_{Log} = \dfrac{P_{Top} - P_{Bottom}}{Ln(\dfrac{P_{Top}}{P_{Bottom}})}$ is taken into account in the calculation of the gas velocity and in k_La expression (Table 2). Pressure is given in atm.

The correlation taking into account the logarithmic pressure has the form:

$$k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d$$

The parameters identified using all $k_L a$ values measured (Figure 3) are reported in Table 6. The effect of pressure is higher than that of the liquid superficial velocity. This suggests that the pressure drop is probably an important parameter to take into account. In Table 6, the results indicate that the parameter "c" (liquid superficial velocity) can be set to zero. In Table 7 are reported the results of parameters identification assuming a correlation of the of the form

$$k_L a = a.(u_G)^b.(P_{Log})^d$$

Parameters identification for all $k_L a$ values (r^2=0.98)				
	Value	Standard Error	t-ratio	Prob(t)
a	2614,97	5,74%	17,43	0,0
b	0,6523	1,49%	66,96	0,0
c	-0,00274	-147,24%	-0,68	0,50
d	-0,5445	-21,14%	-4,73	0,0

Table 6 : $k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.

Parameters identification for all $k_L a$ values (r2=0.98)				
	Value	Standard Error	t-ratio	Prob(t)
a	2671,34	4,76%	20,9894	0,0
b	0,6526	1,49%	67,2342	0,0
d	-0,5548	-20,46%	-4,8882	0,0

Table 7 : $k_L a = a.(u_G)^b.(P_{Log})^d$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.

If it appears here that the pressure has a non negligible effect, this result must be **carefully** considered as the pressure P_{Log} ranges between 1 and 1.2 atm with an average of 1.08. The values lie in a narrow range what reduces the accuracy of the analysis of the influence of the pressure.

The fact that the parameter of the pressure "d" is negative suggest that it will be better to study the influence of the power dissipated and of the pressure drop.
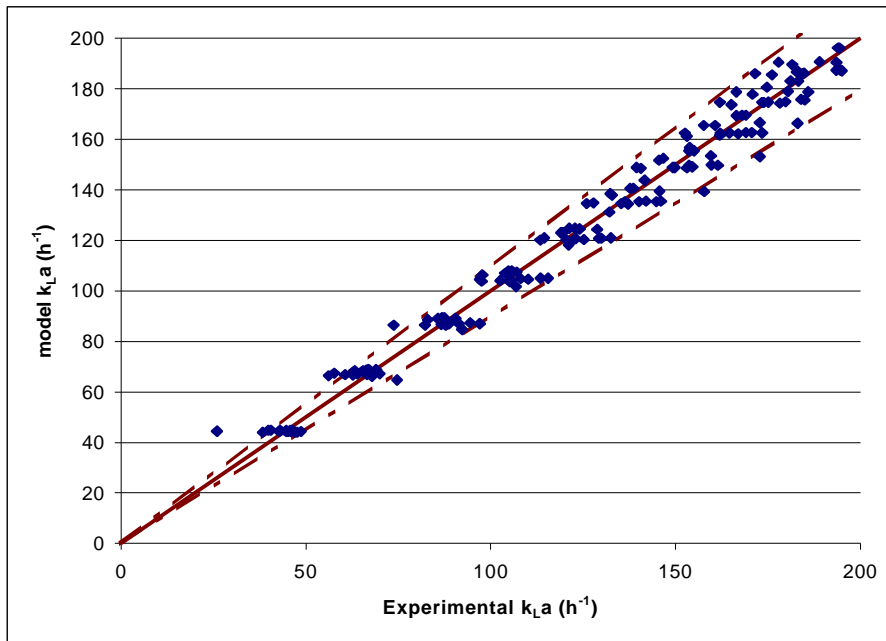
Figure 3 : Comparison between experimental and calculated $k_L a$ value

for the correlation $k_L a = a.\left(u_G\right)^b.\left(u_L\right)^c.\left(\Pr essure\right)^d$ with parameters of

Table 6. Dashed lines indicate the +/-10% area

In conclusion, the effect of pressure is not sufficiently important to be accurately used in a correlation for the condition in which the C50 column is operated, even if it appears that the pressure could play a role.

The simple relation $k_L a = a.\left(u_G\right)^b$ must be used.

III.2.3 Correlation $k_L a = a.\left(u_G\right)^b$

The results of parameter identification for the correlation $k_L a = a.\left(u_G\right)^b$ are given in Table 8 and in Figures 4. The correlation gives a very good fitting of all the experimental values obtained with the C50 column.

Parameters identification for all calculated $k_L a$ values (r^2=0.978)				
	Value	Standard Error	t-ratio	Prob(t)
a	2335,91	4,21%	23,7684	0,0
b	0,6340	1,51%	66,0099	0,0

Table 8 : $k_L a = a.\left(u_G\right)^b$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.
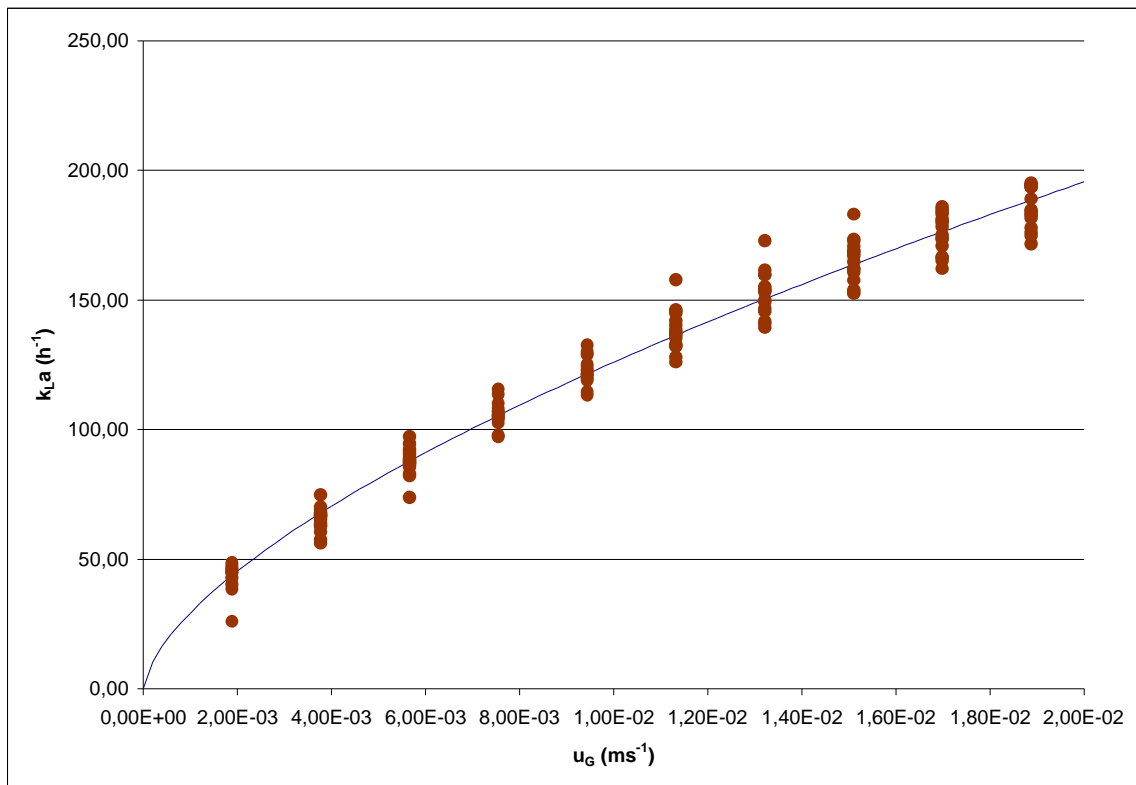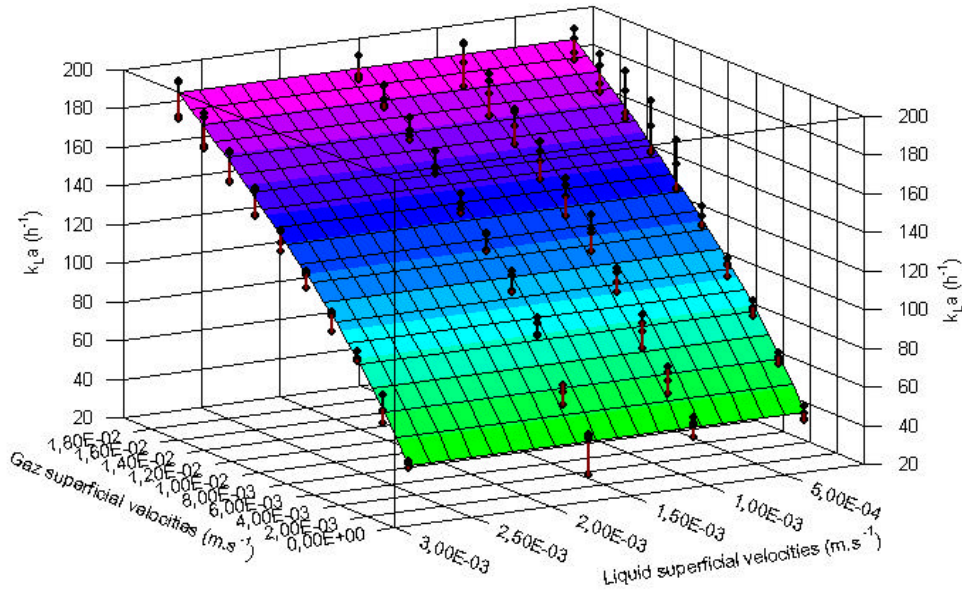
Figures 4 : Fitting of the all experimental values obtained for the C50 column with the correlation $k_L a = a.(u_G)^b$ and the parameters reported in Table 8.

III.2.4 Analysis of the influence of the volumes on the $k_L a$ measurement

As can be seen in Table 4, and more in Figure 5, the influence of the liquid volume is not negligeable (comparison of $k_L a$ and $k_L a°$).

The $k_L a°$ value calculated is the LOWEST value that can be obtained, but it must be kept in mind that this value has no-sense as it supposes that there is no gas volume in the bed.

The results presented in Figure 5 and the calculation of $k_L a°$ serve only to illustrate the effect of the variation of the gas volume in the fixed bed column. As concluded in TN 63.1, we were not able to determine this volume with RTD experiments and then we use the hold-up value as an estimation of this volume.

The determination of the gas volume is a weakness in the experimental results presented here, but as the experiments were repeated by increasing or decreasing the gas flow rate (i.e. variation of the "history of the column") and as the results obtained are consistent, it can be concluded that the gas volume in the column is relatively the same for given operating conditions. Moreover as the gas volume is a physical parameter linked to the pressure it is attempted that by taking into account the pressure and the pressure drop in the column, we will be able to obtained reliable correlations for any kind of operating conditions, even if the choice of the hold-up as an estimation of the gas volume can not be checked.
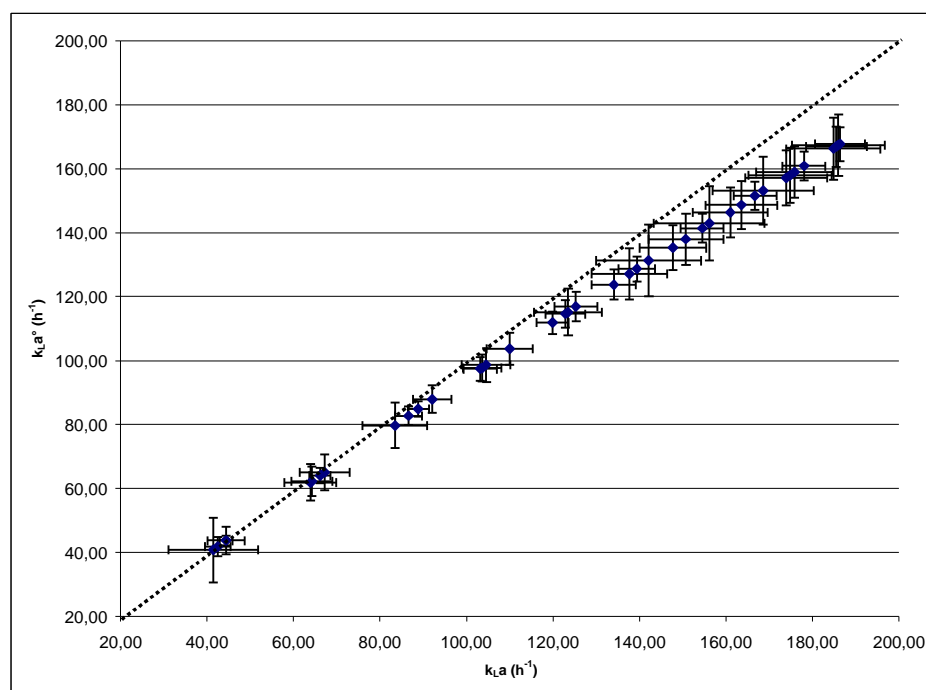

Figure 5 : $k_L a$ and $k_L a°$ - analysis of the volume effect on $k_L a$ calculation. Horizontal and vertical lines represent respectively the relative deviation from the averaged values for $k_L a°$ and $k_L a$.

III.3 C150 results analysis : k_La and flow rates (superficial velocities)

Experiments were performed for 3 different liquid flow rates (9. $l.h^{-1}$; 4.5 $l.h^{-1}$, 2.3.$l.h^{-1}$) and for 11 gas flow rates (from 0.1 to 15 $l.min^{-1}$). Details of the results of the experiments are presented in annexe I, and a summary with the averaged k_La values is reported in Table 8.
For the gas flow rates greater than 3 $l.min^{-1}$ the compressor is used in the gas loop (TN 55.2) in order to control the pressure in the column. The pressure is maintained for the top of the column to the atmospheric pressure. This allows to consider that the hold-up measured for these conditions can be assumed.
The liquid flow rates used correspond to a range of residence times of 43 to 138 min.

It can be observed that for given operating conditions, the 3 values of k_La are very closed (most of then are about +/- 1% to +/- 10%), indicating a good repeatability and then a good accuracy of the measurements, whatever is the history of the operating conditions on the column. Then the averaged k_La value calculated is representative of the measurements performed for in the different series. This averaged value and the standard deviation are reported in Table 9.

Note : It was not possible to perform experiments with gas flow rates higher than 15 l.min-1, as for such gas flow rates the sulphite solution is too quickly exhausted to reach a reliable steady-state for gas balance which is necessary to fulfil the assumption of the models (Table 2).

UG (m/s)	UL (m/s)	mean $k_L a$ (h^{-1})	absolute deviation	%deviation
2.48E-04	3.74E-04	23	0.02	0.09%
7.45E-04	3.74E-04	36	4.98	14.02%
1.49E-03	3.74E-04	44	10.29	23.36%
1.99E-03	3.74E-04	58	5.10	8.77%
2.48E-03	3.74E-04	63	7.40	11.78%
7.45E-03	3.74E-04	121	17.61	14.61%
1.24E-02	3.74E-04	156	16.63	10.66%
1.99E-02	3.74E-04	206	15.51	7.52%
2.48E-02	3.74E-04	236	15.33	6.50%
3.23E-02	3.74E-04	283	13.31	4.71%
3.72E-02	3.74E-04	312	6.84	2.19%
4.47E-02	3.74E-04	339	2.10	0.62%
2.48E-04	9.78E-05	22	3.52	15.89%
7.45E-04	9.78E-05	35	5.25	14.99%
1.24E-03	9.78E-05	42	4.75	11.37%
1.99E-03	9.78E-05	52	6.53	12.44%
2.48E-03	9.78E-05	59	8.02	13.52%
7.45E-03	9.78E-05	114	6.92	6.09%
1.24E-02	9.78E-05	159	7.73	4.86%
1.99E-02	9.78E-05	212	8.44	3.99%
2.48E-02	9.78E-05	249	16.48	6.63%
3.23E-02	9.78E-05	290	19.58	6.76%
3.72E-02	9.78E-05	317	22.19	7.01%
2.48E-04	2.11E-04	24	0.54	2.26%
7.45E-04	2.11E-04	39	0.49	1.26%
1.24E-03	2.11E-04	50	2.37	4.72%
1.99E-03	2.11E-04	63	0.95	1.51%
2.48E-03	2.11E-04	70	1.03	1.47%
7.45E-03	2.11E-04	131	6.22	4.76%
1.24E-02	2.11E-04	180	4.47	2.48%
1.99E-02	2.11E-04	235	10.62	4.52%
2.48E-02	2.11E-04	269	10.12	3.76%
3.23E-02	2.11E-04	314	12.79	4.08%
3.72E-02	2.11E-04	335	15.06	4.50%

Table 9 : Summary of $k_L a$ measurements on C150 column for different gas and liquid flow rates. The border lines indicates the zone of superposition of gas superficial velocity with the C50 column.

III.3.1 Correlation for $k_L a$ calculation from superficial velocities

As previously with the C50 column experiments, the parameters for the correlation $k_L a = a.(u_G)^b.(u_L)^c$ were identified from our C150 experiments using mean $k_L a$ values calculated (including the standard deviation for each value) (Figure 6.1) and using all the value measured (Figure 6.2). The results of the parameters identification are reported in Table 10.
At the contrary of the previous C50 analyses, the identification using all the $k_L a$ values calculated is not comparable to these performed using the averaged $k_L a$ (4 values for each condition) for the C150 column. It is more reliable to use the parameters obtained by using all the values rather than using averaged values.

In the range of operating conditions tested, the gas flow is the more important parameter. The liquid flow has quite no effect (high probability that the parameter c is equal to 0).
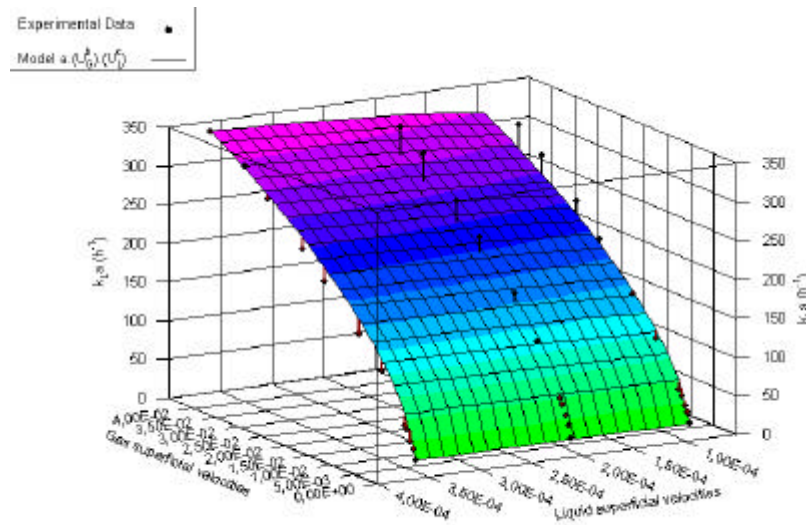
Figure 6.1 : Parameters correlation identification for the averaged k_La values calculated (dots). (r^2= 0.997)
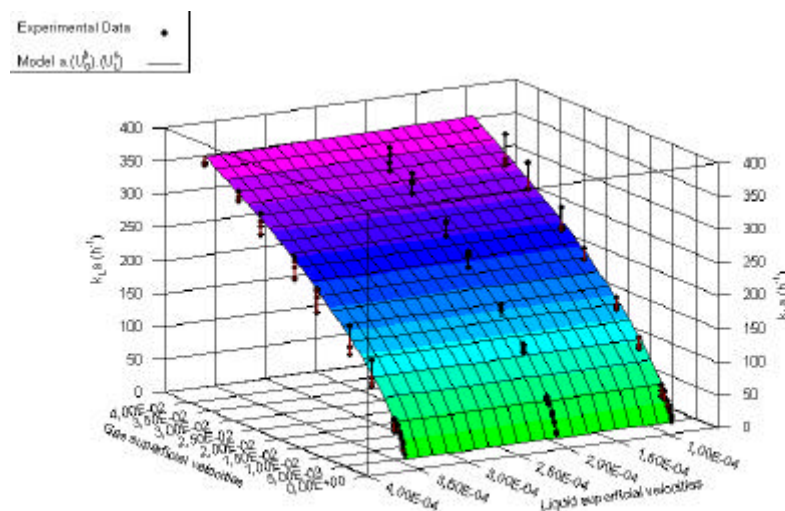
Figure 6.2 : Parameters correlation identification for all k_La values calculated (dots). (r^2= 0.985)

Parameters identification for averaged k_La values (r^2=0.998)			
	Value	Standard Error	t-ratio	Prob(t)
a	2788,79	13,48%	7,4162	0,000
b	0,5193	0,28%	358,4562	0,000
c	0,0620	26,58%	3,7617	0,001
Parameters identification for all calculated k_La values (r^2=0.985)			
	Value	Standard Error	t-ratio	Prob(t)
a	1976,84	10,05%	9,95	0
b	0,5853	1,70%	58,89	0
c	-0,0115	-96,80%	-1,03	0,303

Table 10 : $k_L a = a.(u_G)^b.(u_L)^c$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.

III.3.2 Correlation for $k_L a$ calculation from superficial velocities and pressure

The correlation taking into account the logarithmic pressure has the form:

$$k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d \qquad \text{with } P_{Log} = \frac{P_{Top} - P_{Bottom}}{Ln(\frac{P_{Top}}{P_{Bottom}})} \text{ (in atm)}$$

The parameters identified using all $k_L a$ values measured (Figure 7) are reported in Table 11.

Parameters identification for all $k_L a$ values (r^2=0.991)				
	Value	Standard Error	t-ratio	Prob(t)
a	2259,20	7,52%	13,2971	0,000
b	0,5809	1,22%	82,2271	0,000
c	0,0010	818,58%	0,1222	0,903
d	-1,5219	-14,71%	-6,7973	0

Table 11 : $k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.
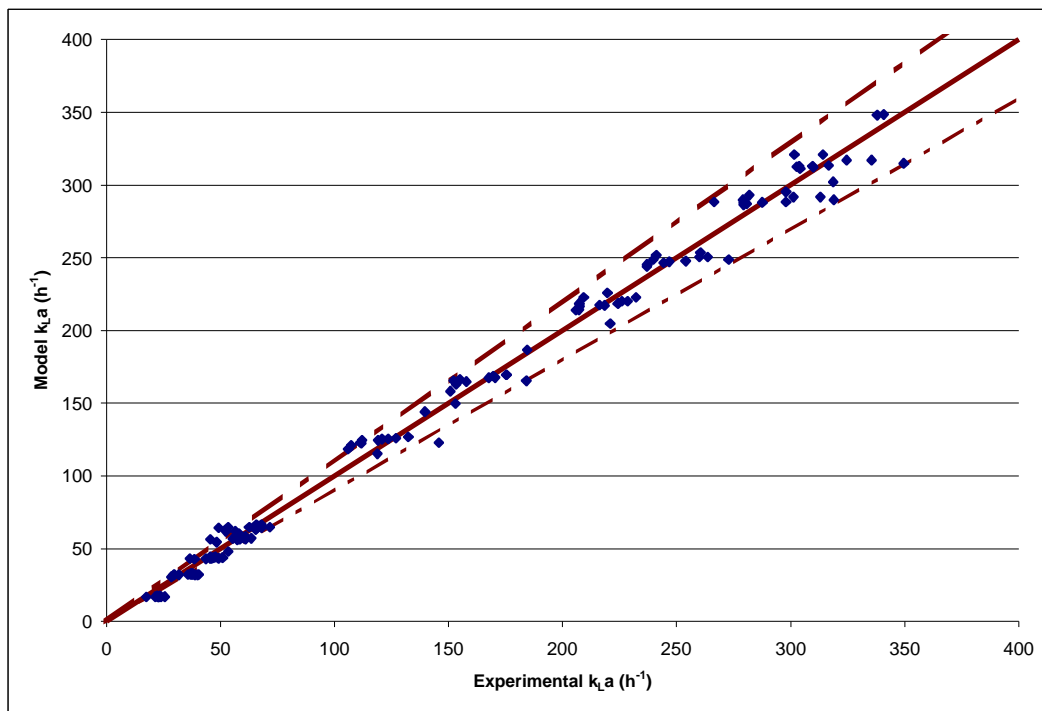
Figure 7 : Comparison between experimental and calculated $k_L a$ values for the correlation $k_L a = a.(u_G)^b.(u_L)^c.(\text{Pr } essure)^d$ with parameters of Table 11. Dashed lines indicate the +/-10% area.

As observed previously with C50 experiments, the effect of pressure is higher than this of the liquid superficial velocity. In Table 11, the results indicate that the parameter "c" (liquid

superficial velocity) is negligible. In Table 12 are reported the results of parameters identification assuming a correlation of the of the form : $k_L a = a.(u_G)^b.(P_{Log})^d$

Parameters identification for all $k_L a$ values (r2=0.991)				
	Value	Standard Error	t-ratio	Prob(t)
a	2240,01	2,70%	37,0128	0,000
b	0,5810	1,21%	82,7616	0,000
d	-1,5155	-14,32%	-6,9838	0,000

Table 12 : $k_L a = a.(u_G)^b.(P_{Log})^d$ - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.

The influence of pressure seems more important in the C150 than in the C50, but as for the C50 column, even if an effect of the pressure exists, the real effect of the parameter in the correlation is low as the logarithmic pressure is about 1.04 +/- 0.02 atm. As for the C50 column the parameter "d" of the pressure is negative what is consistent with the variation of dissipated power.

III.3.3 Correlation $k_L a = a.(u_G)^b$

As with the previous experiments on C50 column, it appears then that the simplest correlation $k_L a = a.(u_G)^b$ can be applied to predict accurately the $k_L a$ in our fixed bed, for the operating conditions used. The parameters identified for this correlation are reported in Table 13.

Parameters identification for all calculated $k_L a$ values (r^2=0.985)				
	Value	Standard Error	t-ratio	Prob(t)
a	2176,11	3,73%	26,8092	0,00
b	0,5847	1,70%	58,9305	0,00

Table 13 : $k_L a = a.(u_G)^b$. - Results of parameters identification Prob(t) is the probability that the parameter value is equal to 0.
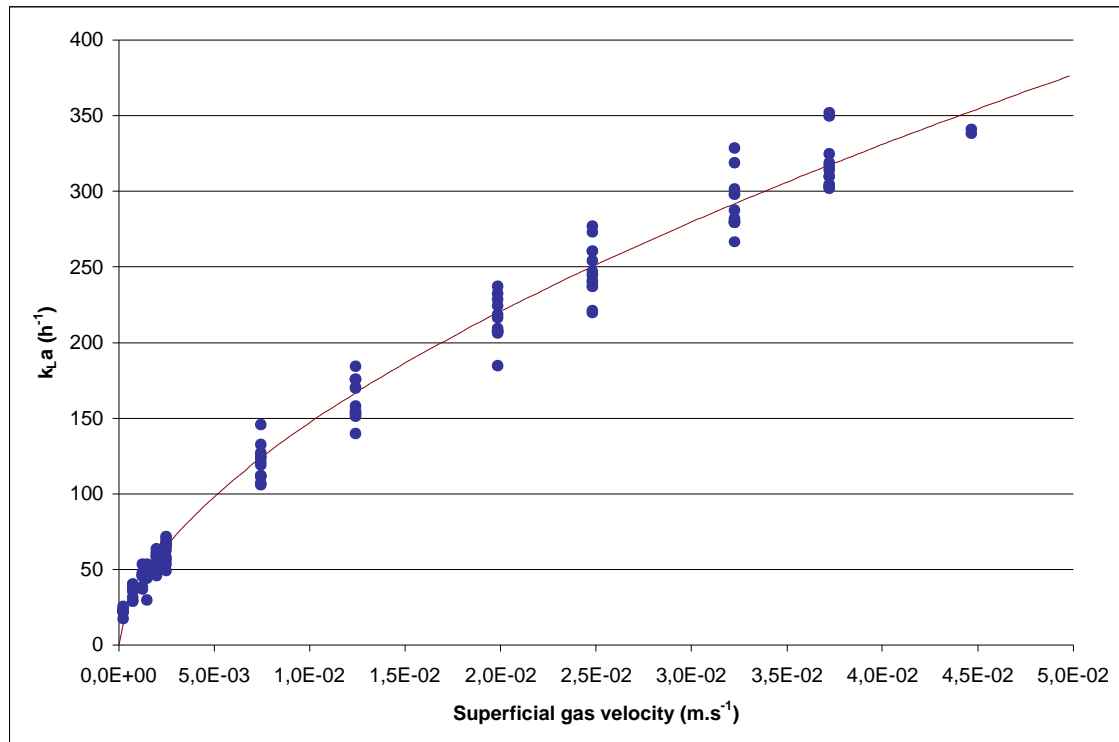
Figure 8 : Fitting of the all experimental values obtained for the C150 column with the correlation $k_L a = a.(u_G)^b$ and the parameters reported in Table 13.

III.4 C50 and C150 : k_La, flow rates and column design

In order to analyse the influence of the column design, all the results obtained with the two columns (160 values for the C50 and 140 values for the C150) are compiled together and four kinds of correlation were tested :

> 1 – the simple correlation involving only superficial velocities
> 2 – the correlation involving superficial velocities and pressure, which have been successfully used for the previous individual analyses of the results on the two columns.
> 3 – a correlation introducing a column design parameter.
> 4 – the simplest correlation previously obtained for the two columns associated to the column design parameter.

<u>*III.4.1 Correlation for k_La calculation from superficial velocities :*</u> $k_L a = a.(u_G)^b.(u_L)^c$

The results of the identification of the parameters of the correlation are reported in Table 14 and in Figure 9.

Figure 9 : Parameters correlation identification for the averaged k_La values calculated (dots). ($r^2 = 0.983$). Parameters identified are in Table 12.

Parameters identification for $k_L a$ values of C50 and C150 (r^2=0.983)				
	Value	Standard Error	t-ratio	Prob(t)
a	1785,27	4,81%	20,7908	0,00
b	0,6263	1,07%	93,4204	0,00
c	-0,0374	-10,69%	-9,3545	0,00

Table 14 : $k_L a = a.(u_G)^b.(u_L)^c$ - Results of parameters identification. Prob(t) is the probability that the parameter value is equal to 0.
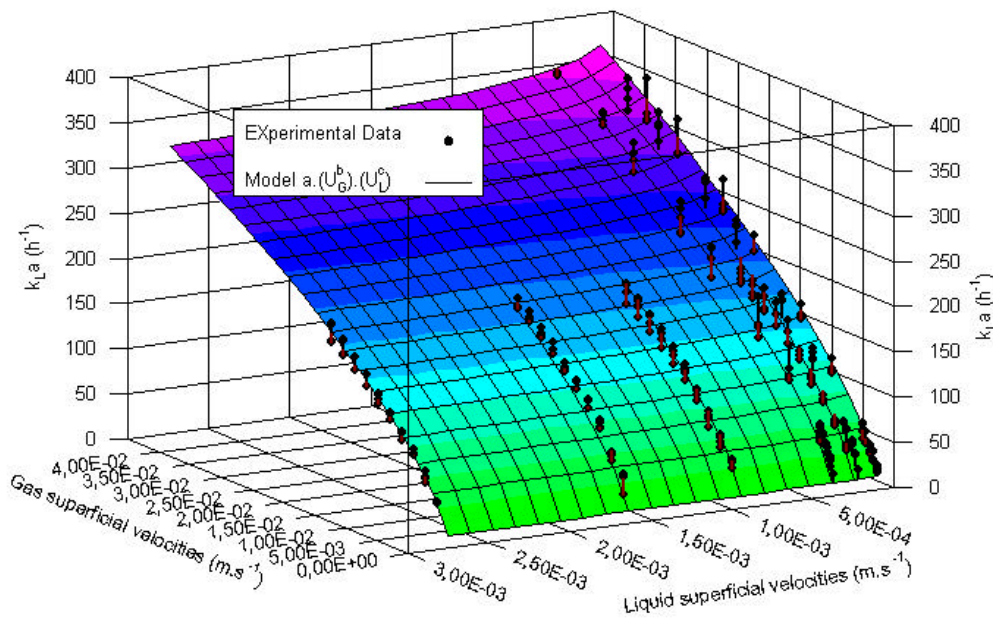
III.4.2 Correlation for $k_L a$ calculation from superficial velocities and pressure

The correlation taking into account the logarithmic pressure has the form:

$$k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d \qquad \text{with } P_{Log} = \frac{P_{Top} - P_{Bottom}}{Ln(\frac{P_{Top}}{P_{Bottom}})} \text{ (in atm)}$$

The results of the identification of the parameters of the correlation are reported in Table 15 and in Figure 10. It can be noticed that on the contrary of the individual analyses of the experiments, the liquid velocity has a low but apparently non-null (Prot(t) close to zero) influence in the expression of this correlation.
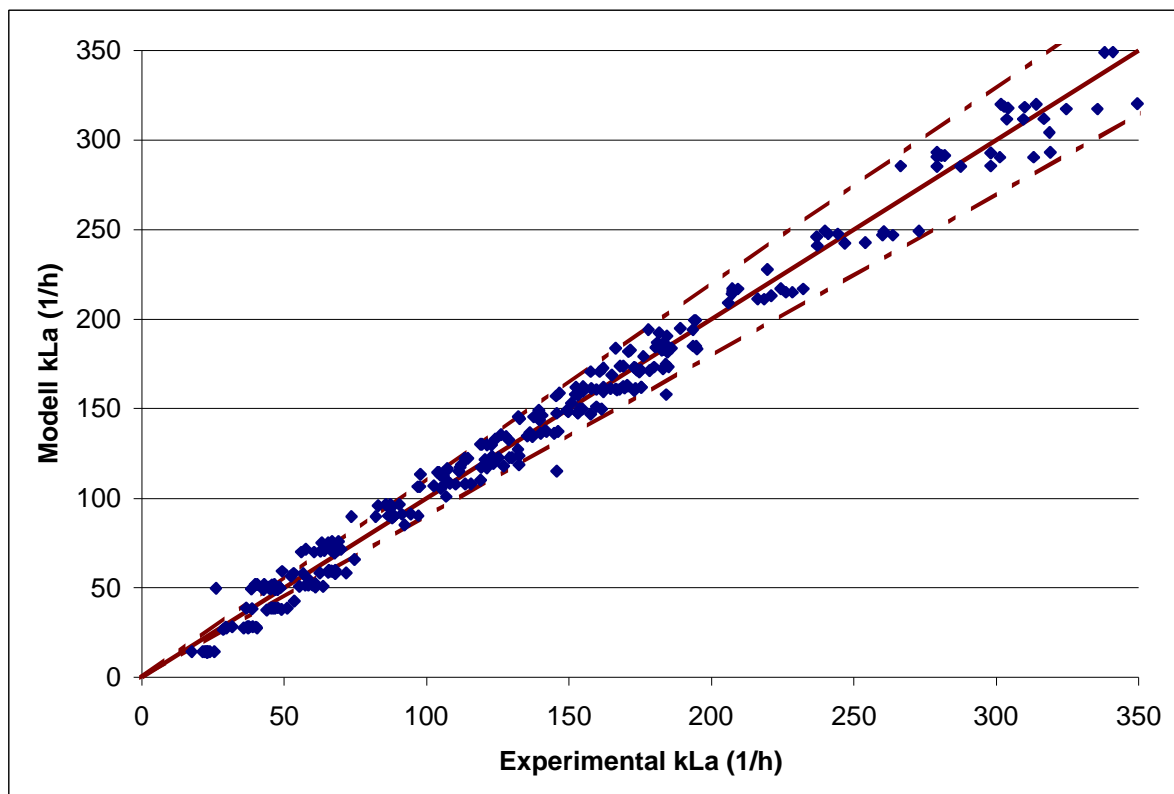

Figure 10 : Comparison between experimental and calculated $k_L a$ values for the correlation $k_L a = a.(u_G)^b.(u_L)^c.(Pr essure)^d$ with parameters of Table 15. Dashed lines indicate the +/- 10% area.

Parameters identification for k_La values of C50 and C150 (r^2=0.986)				
	Value	Standard Error	t-ratio	Prob(t)
a	2175,80	4,60%	21,7596	0,00
b	0,6190	0,93%	107,7645	0,00
c	-0,0167	-24,16%	-4,1390	>0,00
d	-1,0354	-10,26%	-9,7464	0,00

Table 13 : $k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d$ - Results of parameters identification. Prob(t) is the probability that the parameter value is equal to 0.

III.4.3 Correlation for k_La calculation from superficial velocities, pressure and column diameter

The adimensionnal design characteristic of the column $\dfrac{d_P}{D}$ is used. D is the column diameter and d_P is the particle (i.e. beads) diameter. The expression of the correlation is of the same kind of the previous ones :

$$k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d.\left(\frac{d_P}{D}\right)^e$$

The results of the identification of the parameters for this correlation are reported in Table 15 and in Figure 11. By introducing the column characteristic $\dfrac{d_P}{D}$, the influence of the liquid superficial velocity (parameter c= -0.0039 +/-112%) becomes negligible what is more in agreement with the previous individual analysis of the columns (see II and III).

Then in Table 16 are presented the parameters of a correlation of the form:

$$k_L a = a.(u_G)^b.(P_{Log})^d.\left(\frac{d_P}{D}\right)^e$$

without the liquid superficial velocity. The results in terms of k_La values predicted compared to the experimental ones are comparable to the correlation including the liquid flow (Figure 11).

Parameters identification for k_La values of C50 and C150 (r^2=0.988)				
	Value	Standard Error	t-ratio	Prob(t)
a	1762,82	5,40%	18,5220	0,00
b	0,6024	0,97%	103,1772	0,00
c	-0,0039	-112,30%	-0,8905	0,37
d	-0,6862	-16,70%	-5,9883	0,00
e	-0,0700	-16,04%	-6,2343	0,00

Table 15 : $k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d.\left(\dfrac{d_P}{D}\right)^e$ - Results of parameters identification. Prob(t) is the probability that the parameter value is equal to 0.

Parameters identification for k_La values of C50 and C150 (r^2=0.988)			
	Value	Standard Error	t-ratio	Prob(t)
a	1533,05	4,18%	23,8967	0,0000
b	0,5979	0,98%	102,3740	0,0000
d	0,0142	8,85%	11,2994	0,0000
e	-0,1014	-7,88%	-12,6845	0,0000

Table 16 : $k_L a = a.(u_G)^b.(P_{Log})^d.\left(\dfrac{d_P}{D}\right)^e$ - Results of parameters identification. Prob(t) is the

probability that the parameter value is equal to 0.

Figure 13 : Comparison between experimental and calculated k_La values for the correlation

$k_L a = a.(u_G)^b.(u_L)^c.(P_{Log})^d.\left(\dfrac{d_P}{D}\right)^e$ with parameters of Table 15. Dashed lines indicate the +/-

10% area.

III.4.4 Correlation $k_L a = a.(u_G)^b.\left(\dfrac{d_P}{D}\right)^c$

The individual analysis of the results for each column has demonstrated that in the conditions
in which the column were operated, a simple correlation involving only the gas superficial

velocity was sufficient to predict a reliable k_La value. Then for the same reasons, the previous

correlation $k_L a = a.(u_G)^b.(P_{Log})^d.\left(\dfrac{d_P}{D}\right)^e$ can be reduced to $k_L a = a.(u_G)^b.\left(\dfrac{d_P}{D}\right)^e$. The results

of identification for this simplest correlation are reported in Table 17 and in Figures 14. This correlation gives reliable predictive values for the two columns C50 and C150 in the operating range conditions used :

- u_G : 2.5 10^{-4} 4.5 10^{-2} m.s^{-1}
- u_L : 2.8 10^{-5} – 1.6 10^{-3} m.s^{-1} (RT 6 min to 138 min)

Parameters identification for all C50/C150 k_La values (r^2=0.987)				
	Value	Standard Error	t-ratio	Prob(t)
a	1480,99	4,33%	23,0997	0,00
b	0,5979	1,03%	96,9265	0,00
c	-0,1153	-6,78%	-14,7391	0,00

Table 17 : value of the parameters identified for all experimental k_La obtained with C50 and C150 columns

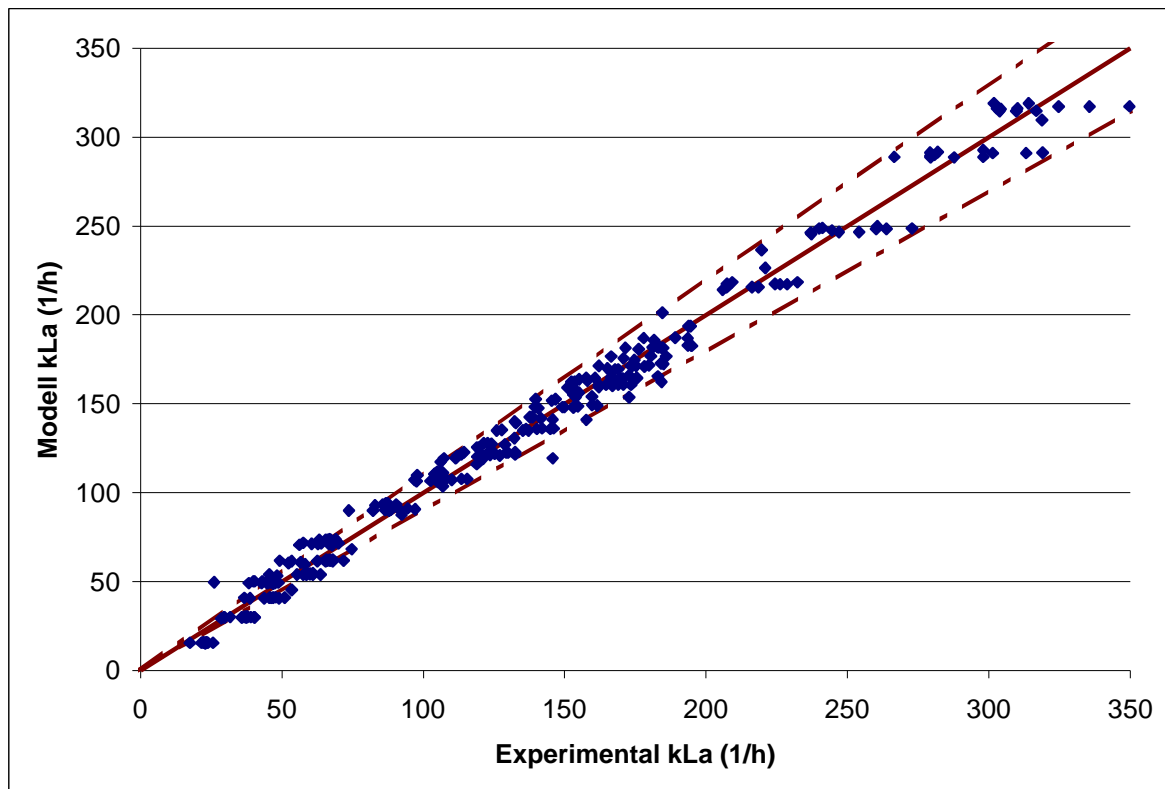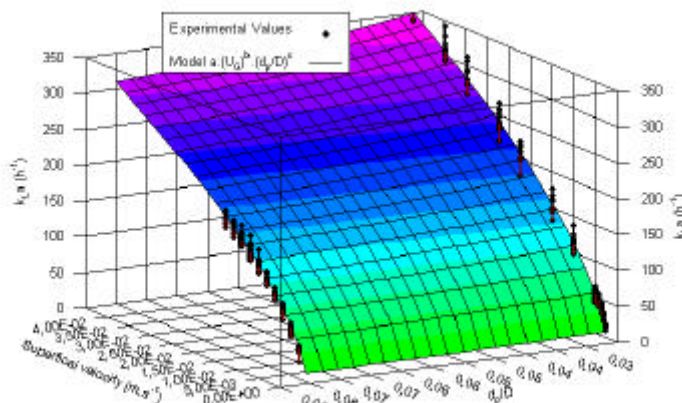Figure 14.1 : Parameters identification (Table 17) for all the k_La values (dot). (r^2= 0.987)

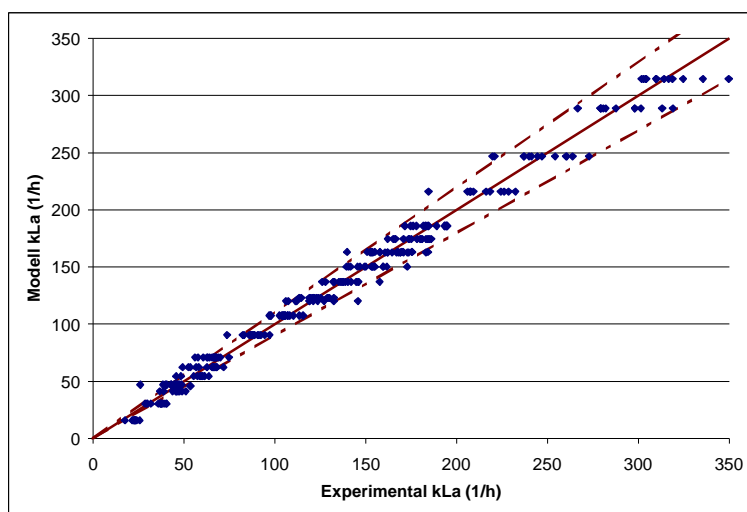

Figure 14.2 : Comparison between experimental and calculated k_La values for the correlation

$$k_L a = a.(u_G)^b.\left(\frac{d_P}{D}\right)^c$$

with parameters of Table 17. Dashed lines indicate the +/-10% area.

IV Comparison with identification of k_La in TN 39.2

In technical note 39.2 (NitriSim Validation), a the identification of a k_La value inside the fixed bed of UAB bench column was tried from biological nitrifying experiments. The identifications were performed using 6 biological steady-state experiments, called M1 to M6 (report to TN 39.2 for details about the experiments). It must be emphasised that the previous estimations of k_La from biological experiments were indirect and filtered by the biological growth parameters. But it is of course interesting to compare the results obtained in this previous work with the correlation established here.

In Table 18 and Figure 15 are reported the results of this comparison. The correlation established in section III.4.4 was used :

$$k_La = 1480.99.(u_G)^{0.5979}\left(\frac{d_P}{D}\right)^{-0.1153} \quad (k_La \text{ in } h^{-1})$$

In order to compensate the difference of temperature between the biological experiments (30°C) and the temperature for which our correlation was established (20°C) the theoretical factor of 1.12 is applied (report to II.3.3).

The results obtained in TN 39.2 are consistent with the values predicted by the correlation. It must be outlined that the experiments M1 and M4 have been already considered in TN 39.2 as inconsistent with the other biological experiments (M2, M3 M5 and M6).

Biological Experiment	Gas flow Rate (l.min⁻¹)	UG (m.s-1) (ε=0.55)	TN 39.2 k_La (h_{-1}) Identification result	K_La (h^{-1}) Correlation C50/C150 20°C	30°C
M1	40	0,00106878	67	30	33,6
M2	100	0,00267195	56	51	57,12
M3	9	0,00024048	23	12	13,44
M4	9	0,00024048	34	12	13,44
M5	15	0,00040079	24	16,5	18,48
M6	40	0,00106878	36	30	33,6

Table 18 : Comparison of k_La value identified in TN 39.2 with predicted k_La using the correlation established in this work.
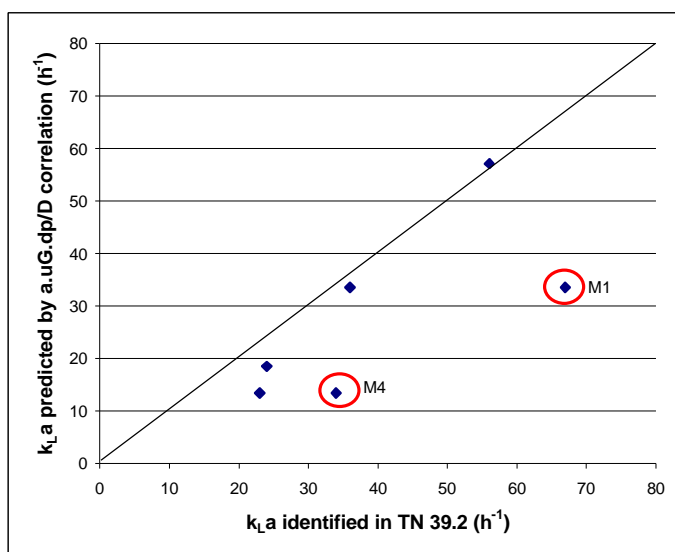

Figure 15 : comparison between k_La value identified in TN 39.2 and the value that are predicted by the correlation

V Conclusion

Experimental measurements of k_La in fixed bed columns C50 and C150 were done. The C50 column is comparable to the nitrifying bench columns while the C150 column is comparable to the nitrifying pilot column of UAB.

The analysis of the results, for each column separately and for the column together indicates that :

- the liquid superficial velocity has no influence on the k_La in the operating conditions used.
- The pressure (logarithmic pressure, representative of the pressure inside the column) plays a role, but can be neglected as were performed a ambient pressure with only small variations. Nevertheless the results suggest that more accurate correlation could be obtained by taking into account the pressure drop (Deront et al. 1998) or an equivalent parameter such as the dissipated power.
- The k_La in the two columns can be accurately predicted using the simple correlation

$$k_L a = a.(u_G)^b \left(\frac{d_P}{D} \right)^c \qquad (k_L\text{a in h}^{-1})$$

  with

1481	4,33%	(a=0.4139 for k_La expressed in s^{-1})
0,5979	1,03%	
-0,1153	6,78%	

  and u_G , P_{log} dp and D being respectively the gas superficial velocity (m.s^{-1}, the beads diameter (m) and the column diameter (m). The experiments were performed at ambient temperature (20°C +/- 1.5°C) and the ranges of operating were:
  u_G [1.89 10^{-3} - 1.89 10^{-2}] and u_L [2.13 10^{-4} - 2.75 10^{-3} m.s^{-1}] for the C50
  u_G [2.84 10^{-4} - 3.72 10^{-2}] and u_L [3.44 10^{-5} - 3.61 10^{-4} m.s^{-1}] for the C150

The gas volume in the fixed bed has a non negligible influence as it is a parameter in the equation used to calculate the k_La from the gas balance analysis. It was previously noticed that this volume cannot be measured using RTD methods, then the gas hold-up measured without liquid flow and with the top of the column at ambient pressure is used. It can be foreseen that taking into account parameters such as pressure, pressure drop and dissipated power will have a corrective effect on the possible variation of gas volume.

References

Danckwerts H. (1970), Gas liquid reactions, Mc Graham Hills – N.Y.

de Ory I., Romero L.E. and Cantero D. (1999) Laboratory scale equipment for the determination of kLa in bioreactors. Biprocess Engineering 20 73-75.

Deront M., Samb F.M., Adler N. and Peringer P. (1998) Volumetric oxygen mass transfer coefficient in an upflow cocurrent packed-bed Bioreactor. Chemical Eng. Science. 53, 7, 1321-1330

Poughon L, Duchez D, Cornet J.F. and Dussap C.G. k_La determination : comparative study for a gas mass balance method. Submitted for publication. Bioprocess and Biosystem Engineering. 2002

Shumpe A. (1993) The estimation of gas solubilities in salts solutions. Chem Eng. Science. 48, 1: 153-158.

Annexe I : Experimental results of series of experiments performed on C50 column
Up : increase of gas flow rate in the experimental serie
Down : decrease of gas flow rate in the experimental serie

UG (m/s)	UL (m/s)	Experimental Serie 1 (up) kla (h-1)	Experimental Serie 2 (down) kla (h-1)	Experimental Serie 3 (up) kla (h-1)	Experimental Serie 4 (down) kla (h-1)
1,89E-02	2,75E-03	174,72	176,11	194,37	193,94
1,70E-02	2,75E-03	166,38	165,12	183,18	181,11
1,51E-02	2,75E-03	153,92	153,08	168,99	167,92
1,32E-02	2,75E-03	141,63	140,62	155,02	153,65
1,13E-02	2,75E-03	132,08	127,77	138,60	137,65
9,44E-03	2,75E-03	121,11	114,46	122,82	121,31
7,55E-03	2,75E-03	106,88	97,04	105,72	104,76
5,67E-03	2,75E-03	92,35	88,74	87,55	86,80
3,78E-03	2,75E-03	74,68	60,57	67,23	66,28
1,89E-03	2,75E-03		42,83	45,77	44,67
1,89E-02	1,59E-03	194,95	183,08	184,67	182,71
1,70E-02	1,59E-03	184,90	173,82	175,08	178,25
1,51E-02	1,59E-03	173,44	161,95	164,55	166,95
1,32E-02	1,59E-03	161,49	149,81	153,66	153,10
1,13E-02	1,59E-03	144,85	135,30	140,13	137,11
9,44E-03	1,59E-03	129,99	120,53	129,20	121,53
7,55E-03	1,59E-03	113,48	105,63	115,49	105,15
5,67E-03	1,59E-03	94,51	88,66	97,13	87,90
3,78E-03	1,59E-03	57,56	67,66	63,95	67,79
1,89E-03	1,59E-03	26,02	47,64	45,18	46,88
1,89E-02	9,25E-04	194,61	193,46	184,30	171,53
1,70E-02	9,25E-04	184,03	179,79	173,43	162,04
1,51E-02	9,25E-04	170,68	168,95	162,10	152,46
1,32E-02	9,25E-04	159,68	154,62	149,20	139,36
1,13E-02	9,25E-04	146,11	142,00	136,35	125,99
9,44E-03	9,25E-04	132,45	125,18	122,91	113,37
7,55E-03	9,25E-04	102,57	110,07	108,07	97,61

5,67E-03	9,25E-04	86,56	91,29	73,69	82,17
3,78E-03	9,25E-04	66,64	69,98	56,15	62,71
1,89E-03	9,25E-04	45,87	48,67	38,42	44,75
1,89E-02	2,14E-04	181,61	177,87	188,96	193,47
1,70E-02	2,14E-04	170,79	166,40	180,44	185,88
1,51E-02	2,14E-04	160,72	157,61	172,84	183,05
1,32E-02	2,14E-04	146,66	145,50	159,58	172,77
1,13E-02	2,14E-04	132,26	132,78	145,74	157,73
9,44E-03	2,14E-04	119,00	119,54	124,13	128,78
7,55E-03	2,14E-04	103,86	104,29	97,80	106,96
5,67E-03	2,14E-04	87,25	85,70	83,04	90,46
3,78E-03	2,14E-04	66,77	65,44	63,18	69,04
1,89E-03	2,14E-04	43,00	39,92	40,50	46,51

Annexe I : Experimental results of series of experiments performed on C150 column
Up : increase of gas flow rate in the experimental serie
Down : decrease of gas flow rate in the experimental serie

UG m/s	UL m/s	Experimental Serie 1 (up)	Experimental Serie 2 (down)	Experimental Serie 3 (up)	Experimental Serie 4 (down)	Additionnal experiments
		kla (h-1)	kla (h-1)	kla (h-1)	kla (h-1)	kla (h-1)
2,48E-04	3,61E-04	22,91305566	22,88526908			
7,45E-04	3,61E-04	40,36973303	35,77808813	37,33964432		28,62585557
1,49E-03	3,61E-04	53,49679981	43,78803597	49,13951833	29,81274375	
1,99E-03	3,61E-04	61,07684285	55,42170357	63,56849111	52,436911	
2,48E-03	3,61E-04	68,0113723	62,61696614	71,82688146	58,05815782	53,43822419
7,45E-03	3,61E-04	145,7252846	111,3693677	118,9209493	106,0679732	
1,24E-02	3,61E-04	184,1696723	152,2810598	153,1455806	139,7328887	150,9096193
1,99E-02	3,61E-04	218,5440504	205,9452426	216,1830528	184,5251653	
2,48E-02	3,61E-04	246,8649134	237,0578115	254,0842506	219,6593772	220,9426234
3,23E-02	3,61E-04	287,568021	279,2653303	297,9920879	266,5005921	
3,72E-02	3,61E-04	309,6166991	303,7219142	316,664034	318,6873478	
4,47E-02	3,61E-04	337,972685		340,9481787		
2,48E-04	9,44E-05	17,48694292	21,52512469	25,61482899	23,86446516	
7,45E-04	9,44E-05	29,45296255	31,69980466	38,88466585	40,0979427	
1,24E-03	9,44E-05	38,68093724	36,74008231	45,45788553	46,15513241	
1,99E-03	9,44E-05	48,32459882	45,55366989	57,48346085	58,61703998	
2,48E-03	9,44E-05	56,55365908	49,1974142	65,38614405	66,1040841	
7,45E-03	9,44E-05	107,2898582	112,0831051	123,5022827	111,7290211	
1,24E-02	9,44E-05	153,409083	155,011195	170,4526074	157,939587	
1,99E-02	9,44E-05	207,2103	207,4263952	224,2974157	207,62232	
2,48E-02	9,44E-05	236,9670942	239,8976942	272,8129567	244,4297184	
3,23E-02	9,44E-05	279,2718863	279,1668033	318,8583393	280,7100795	
3,72E-02	9,44E-05	304,2126297	302,6999843	349,5516524	309,9571291	
2,48E-04	2,10E-04	23,561036	24,232889	23,30795384	24,44645034	
7,45E-04	2,10E-04	39,75682653	38,62100697	39,42947581	39,01768428	
1,24E-03	2,10E-04	53,53164514	49,2066232	50,087862	48,01852775	
1,99E-03	2,10E-04	63,3283547	62,6975868	64,16484991	61,91458796	

2,48E-03	2,10E-04	70,78178405	69,97566377	71,38674119	68,99978001
7,45E-03	2,10E-04	124,9463247	126,3404554	133,2559019	138,2887182
1,24E-02	2,10E-04	175,9322505	177,0341523	184,2244754	184,1548126
1,99E-02	2,10E-04	237,2441152	239,7152974	219,7433927	243,8698091
2,48E-02	2,10E-04	276,666317	272,8843986	254,3688993	273,4741935
3,23E-02	2,10E-04	328,4718875	316,1366422	297,3866682	312,8320645
3,72E-02	2,10E-04	351,9760341	340,5528748	329,6945836	316,7312816