PROJECT NUMBER: 101018756

ACRONYM: GTCLC-NEG

PROJECT TITLE: Development of an innovative Gas Turbine Chemical Looping Combustor for Carbon Negative Power Generation

DELIVERABLE TITLE: Particle Model

DELIVERABLE NUMBER: d3.1

Lead Beneficiary: CSIC

Work Package: WP3

Dissemination level: Public

Type: Report

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SECTION 1: INTRODUCTION TO PARTICLE MODELING IN PRESSURISED CHEMICAL LOOPING

The particle modeling of the oxygen carriers produced and characterized in WP 1 is based on two publications realized at the Instituto de Carboquimica, CSIC, see [1, 2]. These works are based also on the theory developed by Levenspiel [3] when speaking of reactions catalyzed by solids and the pore diffusion resistance combined with surface kinetics. While developing the particle model in this project we focused on the most interesting oxygen carrier that we have tested, which is NiO18 loaded on alpha alumina. This is recognized to have a plate like geometry. See figure 1.

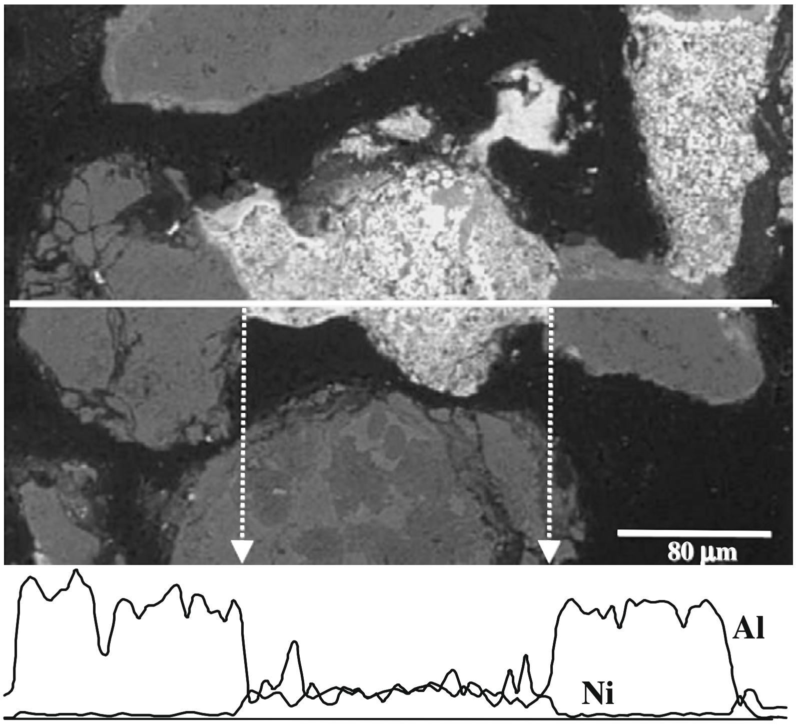

Figure 1: Plate like geometry of nickel oxide, taken from [4]

The geometries can be in fact granular or plate like, see figure 2.

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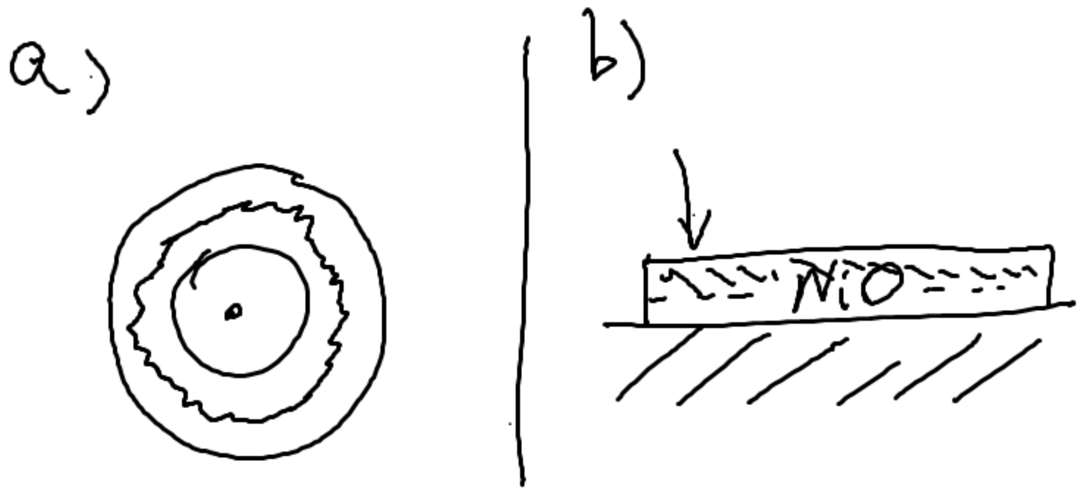

Figure 2: granular (see left) and plate like (see right) geometries

For this kind of geometry the governing equations for the particle model are based on the Shrinking Core Model (SCM):

$$\frac{t}{\tau} = X_r \quad (1)$$

where:

- t is time (s)
- τ is the time for complete solid conversion (s)
- Xr is the solid conversion.

When deriving for time we obtain:

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$$\frac{dX_r}{dt} = \frac{1}{\tau} \quad (2)$$

A nice visualization of the tau is reported in figure 2.

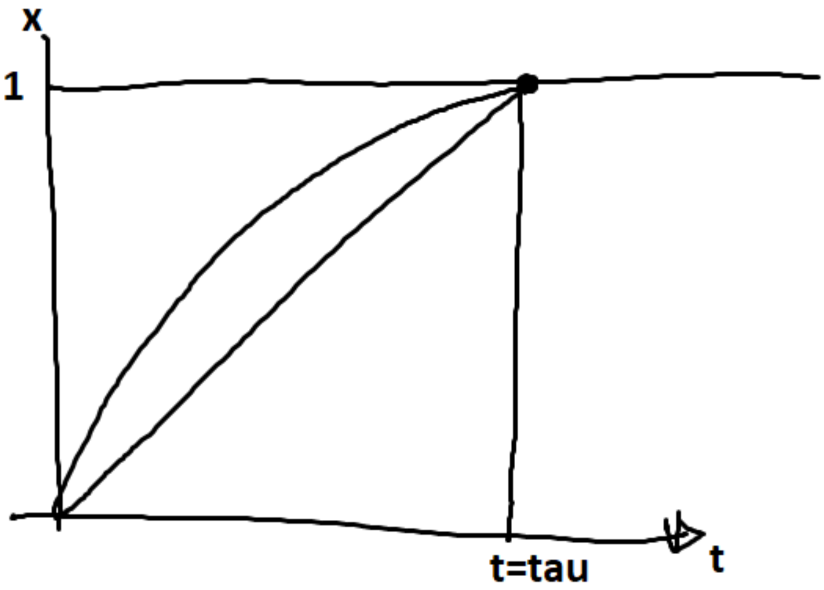

Figure 3: Visualization of the time to complete the reaction (tau)

But we know also that:

$$X = k_r * Pg * t \quad (3)$$

With the above mentioned equation and with the Arrhenius equation we can determine:

- E and A for changing temperatures

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- k_r and d for changing pressures

All these kinetics constants have been derived through the PTGA of the laboratories of Instituto de Carboquimica. CSIC Zaragoza. For the calculation of the E based on the values of the required time for complete conversion, see figures 4 and 5.

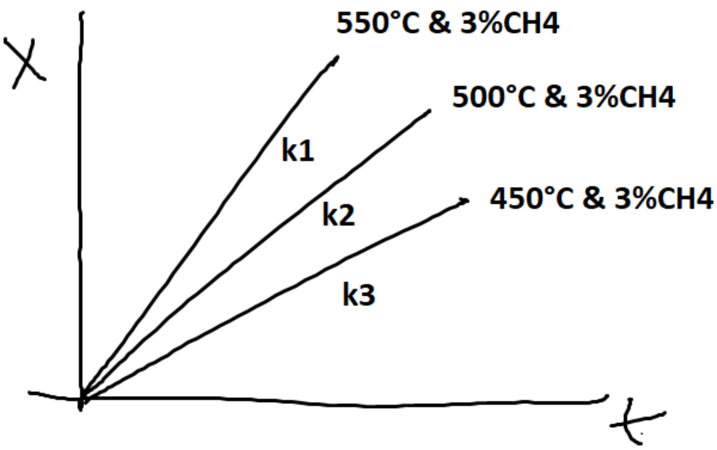

Figure 4: Determination of k values as the slopes of the conversion lines

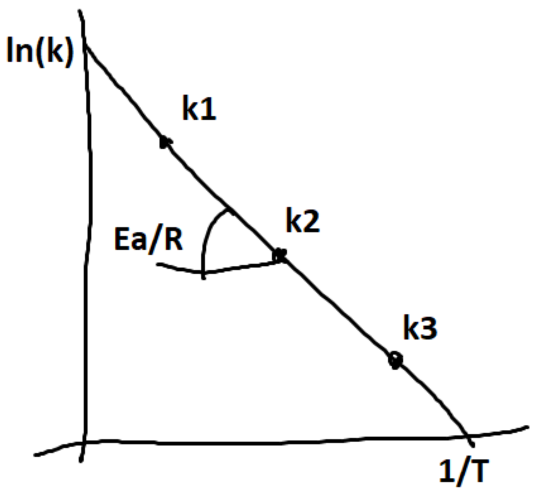

Figure 5: Determination of E

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SECTION 2: CALIBRATION

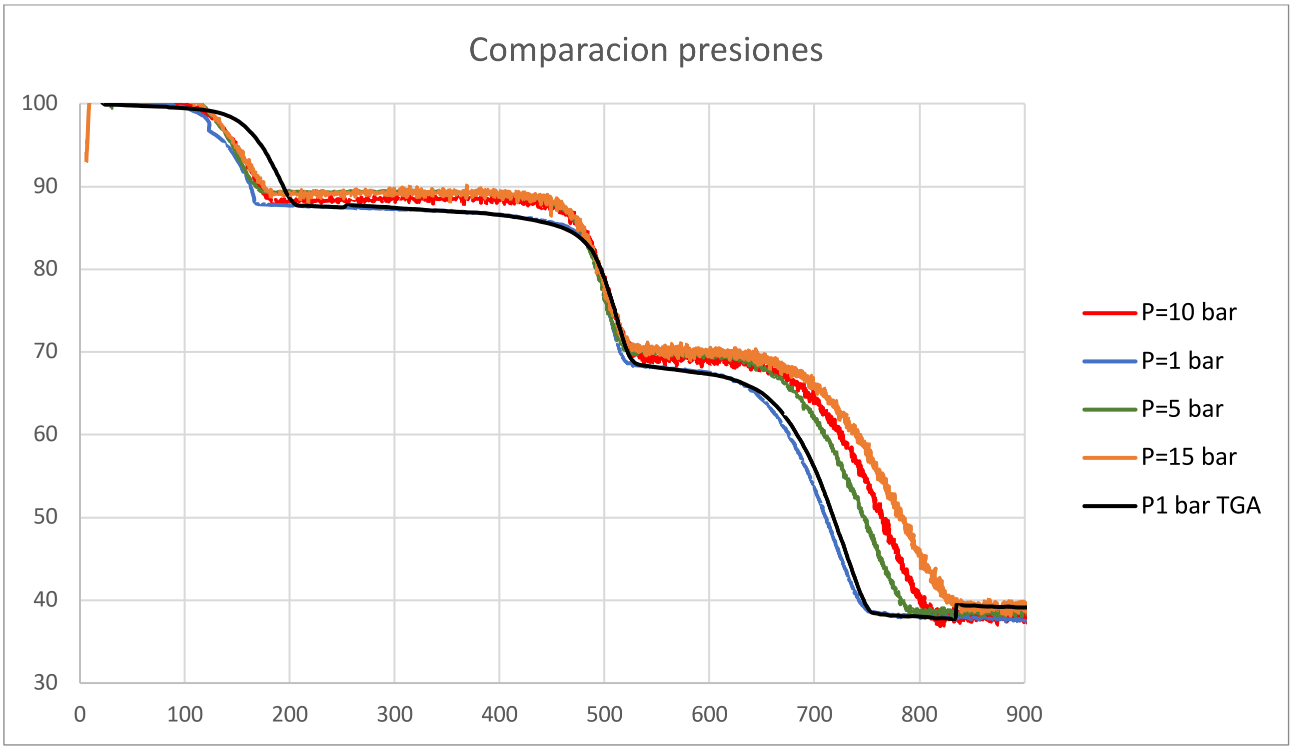

Figure 6: Adjusted curves

Table 1: Adjusted temperature (in the range of 400-600°C)

15 bar	-18°C
10 bar	0°C
5 bar	+6°C
1 bar	+31°C

SECTION 3: EXPERIMENTAL CAMPAIGN FEBRUARY- JULY 2022

The tests performed are reported in Table 2.

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Table 2: Experimental campaign performed at the PTGA

Qt (l/h)	m (mg)	T(ºC)	Pt (atm)	%CH4	%CO2	%N2	Air	PCH4
240	30	475	10	3	19	78	100	0.3
240	50	475	10	3	19	78	100	0.3
240	70	475	10	3	19	78	100	0.3
240	50	475	10	3	19	78	100	0.3
200	50	475	10	3	19	78	100	0.3
175	50	475	10	3	19	78	100	0.3
240	50	500	10	3	19	78	100	0.3
240	50	475	10	3	19	78	100	0.3
240	50	450	10	3	19	78	100	0.3
240	50	425	10	3	19	78	100	0.3
240	50	475	1	30	19	51	100	0.3
240	50	475	5	6	19	75	100	0.3
240	50	475	10	3	19	78	100	0.3
240	50	475	15	2	19	79	100	0.3
240	50	475	1	3	19	78	100	0.03
240	50	475	5	3	19	78	100	0.15
240	50	475	10	3	19	78	100	0.3
240	50	475	15	3	19	78	100	0.45

Of the above reported tests the following have been performed: 1,2,3,4,5,6,7,8,9,10,11,12,13,14, 15,17, 16 ,17, 18.

The tests have been indicated with the following codes:

- 220222_ni18_475_550t_50 (which corresponds to test number 15, which has to be repeated)

- 220315_ni18_500_10bar_30mg (which corresponds to test number 1)

- 220316_ni18_500_10bar_50mg (which corresponds to tests number 2,4,8,13,17)

- 220317_ni18_425-525_10bar_50mg (which correspond to tests number 7,9,10)

- 220426_ni18_500t_50g (which corresponds to sample 5 and 6);

- 220427_ni18_475-550_1-10bar_50mg (which corresponds to 16,18 and 11)

- 220428_Ni18_500-524T_5-15bar_50g_2-6Ch4 (which corresponds to 12 and 14)

- 220429_ni18_506t_10bar_70g (which corresponds to test 3)

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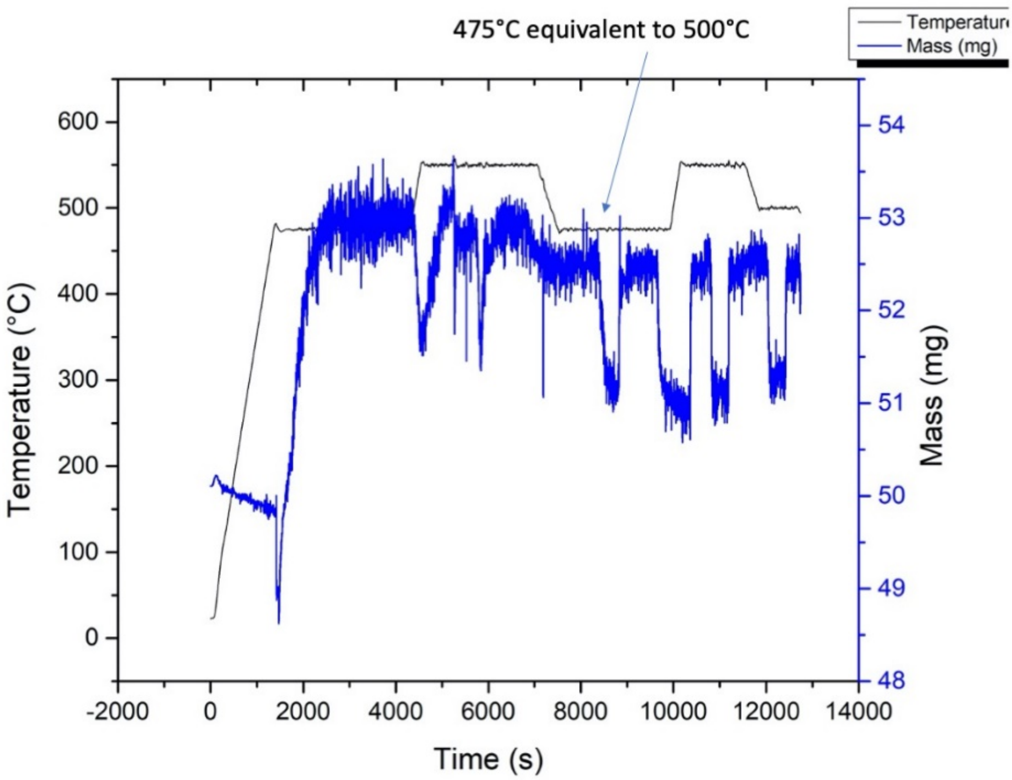

Figure 7: 220222_ni18_475_550t_50

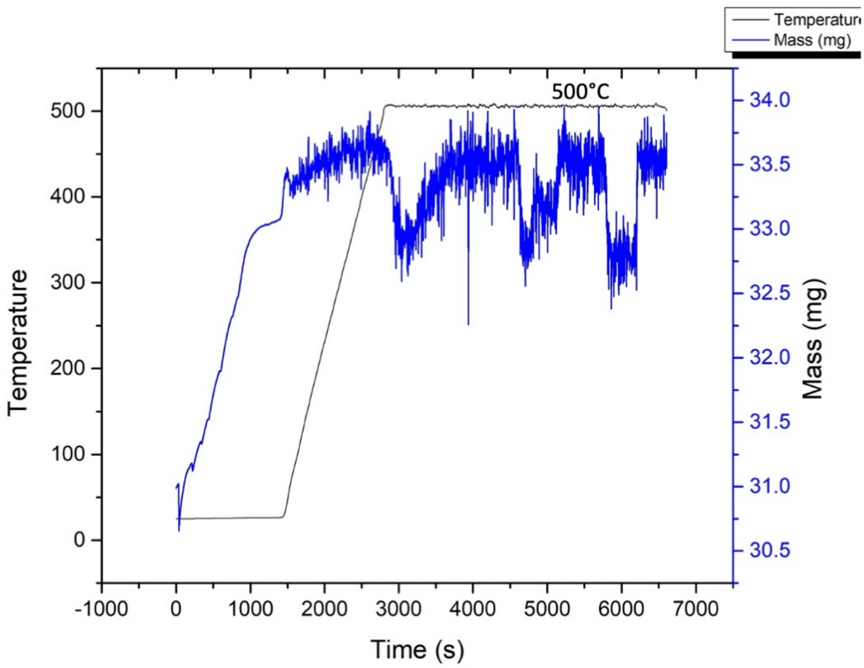

Figure 8: 220315_ni18_500_10bar_30mg

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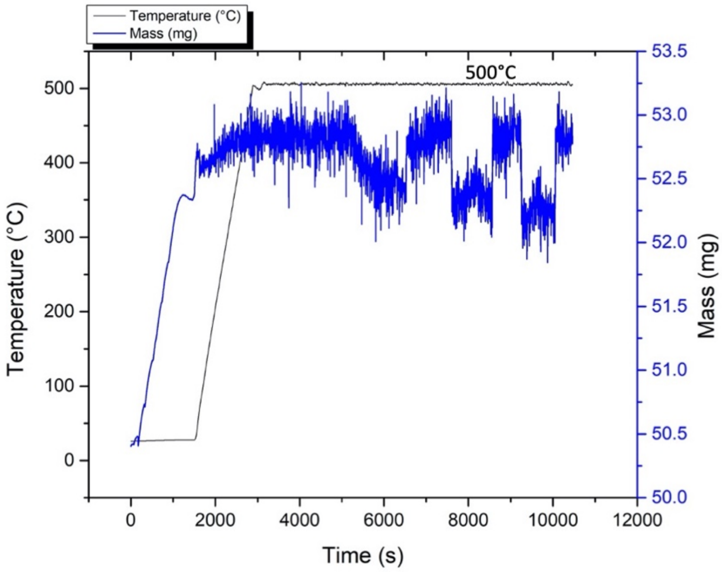

Figure 9: 220316_ni18_500_10bar_50mg

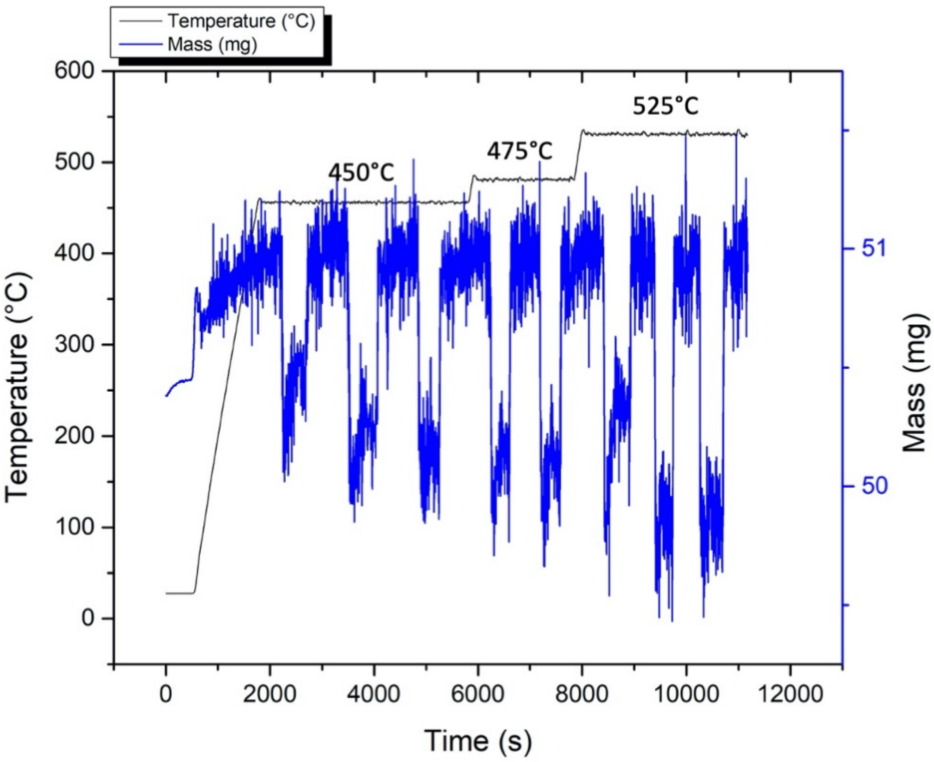

Figure 10: 220317_ni18_425-525_10bar_50mg

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SECTION 4: DATA ELABORATION

The collected data where available in a .csv file. This was opened with excel and then the command data in column was selected to order the data in each column, based on the coma used as a separator and changing the points into comas to have the EU notation of decimal digits. See next figure.

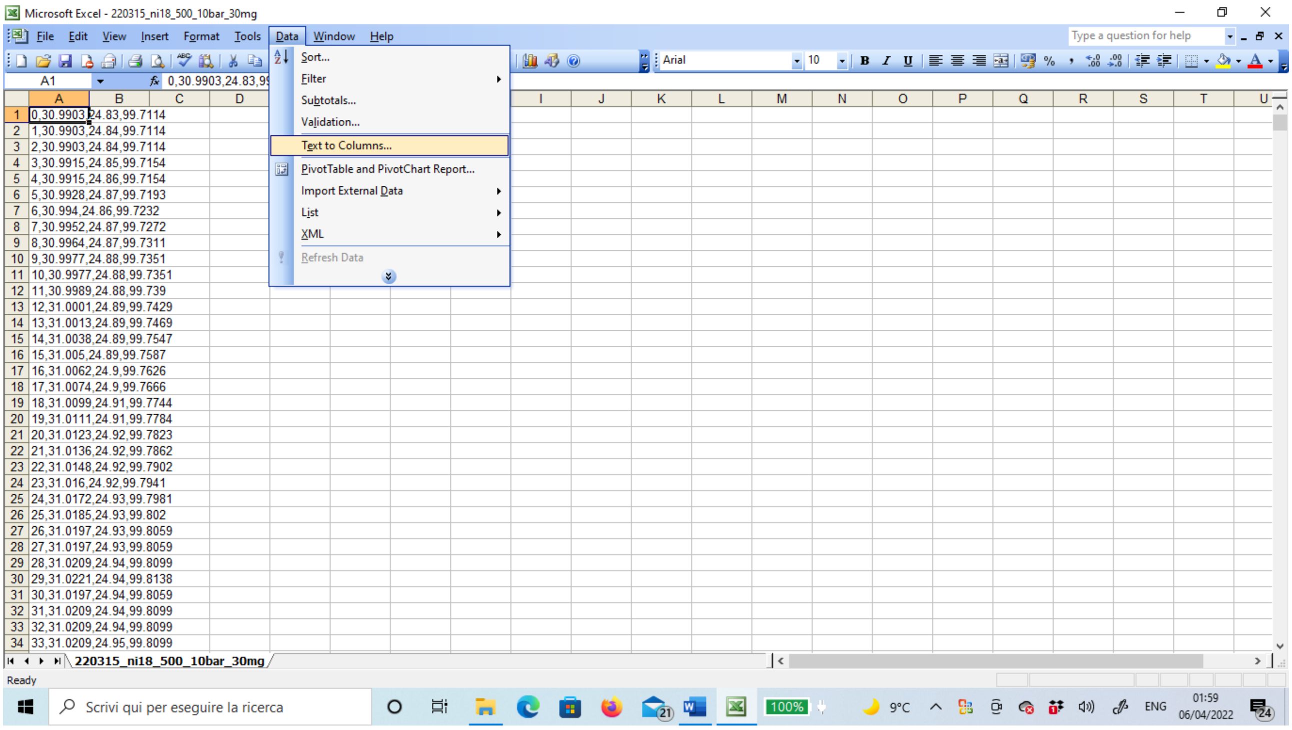

Figure 11: File .csv obtained from PTGA experiments

The final polished data are shown in next figure.

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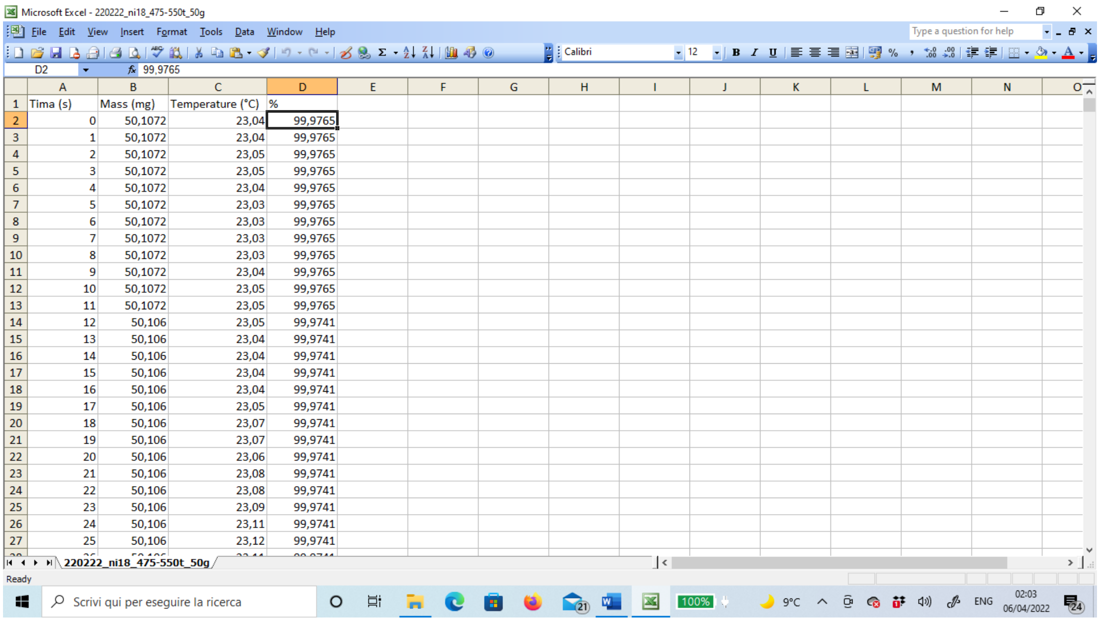

	Tima (s)	Mass (mg)	Temperature (°C)	%
2	0	50,1072	23,04	99,9765
3	1	50,1072	23,04	99,9765
4	2	50,1072	23,05	99,9765
5	3	50,1072	23,05	99,9765
6	4	50,1072	23,04	99,9765
7	5	50,1072	23,03	99,9765
8	6	50,1072	23,03	99,9765
9	7	50,1072	23,03	99,9765
10	8	50,1072	23,03	99,9765
11	9	50,1072	23,04	99,9765
12	10	50,1072	23,05	99,9765
13	11	50,1072	23,05	99,9765
14	12	50,106	23,05	99,9741
15	13	50,106	23,04	99,9741
16	14	50,106	23,04	99,9741
17	15	50,106	23,04	99,9741
18	16	50,106	23,04	99,9741
19	17	50,106	23,05	99,9741
20	18	50,106	23,07	99,9741
21	19	50,106	23,07	99,9741
22	20	50,106	23,06	99,9741
23	21	50,106	23,08	99,9741
24	22	50,106	23,08	99,9741
25	23	50,106	23,09	99,9741
26	24	50,106	23,11	99,9741
27	25	50,106	23,12	99,9741

Figure 12: Ordered data

As it can be seen from the above proposed figure, the sampled data consisted of 4 columns reporting

time in seconds

mass in milligrams

temperature in Celsius degrees

and percentage of mass change.

To elaborate the data it has been used the file **220317_ni18_450-525_10bar_50mg** realized together with Dr. Abad on 30th march 2022. In a first moment only the data sampled at 450 have been taken into account as it is shown in the figure below.

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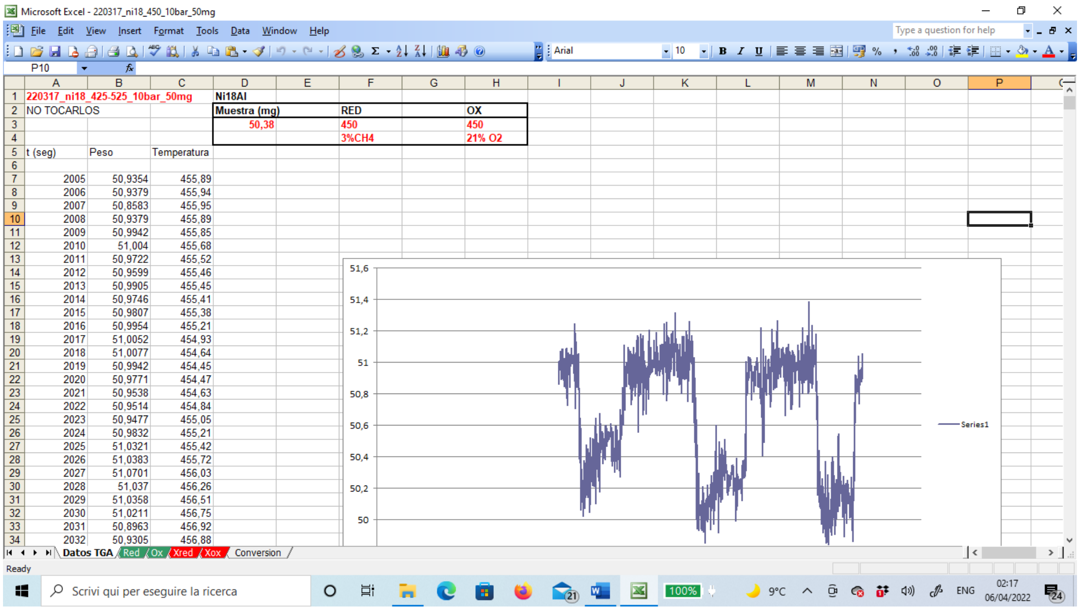

Figure 13: File “220317_ni18_450-525_10bar_50mg”

So in the first section “Datos TGA” the data taken from the PTGA are directly copied and we select only the 3 curves which have been done at the same temperature: 450. We input also:

The mass of the sample in mg

The temperature and the concentration of the reduction gas

The temperature and the concentration of the oxidizing gas

Once all the inputs have been inserted in the first sheet the next one is filled. This is named “Red”.

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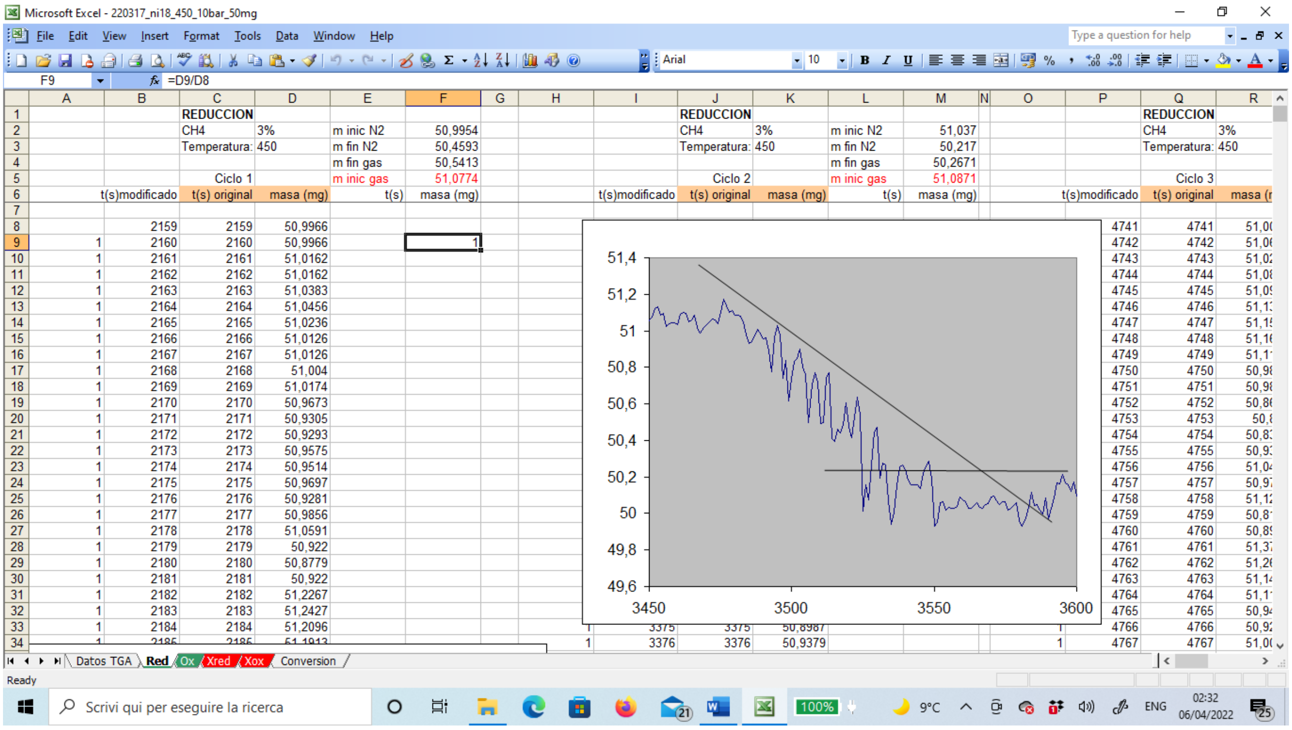

Figure 14: Data elaboration procedure

In the sheet "Red" we copy paste the data already reported in the previous sheet, but we try to select the one which characterize only the change in weight, so for example instead of starting from second 2005 we start from second 2159. Then we have to find three numbers along the decreasing curve of the mass:

m inic N2 50,9954

m fin N2 50,4593

m fin gas 50,5413

m inic gas 51,0774

Where the first number is exactly the mass at which the conversion begins this is identified at the intersection of a declining line which describes the reaction and a horizontal line describing the average mass.

The second number is when the declining line meets a first horizontal line which indicate the equilibrium of mass after the reaction is completed.

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The third number indicates the effect of the change of the flow on the sample inside the PTGA.

The fourth number is given by the sum of the initial mass in nitrogen (m inic N2) plus the difference in weight between the final mass in the gas (m fin gas) and the final mass in nitrogen (m fin N2).

The last data found it is reported as the real beginning of the reaction in the curve and it is identified, taking not also of its corresponding time.

The real end of the reaction period is the part of the curve when constant mass is achieved.

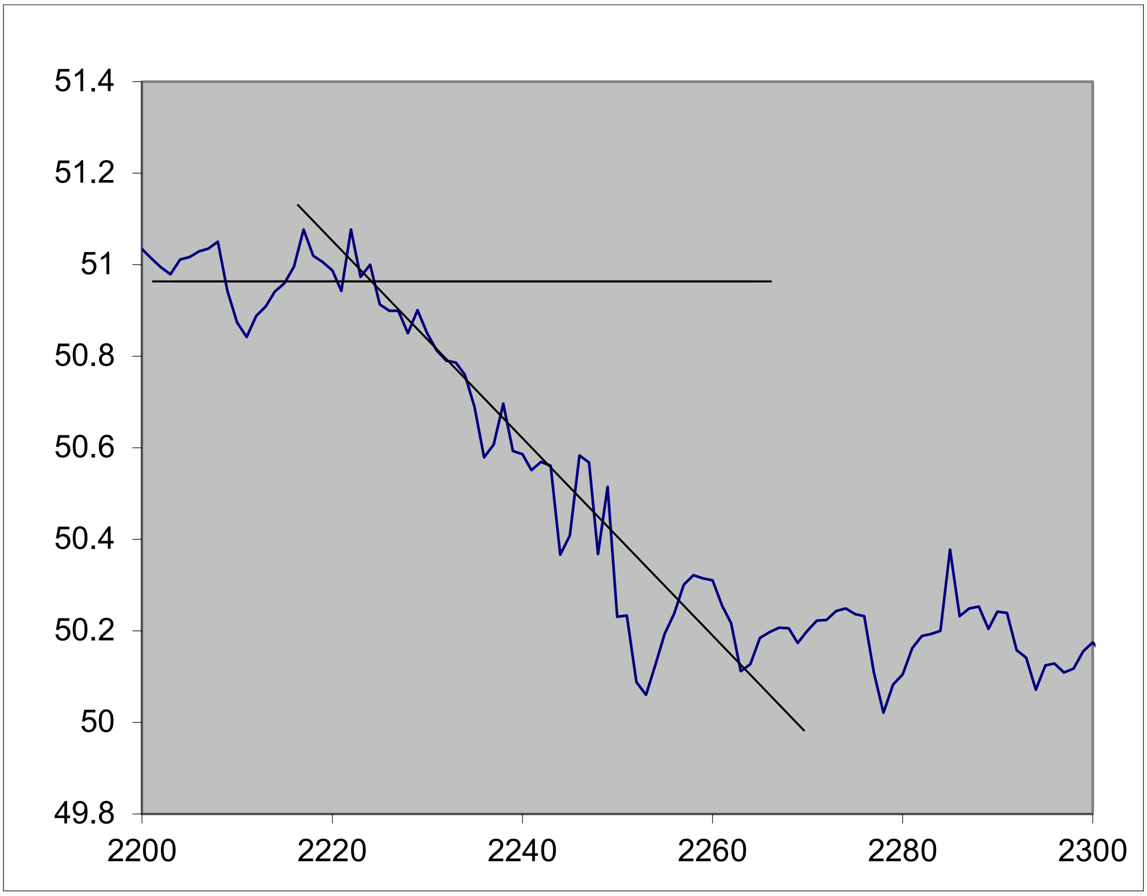

Figure 15: Final curve

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Once the beginning and the end of the reaction have been clearly identified, the following data are calculated.

t(s)	masa (mg)
0	0
1	-0,0584
2	-0,0714
3	-0,0904
4	-0,1346
5	0
6	-0,1034
7	-0,0774
8	-0,1634
9	-0,1774
10	-0,1774
11	-0,2274
12	-0,1762
13	-0,2274
14	-0,2644
15	-0,2874
16	-0,2914
17	-0,3174
18	-0,3884
19	-0,4981
20	-0,47
21	-0,3806
22	-0,4847
23	-0,4908
24	-0,5263
25	-0,5079
26	-0,5165

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27	-0,7111
28	-0,6683
29	-0,4945
30	-0,5092
31	-0,7099
32	-0,563
33	-0,847
34	-0,8433
35	-0,989
36	-1,0171
37	-0,9498
38	-0,8837
39	-0,8396
40	-0,7772
41	-0,7552
42	-0,7625
43	-0,7662
44	-0,8225
45	-0,8604
46	-0,9657
47	-0,9498
48	-0,8923
49	-0,88
50	-0,8702
51	-0,8715
52	-0,9033
53	-0,8776
54	-0,8543
55	-0,8531
56	-0,8335
57	-0,8286

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58	-0,8409
59	-0,8458

Where the first column is still representing the seconds, while the second column is the change in mass calculated through the subtraction of the mass at time i+1 and the mass at time i.

Once these data have been calculated the next step is the calculation of the conversion rate. To do this other input have to be considered, as shown in the following table:

Fichero=	Ni18Al		
Muestra=			
T Calc.=			
Prep.=			
Dp(mm)=	0.1-0.3		
T (C)=	950		
CH4			NiO
CO		Ro	0,200
H2	15	NiO	0,18
H2O		Roc	0,036
CO2		%	3,6
N2	85		
Muestra (mg)	50,38		
var. Peso teo	1,81		

In particular we consider the Ro of nickel (oxygen transport capacity of nickel), the nickel oxide content in the oxygen carrier (NiO), and the oxygen transport capacity of the material (Roc), which is derived by multiplying the oxygen

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transport capacity of nickel oxide for the content of nickel oxide in the oxygen carrier.

In this case:

Roc = NiO_content*Ro = 0.18*0.2 = 0.036 = 3.6%

Based on the weight of the sample, which was 50.38 mg, it is calculated the maximum weight variation (var. Peso teo) by multiplying: 0.036*50.38 = 1.81 mg. This value in the case of reduction reaction is the maximum weight loss which can be achieved.

Once the input parameters have been calculated the data selected in table

	reduccion		
tiempo	peso	tiempo	conversion
0	0	0,0	0
1	-0,0584	1,0	0,03219973
2	-0,0714	2,0	0,03936747
3	-0,0904	3,0	0,04984341
4	-0,1346	4,0	0,07421375
5	0	5,0	0
6	-0,1034	6,0	0,05701116
7	-0,0774	7,0	0,04267566
8	-0,1634	8,0	0,09009307
9	-0,1774	9,0	0,09781218
10	-0,1774	10,0	0,09781218
11	-0,2274	11,0	0,12538044
12	-0,1762	12,0	0,09715054
13	-0,2274	13,0	0,12538044

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14	-0,2644	14,0	0,14578095
15	-0,2874	15,0	0,15846235
16	-0,2914	16,0	0,16066781
17	-0,3174	17,0	0,17500331
18	-0,3884	18,0	0,21415024
19	-0,4981	19,0	0,274635
20	-0,47	20,0	0,25914163
21	-0,3806	21,0	0,20984959
22	-0,4847	22,0	0,2672467
23	-0,4908	23,0	0,27061003
24	-0,5263	24,0	0,29018349
25	-0,5079	25,0	0,28003838
26	-0,5165	26,0	0,28478012
27	-0,7111	27,0	0,39207578
28	-0,6683	28,0	0,36847735
29	-0,4945	29,0	0,27265008
30	-0,5092	30,0	0,28075515
31	-0,7099	31,0	0,39141414
32	-0,563	32,0	0,3104186
33	-0,847	33,0	0,46700631
34	-0,8433	34,0	0,46496626
35	-0,989	35,0	0,54530016
36	-1,0171	36,0	0,56079352
37	-0,9498	37,0	0,52368665
38	-0,8837	38,0	0,48724141
39	-0,8396	39,0	0,46292621
40	-0,7772	40,0	0,42852102
41	-0,7552	41,0	0,41639098
42	-0,7625	42,0	0,42041595
43	-0,7662	43,0	0,422456
44	-0,8225	44,0	0,45349786

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45	-0,8604	45,0	0,4743946
46	-0,9657	46,0	0,53245335
47	-0,9498	47,0	0,52368665
48	-0,8923	48,0	0,49198315
49	-0,88	49,0	0,48520136
50	-0,8702	50,0	0,47979798
51	-0,8715	51,0	0,48051475
52	-0,9033	52,0	0,49804817
53	-0,8776	53,0	0,48387808
54	-0,8543	54,0	0,47103127

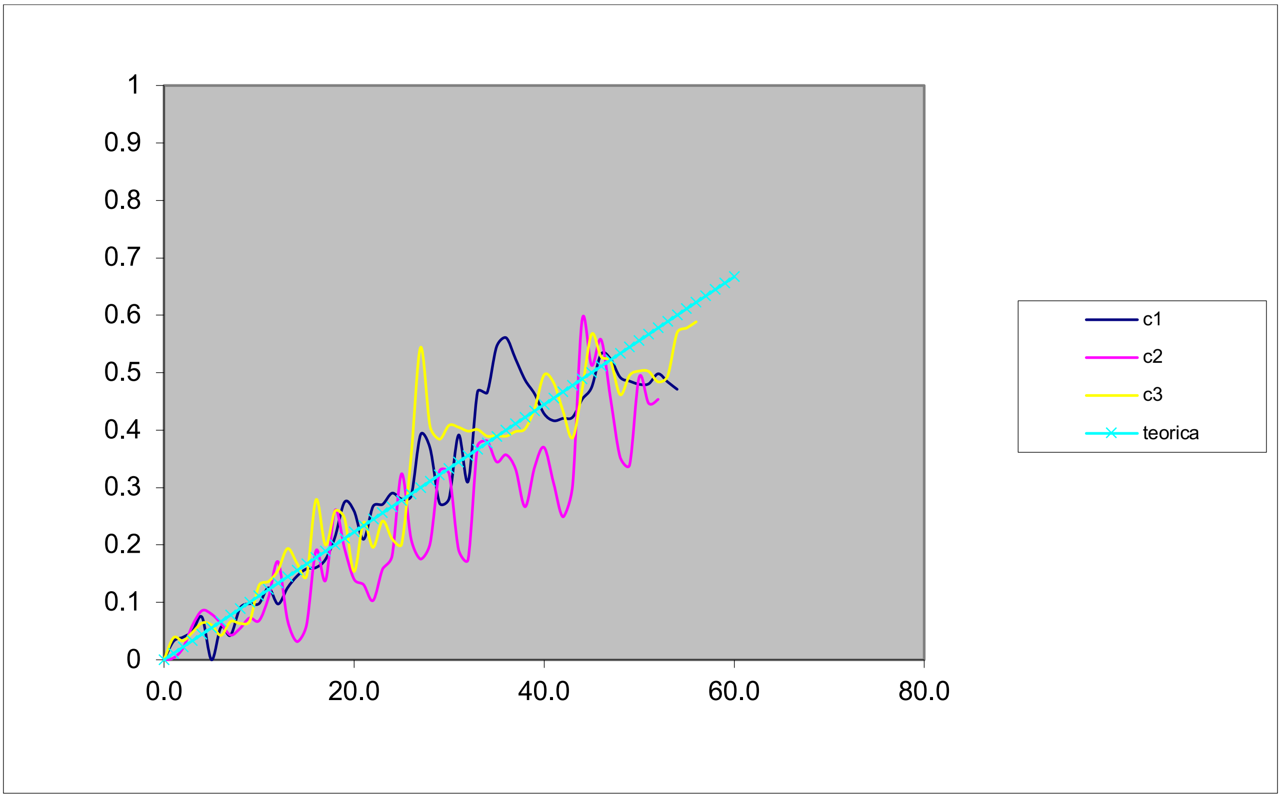

Figure 16: determination of tau

The detailed data are reported in the table below.

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tau	90
Teorica	
t(s)	X
0	0
1	0,01111111
2	0,02222222
3	0,03333333
4	0,04444444
5	0,05555556
6	0,06666667
7	0,07777778
8	0,08888889
9	0,1
10	0,11111111
11	0,12222222
12	0,13333333
13	0,14444444
14	0,15555556
15	0,16666667
16	0,17777778
17	0,18888889
18	0,2
19	0,21111111
20	0,22222222
21	0,23333333
22	0,24444444
23	0,25555556
24	0,26666667
25	0,27777778
26	0,28888889

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27	0,3
28	0,31111111
29	0,32222222
30	0,33333333
31	0,34444444
32	0,35555556
33	0,36666667
34	0,37777778
35	0,38888889
36	0,4
37	0,41111111
38	0,42222222
39	0,43333333
40	0,44444444
41	0,45555556
42	0,46666667
43	0,47777778
44	0,48888889
45	0,5
46	0,51111111
47	0,52222222
48	0,53333333
49	0,54444444
50	0,55555556
51	0,56666667
52	0,57777778
53	0,58888889
54	0,6
55	0,61111111
56	0,62222222
57	0,63333333

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58	0,64444444
59	0,65555556
60	0,66666667

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2. Garcia-Labiano, F., et al., *Effect of pressure on the behavior of copper-, iron-, and nickel-based oxygen carriers for chemical-looping combustion.* Energy & Fuels, 2006. **20**(1): p. 26-33.
3. Levenspiel, O., *Chemical reaction engineering*. 1998: John wiley & sons.
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