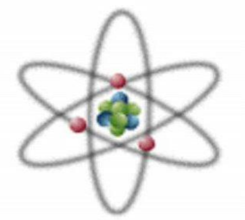
Determination of biogenic fraction of waste on the base of ^{14}C measurement

Method



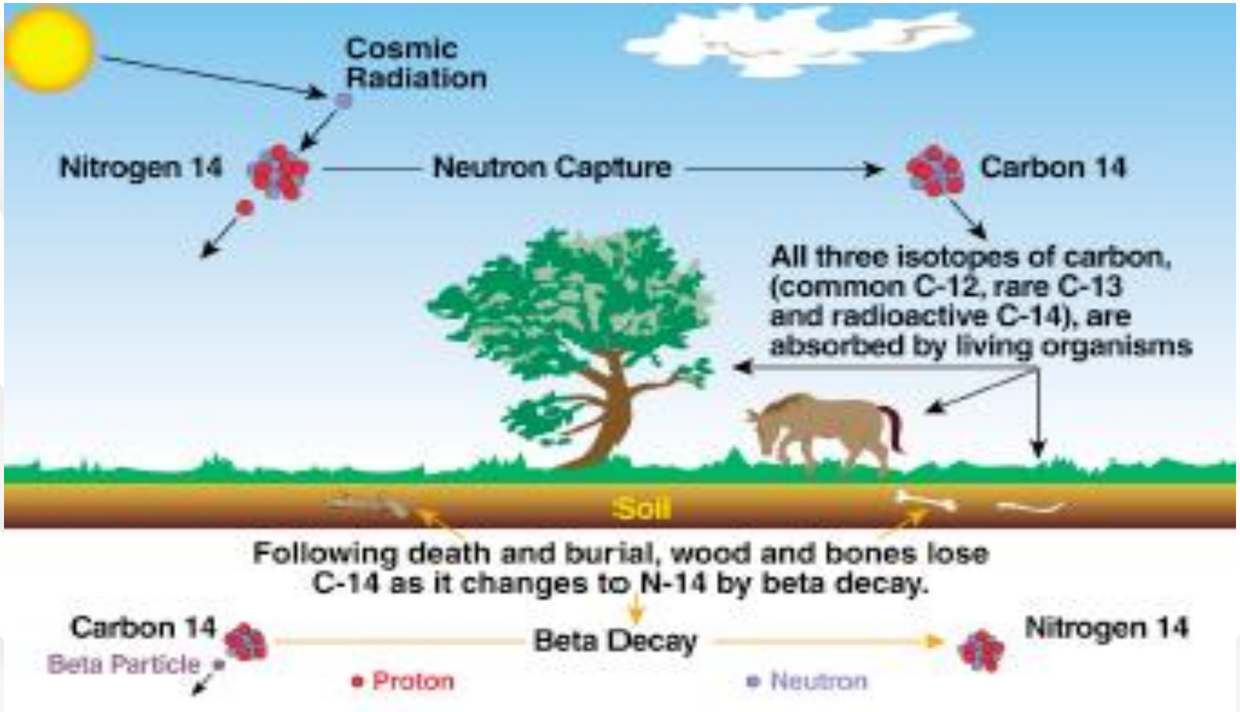
Carbon has 3 isotopes

2 stable: ^{12}C e ^{13}C

<u>1 radioactive: ^{14}C</u>

<u>13,56 DPM/g C</u>

Half-life of 5730 years
(beta radiation)



- The modern carbon (biogenic origin) contains the same ^{14}C atmospheric concentration and then they have the same radioactivity
- The fossil carbon does not contain ^{14}C and it has an activity equal to zero

^{14}C mesurament methods

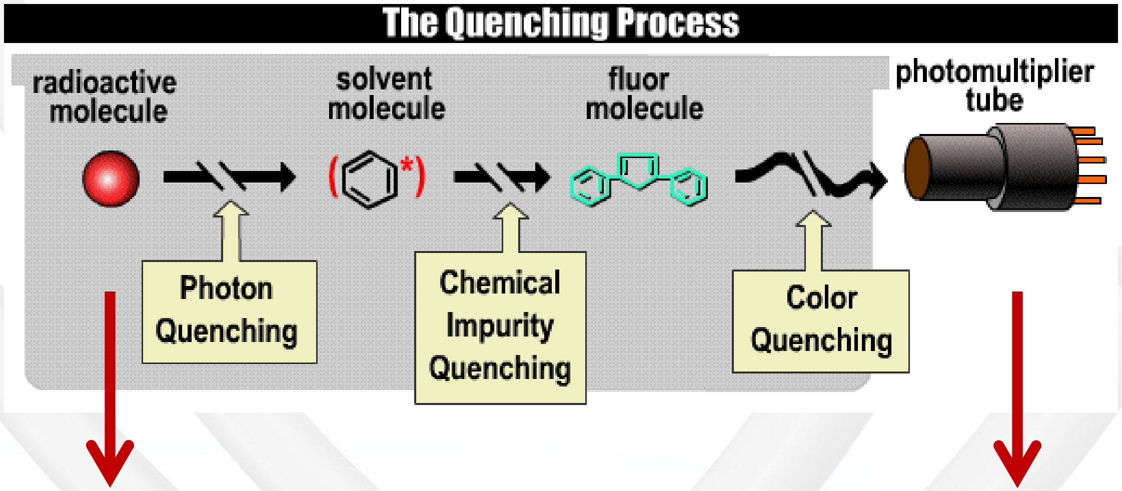
(pr EN 15440 e ASTM 6866)

1. Proportional Scintillation Method (PSM)
2. Beta Ionisation (BI)
3. Accelerated Mass Spectrometry (AMS)

Although characterized by different degrees of precision (ASTM 6866), the three methods are considered equivalent for the standard purpose.

Proportional Scintillation counter Method (PSM)

The measurement principle is based on the fact that the particles of 14C, interact with the liquid scintillator, generating, in a proportionate manner, a light radiation which is measured instrumentally using **Liquid Scintillation Counter (LSC).**



dpm

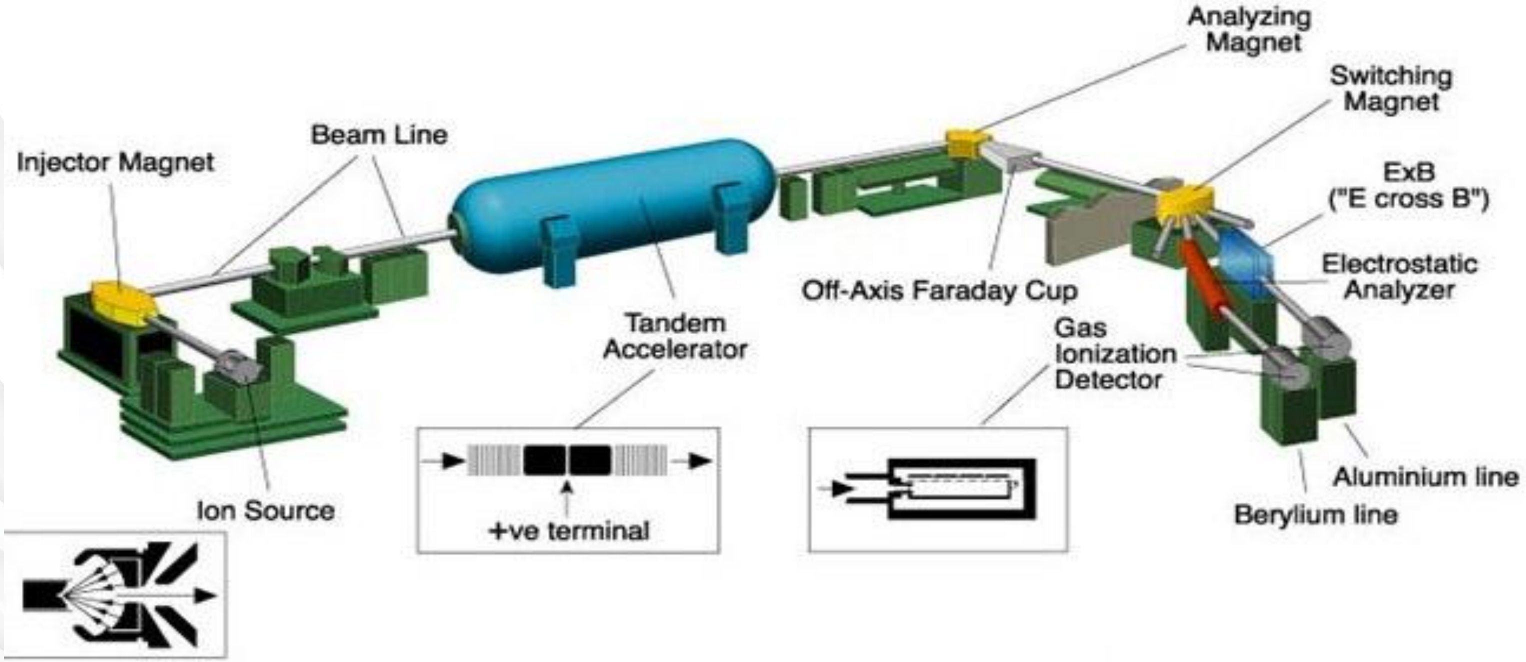
cpm

$$\textbf{Efficienza} = \frac{\textbf{cpm}}{\textbf{dpm}}$$

The results (formally expressed in dpm, or disintegrations per minute) were converted to biomass C percentage compared to the total C content.

Accelerator Mass Spectrometry (AMS)

The atoms are converted into a beam of ions that are accelerated by an electric field, deflected by a magnetic field (in relation to the mass) and measured by the ion detector which determines the relative isotopic abundance of the ion. The sample of CO2 must be converted to graphite before analysis



The only direct measurement method of the ratio $^{14}C/^{12}C$.

Metodi di misura (pr EN 15440 e ASTM 6866):

A representative solid fuel sample must be submitted to:

1. Combustion of the sample in a calorimetric bomb
2. Combustion of the sample in a tube furnace
3. Combustion of the sample in a laboratory scale combustion apparatus

It does not solve the problem of the need to obtain a analysis sample of the waste, with the consequent problems and difficult to apply to waste very uneven

The CO2 produced is absorbed in an appropriate solution, depending on the method of combustion and analysis methods used

Exemple of laboratory procedure

Analysis sample (1 g)

<u>Calorimeter Bomb</u>

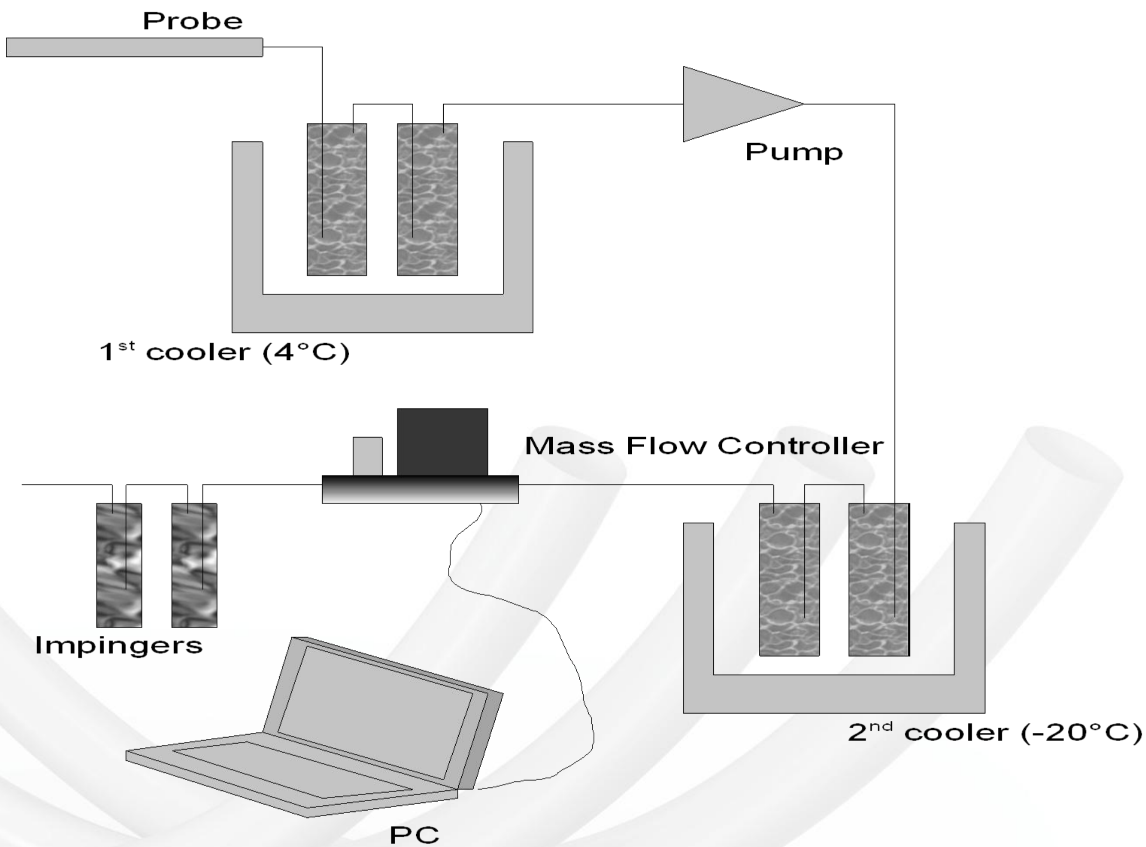
<u>Kit for CO_2 capture</u>

Scintillation Cocktail

<u>Quantulus (LSC)</u>

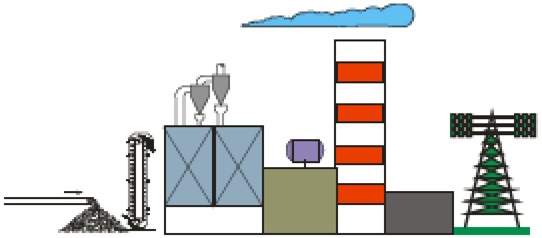
Stack gas method

Still being optimized, but with the advantage of recovering the CO2 directly to the fireplace to avoid the sampling of solid fuel.



The absorption solution composition depends on the method of 14C measurement). It can be KOH for AMS or 3-Methoxy 1-propyl amine for PSM.

Exemple of stack gas method

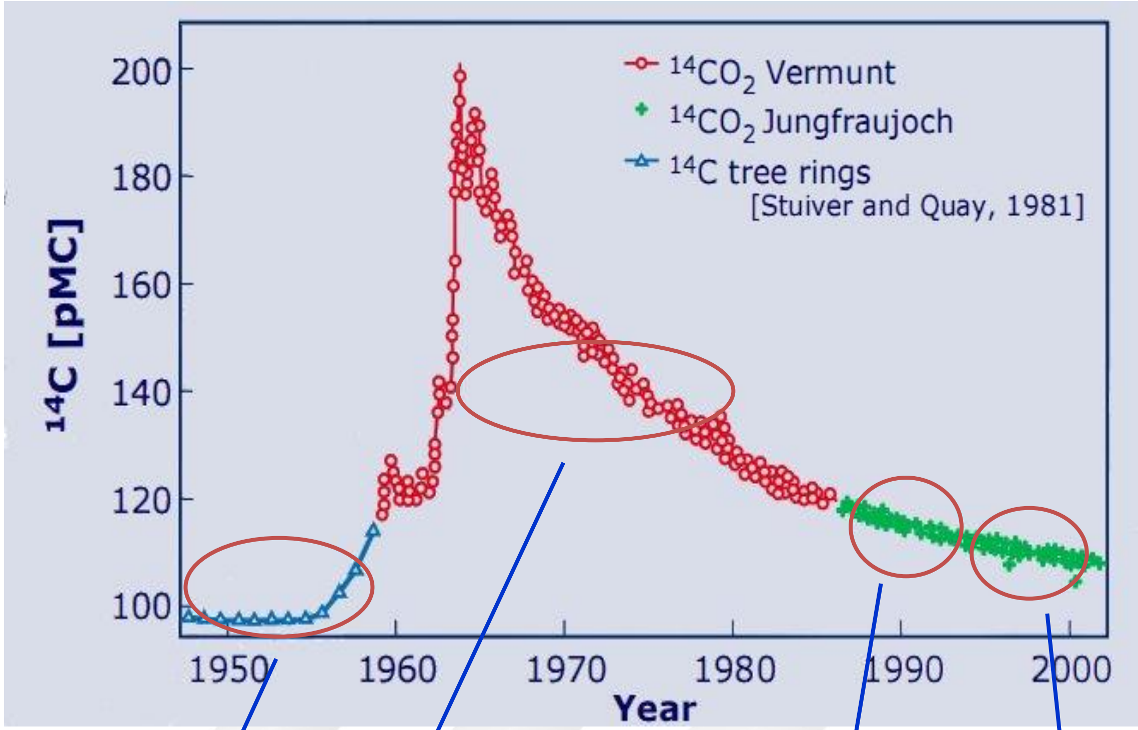


Kit di campionamento a camino

absorption solution

Analisi strumentale con AMS o PSM .

Reference values



Paper and paperboard(25 years)

Building and demolition (70 years)

Recent biomass(0 years)

Packaging and forniture (40 years)

From mass to energy

From mass to energy
(Fellner et al., 2007)

TABLE 1. Chemical Composition of Biogenic and Fossil Organic Matter

moisture- and ash-free content of	unit	biogenic matter			fossil matter		
		symbol	av	sd	symbol	av	sd
C	g/kg	c_{C_B}	468	6.9	c_{C_F}	769	20
H	g/kg	c_{H_B}	66	1.1	c_{H_F}	109	7.0
O	g/kg	c_{O_B}	446	8.3	c_{O_F}	88	22
N	g/kg	c_{N_B}	12	1.6	c_{N_F}	13	5.4
S	g/kg	c_{S_B}	3.3	0.7	c_{S_F}	3	1.1

$$\begin{aligned} \boldsymbol{H} = {} & \dot{m}_B\cdot(34.8\cdot c_{C_B} + 93.9\cdot c_{H_B} - 10.8\cdot c_{O_B} + 6.3\cdot c_{N_B} + 10.5\cdot c_{S_B}) \\ & + \dot{m}_F\cdot(34.8\cdot c_{C_F} + 93.9\cdot c_{H_F} - 10.8\cdot c_{O_F} + 6.3\cdot c_{N_F} + 10.5\cdot c_{S_F}) \end{aligned}$$

From mass to energy

The percentage of energy can be calculated by placing the average chemical composition and calorific value of each of the renewable and fossil fractions. These data are difficult to obtain direct experimental way (especially for SRF), but we can refer to data in the literature.

Molecular weight

Typical average values of fossil and biomass fractions

		Biogenic fraction	Fossil fraction
Chemical formula		$C_1H_{1,7}O_{0,71}N_{0,022}S_{0,0026}$	$C_1H_{1,7}O_{0,09}N_{0,014}S_{0,0015}$
Molecular weight		25,5	15,3
Energy content (weight)	MJ/kg	17,8	36,2
Energy content (moles)	KJ/Mole	454	554
Energetic ratio (weight)	E_f/E_b	2,03	
Energetic ratio (moles)	$(E_f*MW_f)/(E_b*MW_b)$	1,22	

From mass to energy

Percentage of biogenic fraction expressed on a C base :

$$\%C_{BIO} = C_{BIO}/C_{TOT} *100$$

Weight percentuale ot the waste:

$$\%W_{BIO}= (C_{BIO}* PM_B /12) /(C_{BIO}* PM_B/12 + C_F* PM_F/12) * 100$$

Energy percentuale ot the waste :

$$\%E_{BIO}= C_{BIO}\ E_B /(C_{BIO}*E_B + C_F*E_F) * 100$$

C_{BIO} = Biogenic carbon
C_{TOT} =Total carbon
W_{BIO} = Biogenic fraction Weight
MW_B = Molecular weith of biogenic fraction
C_F = Fossil carbon
MW_F = Molecular weith of fossil fraction
E_{BIO} = biogenic fraction energy
E_B = Calorific value of biogenic fraction
E_F = Calorific value of fossil fraction

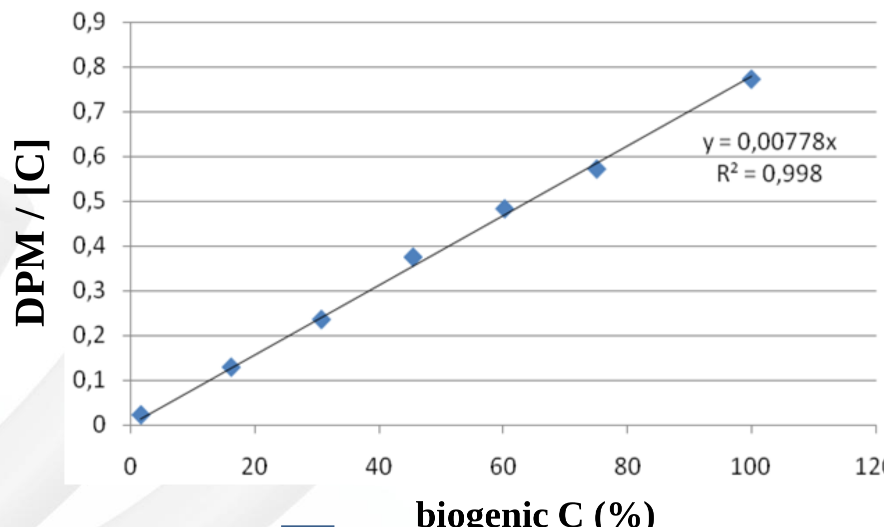
SIBE s.r.l. – Univpm Testing

Calorimeter Bomb

Kit for CO_2 capture

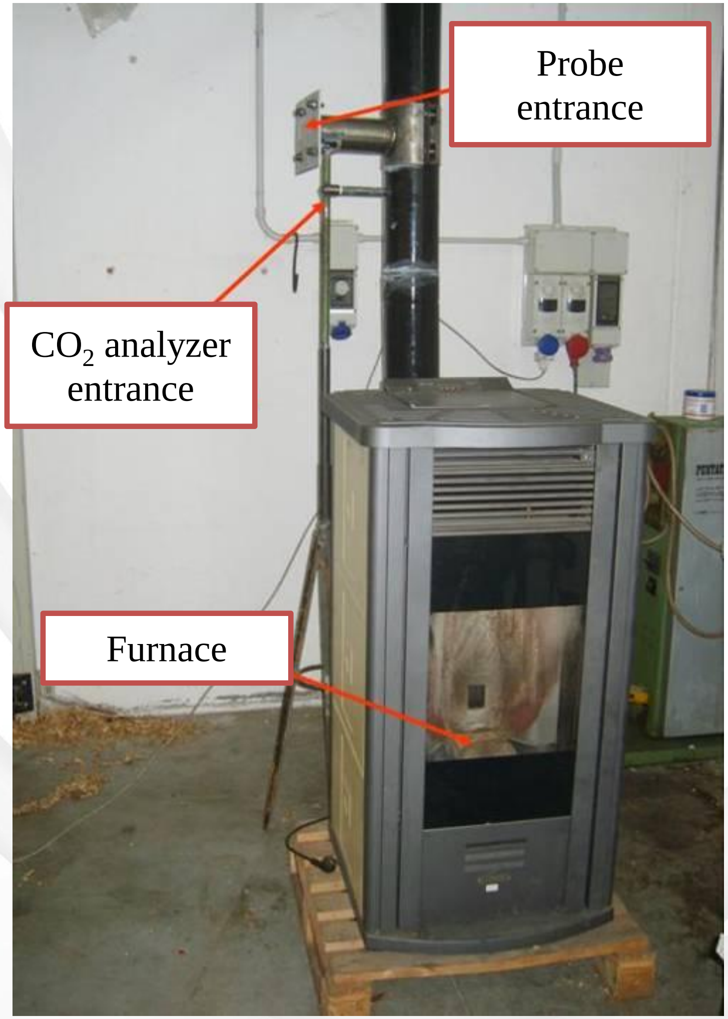
Quantulus

Sample	Natural rubber	Synthetic rubber
(n)	(g)	(g)
1	200	0
2	150	50
3	120	80
4	90	110
5	60	140
6	30	170
7	0	200

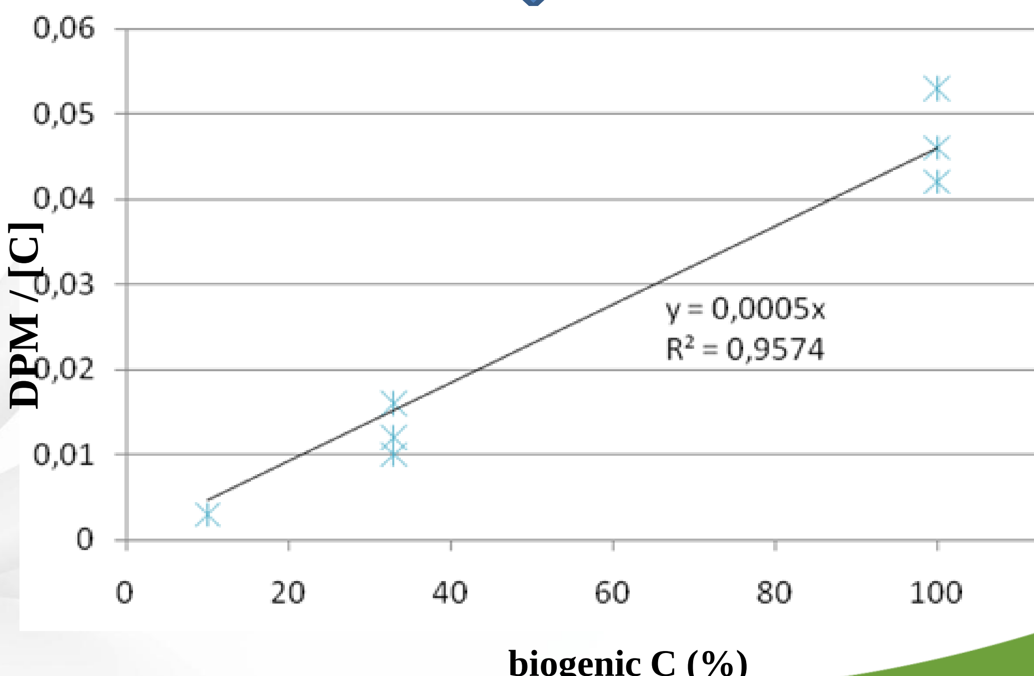


Tire production waste = 54,1% of biogenic carbon

SIBE s.r.l. – Univpm Testing



n. test	Biogenic Carbon (%)	n. test	Biogenic Carbon (%)
1	0	7	33
2	0	8	33
3	0	9	33
4	10	10	100
5	10	11	100
6	10	12	100



SIBE s.r.l. – Univpm Testing

n. test	Biogenic carbon (%)
1	0
2	15
3	40
4	100
5	100
6	100