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Determination of the Biomass Content of End-of-Life Tyres

Leticia Saiz Rodríguez, José M. Bermejo Muñoz,
Adrien Zambon and Jean P. Faure

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Abstract

Studies have been conducted in France and Spain for (1) the validation of sampling methods to achieve representative samples of end-of-life tyre (ELT) materials and (2) the comparison and validation of test methods to quantify their biomass content. Both studies conclude that the ^{14}C techniques are the most reliable techniques for determining the biomass content of end-of-life tyres. Indeed, thermogravimetry and pyrolysis-GC/MS do not lead to results consistent with the theoretical content of biogenic materials present in tyres, and results in both cases differ considerably from the known natural rubber content of the reference samples studied using thermogravimetric analysis. Furthermore, in the two last techniques, natural isoprene cannot be distinguished from synthetic isoprene. Results obtained with radiocarbon analysis based on ^{14}C contents could be used as reference values of the biomass content of the ELTs: in the ranges of 18–22% for passenger car tyres and 29–34% for truck tyres, in line with actual natural rubber and other components content. Additionally, the presence of textile fibres and stearic acid, which are known sources of biomass in the tyre, cannot be evaluated by thermogravimetry and pyrolysis-GC/MS techniques.

Keywords: end-of-life tyres, biomass, natural rubber, reference values, alternative fuel, pyrolysis-GC-MS, thermogravimetry, radiocarbon analysis, isoprene

1. Introduction

End-of-life tyre (ELT) is any pneumatic tyre removed from any vehicle and not selected to be mounted on a vehicle again [1]. Because the end-of-life tyre is a non-reusable tyre in its original form, it enters a waste management system based on product/material recycling and

energy recovery. For that, it is important to know the composition of the tyres and their properties in order to recycle them or recover their energy.

Tyres could be classified according to the type of vehicle in which they are suitable to be mounted, so the main groups established by the industry are passenger car, truck and bus, and agro tyres, all of them included in this chapter.

Tyres are composite materials, essentially made of rubber, metal wire and textile fibres, in Ref. [1]. The rubber component is based on a vulcanized mixture of elastomers with some different chemicals (see **Table 1**), such as carbon black, silica and extender oils which also constitute a high percentage of the tyres.

Their compositions and combustion properties are similar to, or even better than those of coal (see **Table 2**). Due to their high carbon content (60–70%), they have become an interesting alternative fuel with a net calorific value in the range of 26.4–30.2 MJ/kg [2].

The use of secondary fuels is progressively increasing, not only because of its economic benefits, but also because of the environmental advantages of using solid recovered fuels [3]. These include natural resource savings, the preservation of fossil fuels such as petroleum coke, and above all the reduction in net emissions of CO₂ due to the biogenic origin of some components of the tyre, mainly natural rubber. Indeed, according to Directive 2003/87/EC [4], emissions associated with biomass fraction are considered to be neutral with regard to the greenhouse effect.

It also leads to the reduction in other pollutants [5] such as SO_x, mainly because the sulphur content in tyres (1–2%), used for the vulcanization process, is in any case lower than the quantity in most fossil fuels (see **Table 2**).

ELTs contain a fraction of biogenic carbon that mainly comes from their natural rubber content. This is not, however, the only source of biogenic carbon. Most tyre formulations also include stearic acid in small quantities, used as activator of the vulcanization reaction, and

Material	Passenger car tyre (%)	Trucks tyre (%)
Rubber/elastomers	43	42
Carbon black and silica	28	24
Metal	13	25
Textile	5	–
Zinc oxide	2	2
Sulphur	1	1
Accelerators/antidegradants	8	–
Stearic acid	1	n.a
Oils	7	n.a

Table 1. Main components of the passenger car tyre and truck tyre.

Content in % mass				
Major elements (>1%)				
	Passenger car	Truck	Coal	Petroleum coke
Carbon (C)	68 to 70%	60 to 63%	63.9%	84 to 97%
Iron (Fe)	11 to 12%	25 to 27%		0 to 0.2%
Hydrogen (H)	6 to 6.3%	5.3 to 5.6%	3.6%	0 to 5%
Oxygen (O)	3.3 to 3.8%	1.5 to 2.2%		
Silica (Si)	1.5 to 1.9%	0.3 to 0.5%	2%	Nd
Zinc (Zn)	1.3 to 1.5%	1.3 to 1.8%		
NCV (MJ/kg)	30.2	26.4	26	32
Sulphur (S)	1 to 1.5%	1.2 to 1.6%	1.3%	0.2 to 6%
Biomass fraction (% mass)	18.3%	29.1%	0%	0%

Table 2. Elemental analysis of tyres.

also smaller quantities of rayon, a natural fibre used as a reinforcement material in the manufacturing of some tyre carcasses. Nowadays, cotton could only be found in carcasses of older tyres [6, 7].

Despite the range of variation in the formulation of tyres, in practice their composition hardly varies, and thus they are one of the more dependable fuels, coming from wastes.

The greatest variation in biomass content is found among tyres of different types: passenger car tyres, truck tyres or agro vehicle tyres [1].

Each tyre particles obtained from treatment by shredding is quite heterogeneous in terms of biomass content. This intrinsic heterogeneity of tyres particles at the microscopic level is related to their composition. For example, elastomer mixtures are not the same in each part of the tyre (see **Figure 1**).

Although the heterogeneity does not appear at the industrial scale (consumption of around one ton per hour), the microscopic heterogeneity is of importance when it is necessary to take representative laboratory samples and to prepare them for analysis, in order to prevent different results.

In order to quantify the biomass content of an ELT, three analytical techniques have been identified. The first one is a method that determines the biogenic carbon content by measuring the activity of the ¹⁴C isotope, a technique employed in archaeology to date organic materials [8–10]. Another widely used technique for determining the composition of vulcanized elastomers is thermogravimetric analysis (TGA) [11]. This method is based on the measurement of the weight variation of a sample when it is submitted to a progressive increase in temperature in a controlled atmosphere. The third method, pyrolysis-gas chromatography/

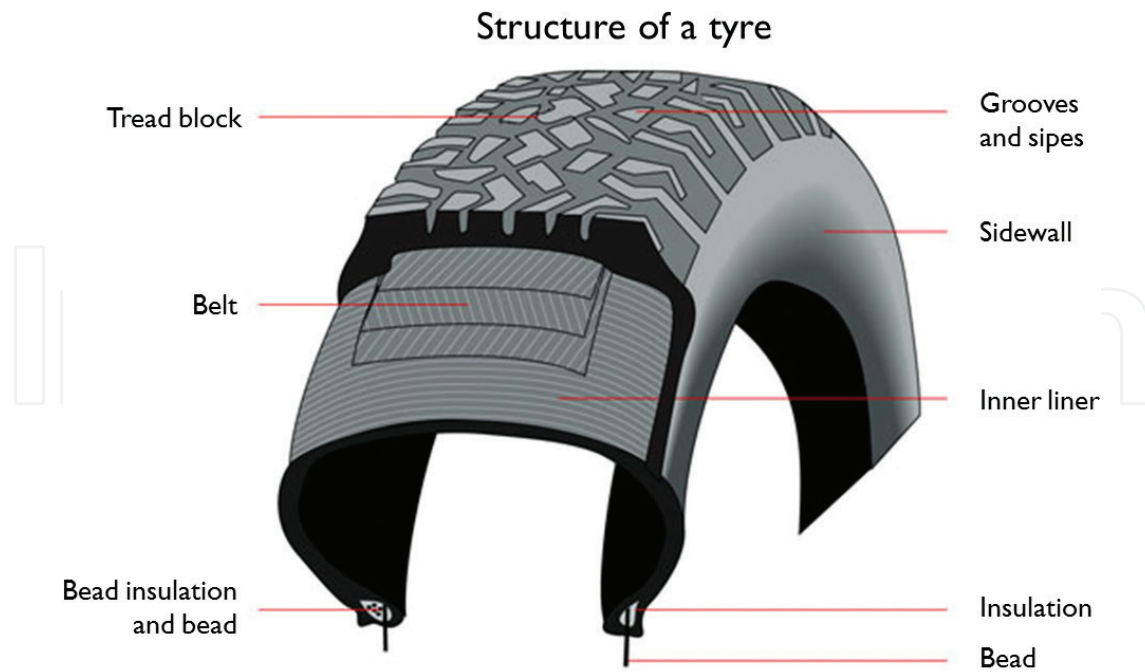


Figure 1. Different layers of a tyre.

mass spectrometry (Py-GC/MS), has been used extensively for qualitative and quantitative identification of polymer blends [12].

The results obtained under sampling, testing and analysis conditions respecting good practices with regards to heterogeneous materials show a remarkable stability in the measured parameters.

This chapter provides first the appropriate methodology to make a selection of test samples from tyres, and secondly, novel information on the use of different technologies for the determination of their biomass content.

Two cases studies conducted independently by ALIAPUR and SIGNUS, in France and Spain, respectively, have probed which techniques are appropriate to measure biomass content in tyres and which are not. Also in both studies reference values of biogenic content have been established, and results are quite close to theoretical values.

This chapter then offers an analysis of the differences between the results of the three techniques as well as the advantages, disadvantages and problems.

2. Sampling procedure for the estimation of biogenic fraction of end-of-life tyres

The management of ELTs to be used as secondary fuel mainly consists of the shredding of relevant quantities of different types of tyres coming from a diverse range of origins.

Shredded material can be stocked in piles, in which each particle contains parts of different layers of the tyre, each with a particular composition. So, the first problem to solve is how to estimate the biomass content taking random portions of materials. If this process is not performed carefully, there is an important risk not to be representative enough of the total stock. This is especially critical if we take into account that any of the used analytical techniques hardly needs a few milligrams of material.

One of the key points for this calculation of biomass content is then the design of a sampling plan which is representative of the big sized lots. In the case of samples taken on the shredding site, the samples will be representative of one to several days of production. Depending on the size of the facility, the sample could represent tens or even hundreds of tons of material.

In the case of samples taken during loading or unloading processes at the storage site, the samples will be representative of several weeks of production; the stocks in this case could even be of thousands of tons of material.

2.1. General criteria for the definition of sampling procedure

The minimum mass to produce a representative laboratory sample from the lot should be determined by the following formula [13]:

$$m_m = \frac{\pi}{6} \cdot d_{95}^3 \cdot s \cdot \lambda \cdot g \cdot \frac{(1-p)}{(Cv)^2 \cdot p} \quad (1)$$

where,

- m_m is the mass of the minimum sample size, in grams as received.
- d_{95} is the nominal top size of a particle (a mass fraction of 95% of the particles are smaller than d_{95}), in mm. This value is measured by means sieves following the method described within CEN/TS 15415:2006 [14].
- s is the shape factor, in mm^3/mm^3 ; reference value of 1.0 in the case of granular materials with nominal size smaller than 50 mm [13].
- λ is the average particle density of the particles in the solid recovered fuel, in g/mm^3 as received [15].
- g is the correction factor for distribution in the particles size. Its value is related to the superior nominal size d_{95} and the minimum size of the particle d_{05} .
- p is the fraction of the particles with a specific characteristic (such as a specific contaminant), in g/g, and is equal to 0.1 [13].
- Cv is the coefficient of variation. Its value is 0.1 [13].

2.2. General criteria for the preparation of laboratory samples

Samples were prepared using a riffle splitter with 14 slots of 27 mm in width, until the mass of the sample is greater than the minimum size of the laboratory sample necessary to guarantee

total representativeness for few milligrams. This must be calculated according to the third-power law [16], which for granular materials is expressed as:

$$m > \alpha \cdot d_{95}^3 \quad (2)$$

where m is the mass retained after each sample division step in grams, d_{95} is the nominal top size in millimetres, and α is a constant over the whole sample preparation procedure for a particular material in g/mm^3 .

Depending on the size of the laboratory sample for each method, a particular number of tests are needed to guarantee the representativeness of the sample.

2.3. Methodology for taking representative samples from ELTs

The preparation of the sample consists in a reduction made in several stages of fragmentation/quartering until the different subpopulations (rubbers, metal wires, textile fibres) are obtained (see **Figure 2**). The standard means and procedures for reducing test samples are carried out in a laboratory with the appropriate equipment (sample division, cryogenic mill...). **Figure 3** shows the flow diagram of the whole process for collection and preparation of the representative sample to obtain a test portion.

Taking into account the size of the average production lots, it was estimated that 1.5 t of whole tyres is the minimum necessary quantity of ELTs. For the Spanish case, four different samples were taken in order to estimate the biomass content by type of tyre.

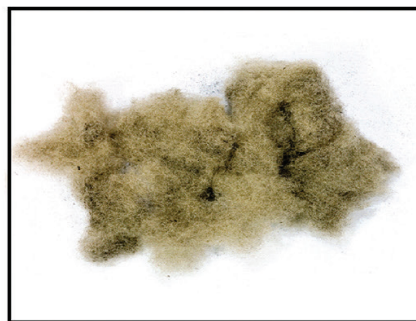
Starting with 1.5 t of tyres, the first step is the shredding of tyres to reduce the size of the sample and to obtain a mix of particles from different tyres. This first-size reduction can be carried out in a primary shredder to obtain pieces within the interval of 35–200 mm.

The sample must be taken at the production platform, using a tool of the open rectangular shovel type by completely cutting the flow of falling material. Samples are considered valid if a total quantity of at least 25 kg is taken per increment to represent a production of 1.5 t.

Elastomer phase



Textile phase



Metal phase



Figure 2. Different fractions of the tyre.

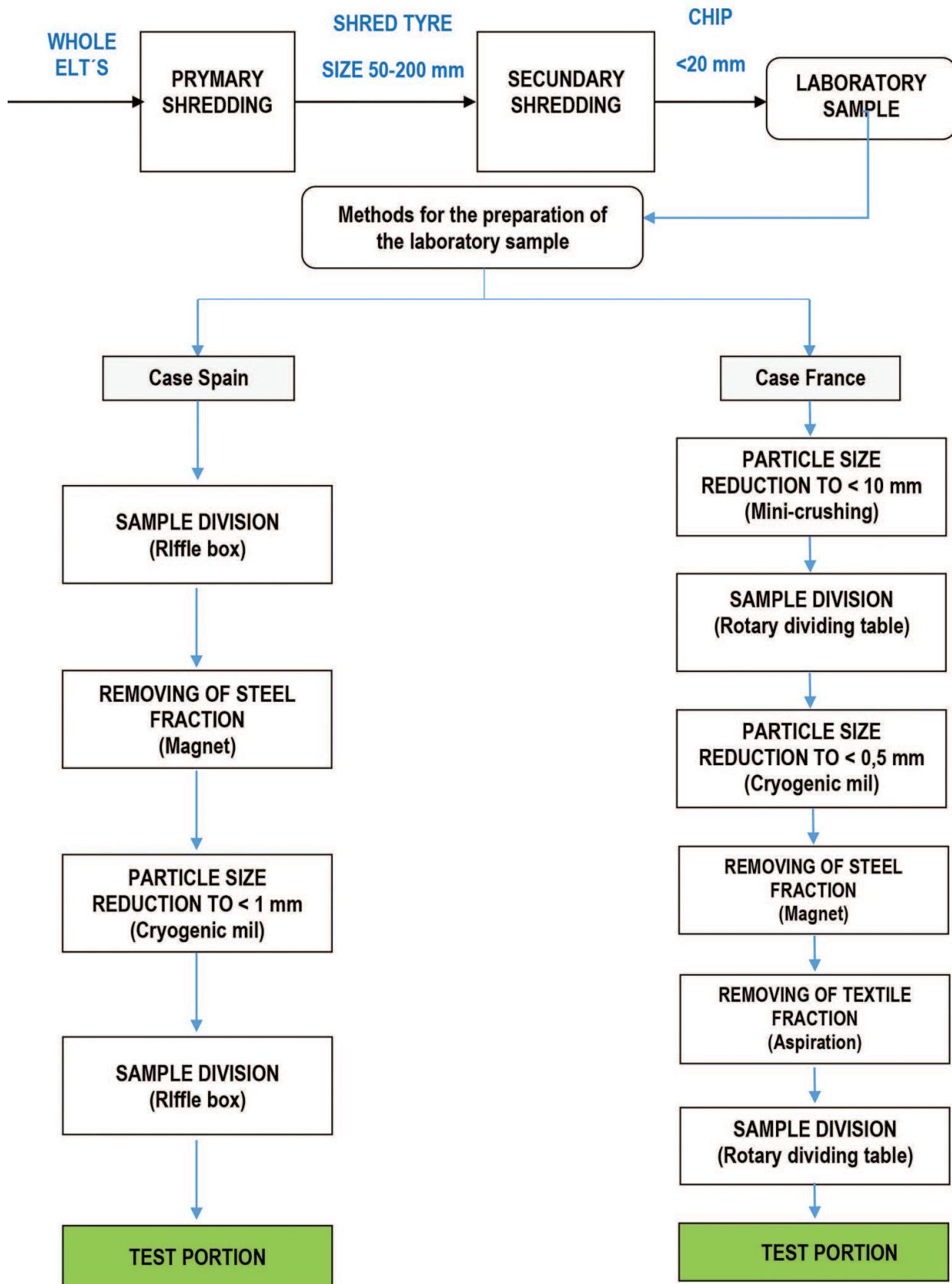


Figure 3. Complete scheme for test sampling preparation.

In a second step, those particles are reduced under a maximum size of 20 mm. The samples produced by this secondary shredder should be taken in smaller portions, at constant intervals of time, called increments.

No less than 24 increments are recommended to achieve a representative sample.

The obtained sample must be quartered to obtain subsamples of a quantity between 1.5 and 3 kg. That is bigger than the minimum quantity necessary for this type of material (around 1.0 kg).

Then the steel fraction should be removed from the sample using a magnet, taking special care in leaving the rest of material (rubber and textile fibres) that should be reduced in particles sized under 1 mm. Different methods could be used for this purpose, especially cryogenics. The obtained product should then be quartered to obtain a test portion.

For the French case, the procedure is similar to the above described (see **Figure 3**).

3. Test methods for the determination of biomass content in tyres

Different test methods were identified in the literature for the determination of natural rubber content in blends that can thus be indirectly used for the quantification of biomass content in tyres [17].

Some of those methods are based on the determination of content in elastomers and are particularly able to distinguish the presence of isoprene, the main component of the natural rubber, among other different elastomers of the rubber blend. This natural rubber has been identified as the main source of biogenic carbon in a tyre; nonetheless, this component is not the only bio-based one. Thus, some of the test methods identified for this chapter are not really conclusive about the total content of biomass in tyres. On the other hand, there are significant differences in the time to analyse the samples (see **Table 3**).

3.1. Pyrolysis-GC/MS

This method is based on the degradation of a sample in an electric furnace at 500–600°C and keeping the sample within this temperature range [18]. This temperature range is recommended to obtain rapid pyrolysis without excessive degradation or carbonization of the rubber sample. However, a temperature of 550°C is advised to obtain the maximum quantity of pyrolysate for NR, IR, BR, SBR, IIR, BIIR and CIIR that are the major elastomeric components of a tyre.

	TGA	Py-GC/MS	¹⁴ C	
			¹⁴ C (LSC)	¹⁴ C (BI)
Test duration	A few hour	A few days	2 months	A few days

Table 3. Test duration of the different methods.

This pyrolysis must be performed passing a stream of nitrogen through the pyrolysis reactor. Nitrogen serves to displace air, prevents oxidation and facilitates the transfer of the pyrolysis products to the gas chromatographer.

The gas chromatographer is equipped with 30-m-long capillary chromatographic column in a fused non-polar-type silica.

The gas chromatographer is coupled to a mass spectrometer operating in scan mode. It detects and registers certain decomposition substances between 35 and 550 atomic mass units (amu).

The pyrolysis-GC/MS carried out in one of the studies is based on ISO standard 7270-2 and requires a calibration curve by pyrolysing the samples with known styrene/butadiene/isoprene ratios.

The approach of this method is to evaluate the natural rubber content in a sample of tyres: It is possible to calculate the total concentration of elastomers in samples and also the concentration in natural elastomers by reporting the result on the previously produced calibration curve.

The authors of this study observed several problems during the application of this method; the main one being related to the non-possibility to distinguish natural isoprene from synthetic isoprene.

One major drawback is that determining the content comparing results with a curve made with different ratio of known samples of styrene/butadiene/isoprene rubbers only gives relative values inside the elastomeric fraction and not in the whole sample. An unrealistic composition on biomass could then be reported with this method.

Another problem derived from the use of PY-GC/MS is the non-detection of other biogenic components of the rubber. A variability of results with pyrolysis temperature and the extraction time in solvents before pyrolysis is also reported. Finally, the presence of brominated butyl could also disturb the results.

Taking into account all these issues, Pyrolysis-GC/MS is then not considered as a valid technique for the evaluation of biogenic content.

3.2. Thermogravimetric analysis (TGA)

This method is based on the continuous measurement of the weight loss of a sample submitted to a ramp of temperature in a controlled atmosphere [11, 19].

In the case of TGA, each type of elastomer has a particular temperature at which the loss of mass occurs. When a sample of vulcanized rubber is tested, some particular peaks appear at specific temperatures.

At lower temperatures, below 300°C, moisture, volatile components derived from plasticizers and other simple chemicals of the rubber blend, volatilize.

In the range from 300 to 525°C most of the elastomers in a tyre rubber blend are degraded by the heat. The first thermal decomposition corresponds to natural rubber NR, and the maximum

weight-loss rate occurs in the 300–400°C interval. Styrene-butadiene SBR maximum weight-loss rate occurs between 420 and 550°C.

One of the studies tried to produce a reference calibration curve based on different binary NR/SBR rubber samples of known composition and the intensity—or height—of the peaks of the DTG curves. Each measurement produces a typical graph of weight loss as a function of the increase in temperature. **Figure 4** shows an example of a weight loss curve for a (NR 75%, SBR 25%) blend and its derivative weight loss curves. This curve shows one minimum per elastomer, H_{NR} and H_{SBR} .

The calibration curve in **Figure 5** represents the relationship between the peak height ratio H_{NR}/H_{SBR} and the NR content of each of the reference samples. The resulting values are adjusted to a second degree polynomial equation [19]:

$$r = \left(\frac{NR}{NR + SBR} \right) \% = a \left(\frac{H_{NR}}{H_{SBR}} \right)^2 + b \left(\frac{H_{NR}}{H_{SBR}} \right) + c \quad (3)$$

$$a = -22.331; b = 84.503; c = 3.0782$$

where r is the percentage of NR in the elastomeric fraction (NR+SBR), H_{NR} is the maximum rate of weight loss in the area where NR decomposes, and H_{SBR} is the maximum rate where SBR decomposes.

Using this calibration curve, the value of r of an unknown sample can be then determined, based on the height of the peaks for NR and SBR.

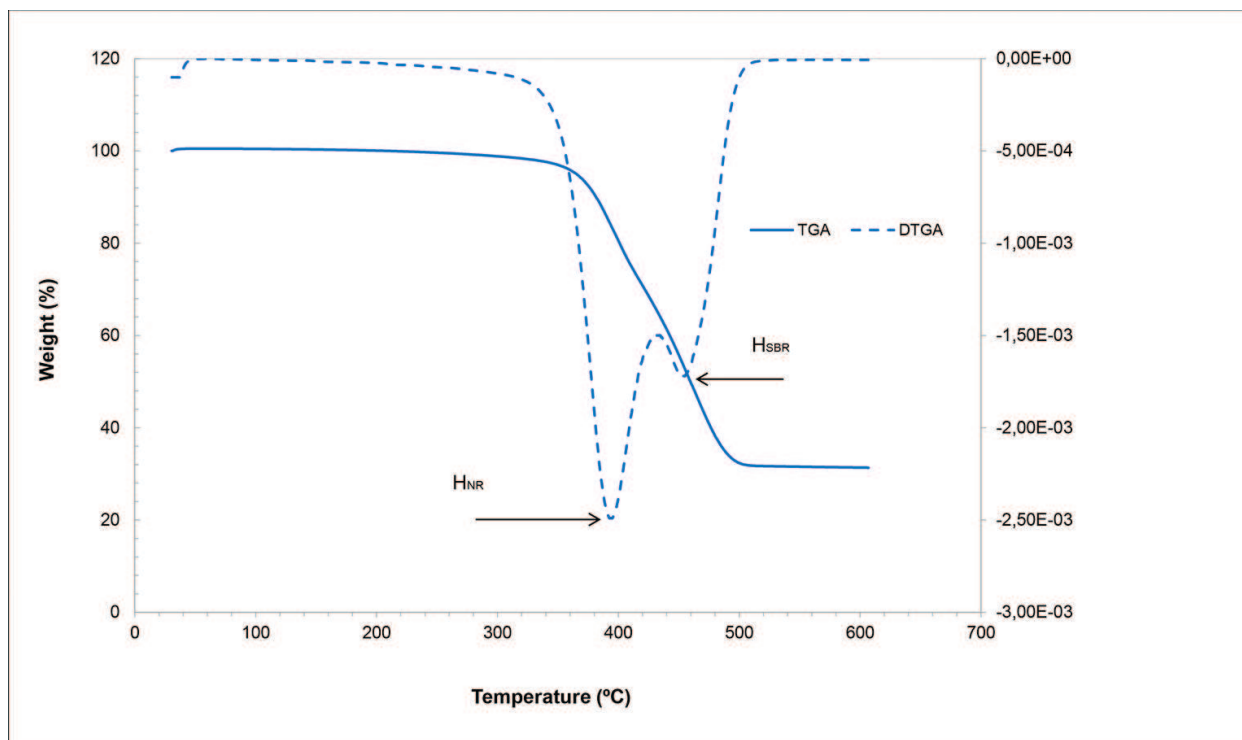


Figure 4. Weight loss and derivative weight loss curve for a polymer blend (NR75%/SBR25%).

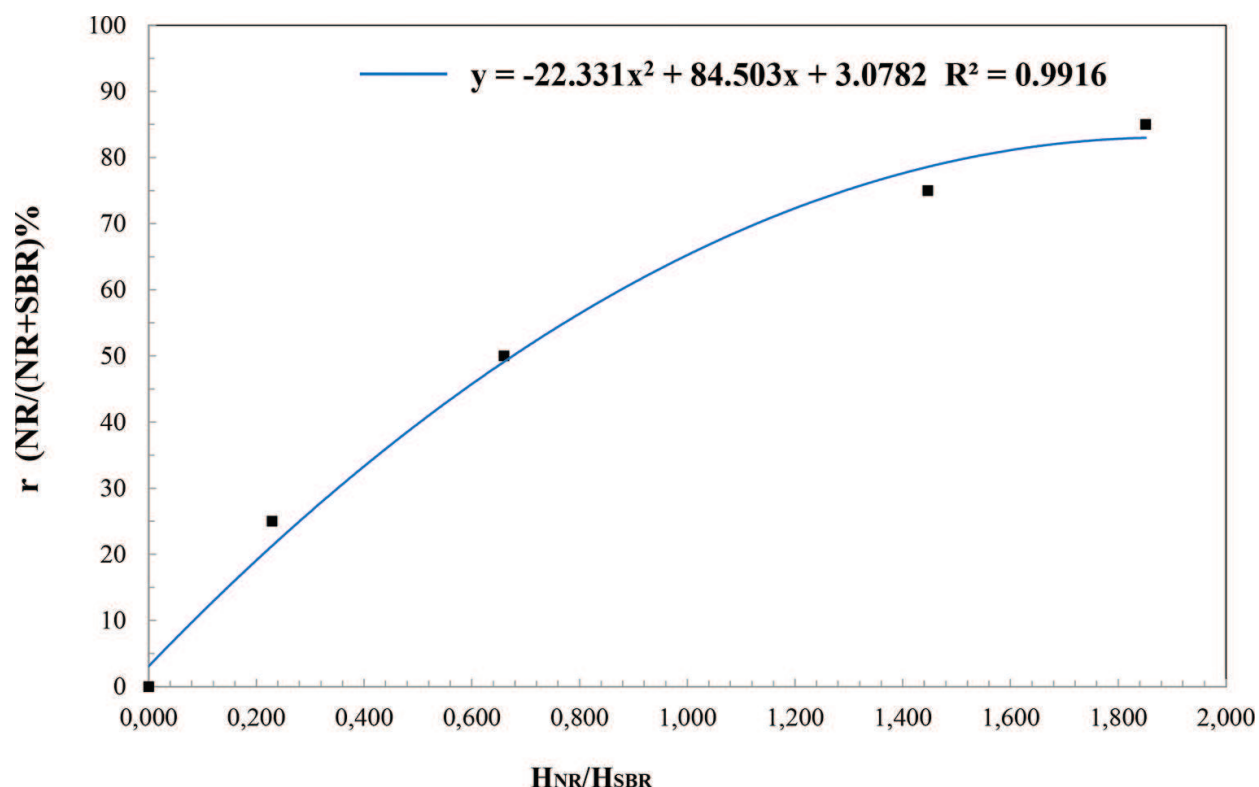


Figure 5. Plot of r (NR/(NR+SBR)%) vs. the peak heights ratio (H_{NR}/H_{SBR}) to determine the biomass content in the tyres studied.

However, it has been reported by authors of this chapter [17] that the correlation of the result for NR obtained by TG analysis and the actual content of NR in samples with known quantities of this elastomer is very bad. Like in the case of PY-GC/MS, this analysis technique is only valid for an estimation of the natural rubber content, independently of the accuracy of the results. Indeed, there is not any possibility to distinguish natural isoprene from synthetic isoprene.

Furthermore, problems derived from the use of this technique start when there is a combination of more than two elastomers in the sample; in such case, the identification and quantification of the elastomers are very difficult because of the overlapping of peaks. Finally, other biogenic components of the rubber, such as cotton or stearic acid, are not detectable by the use of this technique.

Taking into account all these issues, thermogravimetric analysis is then not considered as a valid technique for the evaluation of biogenic content.

3.3. Radiocarbon analysis: ^{14}C methods

The determination of biomass content in different materials using ^{14}C methods is based on analytical procedures used for the determination of the age of carbon contained in materials [8, 9].

Three well-known methods for the determination of ^{14}C content are described in the literature, two of which have been used in the studies made by the authors of this chapter. Those methods are commonly accepted for the determination of the age of objects, especially

employed in archaeology, to date organic materials. The percentage of recent carbon in samples gives an accurate idea of non-fossil carbon content.

This technique is based on the principle that all the carbon atoms in organic materials have either a contemporary origin, proceeding directly or indirectly from the fixation of contemporary atmospheric CO₂ by means of photosynthesis, or a fossil origin and were fixed millions of years ago.

Every living organism contains a quantity of ¹⁴C proportional to the relative abundance of ¹⁴C in the atmosphere. Thus, the percentage of biomass in a material is directly proportional to its ¹⁴C content. Fossil fuels, however, do not contain ¹⁴C, as its half-life is 5,700 years [20, 21].

3.3.1. ¹⁴C/¹²C determination by beta-ionization (BI)

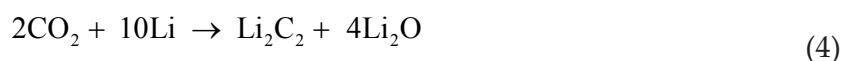
One of the studies used the analysis of the carbon concentration of bio-based origin (Beta ionization method) focusing on the biomass ¹²C assay, considered to be more accurate.

The test has been developed according to standard ASTM D6866-08 and has determined the biogenic carbon content specifically for this purpose.

Particularly, in this case, this test method has been adapted and used for measuring ¹⁴C, in elastomeric fraction and textile fraction.

3.3.2. Liquid scintillation spectrometer (LSC) ¹⁴C determination

Another alternative is the ¹⁴C determination by liquid scintillation spectrometer LSC using butyl-PBD, as scintillation agent, added to benzene (C₆H₆) samples, previously prepared by the following chemical reactions:



CO₂ is then produced in a combustion chamber by burning an appropriate sample of rubber coming from tyre. It was ensured that the reacting CO₂ was only coming from the sample.

The ¹⁴C activity was corrected by the isotopic fractionation according to the directives of the ASTM D6866-05 standard test methods for the determination of biomass content [10]. To do this, the ¹²C/¹³C ratio was established in the stable isotopes laboratory of reference.

4. Discussion of results of the biomass content in tyres

Two different studies have been conducted recently, one in France and the other Spain for the quantification of the biomass content in tyres.

Description of the sample	Spanish case (number of tests)		French case (number of tests)	
	TGA	¹⁴ C (method C)	Py-GC/MS	¹⁴ C (method B)
Passenger car tyres	8	4	8	8
Truck and bus	4	2	4	4
Agro tyres	4	2	–	–
Total number of tests	12	8	12	12

Table 4. Tests are conducted for each method.

In both cases, the purpose of the studies was not only the quantification of the biomass content in tyres but also the validation or not of different techniques for this purpose.

In paragraph 3 of this chapter, three techniques have been compared: PY-GC/MS and TGA were discarded, and techniques related with ¹⁴C determination have been accepted and are highly recommended. **Table 4** shows the number of tests conducted for each method.

Table 5 indicates the content of each sample of tyres in the recycling plant selected to conduct this study in Spain, taking into account the Spanish shared market, in terms of sizes. Lot coded PT140611-1 represents a sample of motorcycle, passenger car, SUV and vans tyres representative in percentage of the market in Spain. The other sample PA140611-2 was randomly taken from a stocked pile of those types of tyres. In addition, two other samples, one corresponding to truck tyres, and other sample with agro tyres were prepared.

Tyres were shredded and reduced to granules following the procedure described in paragraph 2 of this chapter. Samples were appropriately divided using a riffle box with the appropriate number of slots.

After reducing the size of the particles below 20 mm, the steel wires were removed from samples. This process was carried out with a magnet and the percentage of steel in samples is given in **Table 6**. Some rubber particles remain attached to the steel samples, so a calcination of these samples was performed to calculate the actual content of metal wires in the representative samples.

In the same way, the rubber granulates samples were reduced to fine powder, under 1 mm.

Sample code	Description of the sample	Number of tyres	Total weight in tons
PT140611-1	Passenger car tyres of a representative sample of the market	200	1.62
PA140611-2	Random sample of passenger car tyres	190–210	1.58
MC190711-3	Truck and bus	30	1.67
MA190711-4	Agro tyres	30	1.76

Table 5. Samples of different types of tyres (Spanish case).

	% in weight of the steel fraction	% percentage of steel after calcination	% real content per sample
PT140611-1	23	70.25	15.9
PA140611-2	24	62.22	15.1
MC190711-3	36	77.35	27.9
MA190711-4	6	90.15	5.2

Table 6. Percentage of steel fraction (Spanish case).

The French study used a specific laboratory equipment that permits a complete separation of the three different fractions of materials with no contamination between them, starting from shredding stage. So, the phase of calcination of steel fraction was not used. Summary of content of different materials are listed in **Tables 7** and **8**. Then the rubber and textile fractions were also reduced to particles under 1 mm.

In both studies, a cryogenic laboratory mill was used to achieve this particle size total reduction in the samples.

4.1. Results of the ^{14}C analysis

According to the sampling plan, the sample for laboratory test is representative of the lot if quantity is over 66 mg. In the case of liquid scintillation spectrometry, the mass of the sample should be between 10 and 12 g and then, only one single test per sample is necessary. Nevertheless, all the samples have been tested twice to ensure the repeatability of the results.

Results of ^{14}C per sample of rubber and textile using this LSC are shown in **Table 9**.

The percentage of modern carbon is calculated with the following expression.

Sample	Rubber	Metal	Textile
VL1	80.90	12.16	6.93
VL2	82.54	10.05	7.41
VL3	82.30	13.15	4.55
VL4	80.30	13.57	6.13
VL5	83.59	10.77	5.64
VL6	83.08	11.25	5.68
VL7	84.54	12.58	2.89
VL8	84.03	12.28	3.68
Average reference values	82.7	12.0	5.4

Table 7. Summary of content of different fractions per sample in French case (passenger car tyres).

Sample	Rubber	Metal	Textile
PL1	78.74	21.26	0.00
PL2	79.67	20.33	0.00
PL3	73.66	25.50	0.84
PL4	72.55	27.45	0.00
Average reference values	73.1	26.5	0.42

Table 8. Summary of content of different fractions per sample in French case (truck and bus tyres).

$$pMC = \frac{A_{SN}}{A_{ON}} \quad (7)$$

where A_{SN} is the isotopic activity of the sample, standardized for isotopic division, A_{ON} is the activity of the oxalic acid reference, also standardized for isotopic division and pMC is the percentage of modern carbon. Using this Eq. (7), the results of the biomass content in the Spanish study are summarized in **Table 10**.

In general terms, duplicated samples show similar values, all of them are under the limits of tolerance established for this analytical technique.

Table 10 shows the average value of the percentage of biomass in the rubber-textile fraction for each sample. The final result of biomass in the tyres sample, taking into account the content of steel in each one, is written in the **Table 11**.

As a conclusion, the biomass content in the sample corresponding to the passenger car tyres both random and representative to the Spanish share market are exactly the same with an average value of 22.2%.

Sample code	Weight of the sample burned (g)	Yield		Weight of C ₆ H ₆ obtained (g)	Weight of C ₆ H ₆ analyzed (g)	Isotopic division (‰)
		C ₂ H ₂ %	C ₆ H ₆ %			
PT140611-1.1	12,1	99,2%	94,5%	7,4	6,188	-26,6 ± 0,2
PT140611-1.2	9,7	99,9%	97,5%	7,8	6,077	-26,6 ± 0,2
PT140611-2.1	11,2	99,6%	97,8%	8,1	6,123	-27,2 ± 0,2
PT140611-2.2	10,1	99,5%	97,9%	7,6	6,121	-27,7 ± 0,2
MC190711-3.1	10,8	99,3%	97,4%	7,7	6,112	-26,7 ± 0,2
MC190711-3.2	10	99,6%	97,6%	7,7	6,100	-26,7 ± 0,2
MA190711-4.1	9,7	97,9%	98,4%	7,8	6,103	-26,0 ± 0,2
MA190711-4.2	9,9	96,0%	97,5%	7,6	6,127	-26,0 ± 0,2

Table 9. Summary of synthesized samples for ¹⁴C analysis (Spanish case).

Sample	Rubber and textile fraction	
	pMC (%)	Biomass (%)
PT140611-1.1	29,2 ± 0,7	27,2 ± 0,7
PT140611-1.2	27,5 ± 0,7	25,6 ± 0,7
PA140611-2.1	27,8 ± 0,7	25,8 ± 0,7
PA140611-2.2	28,5 ± 0,7	26,5 ± 0,7
MC190711-3.1	50,2 ± 0,7	46,7 ± 0,7
MC190711-3.2	50,9 ± 0,7	47,3 ± 0,7
MA190711-4.1	29,7 ± 0,7	27,6 ± 0,7
MA190711-4.2	30,1 ± 0,7	28,0 ± 0,7

Table 10. Results of ^{14}C analysis for the biomass content in tyres (Spanish case).

Sample	% biomass of the rubber-textile fraction	% biomass of the total sample	Range of biomass content in tyres (%)
Passenger car tyres of a representative sample of the market	26.4	22.2	21.5–22.9
Random sample of passenger car tyres	26.15	22.2	21.9–22.5
Truck and bus	47.0	33.9	33.7–34.1
Agro tyres	27.8	26.4	26.2–26.5

Table 11. Results of biomass content in tyres samples (Spanish case).

Biomass values obtained for tyres samples corresponding to truck and bus tyres resulted in an average percentage of 33.9% by weight, and the average value for biomass content of agro tyres resulted in a 26.4% by weight.

On the other hand, the study carried out in France on several tyre samples, both passenger car, truck and bus tyres, for the determination of biomass content have been tested by the beta-ionization technique.

Results obtained for different types of samples are shown in **Tables 12** and **13**. The value of biomass for passenger car tyre samples is in average 18.3 and 29.1% for the truck and bus samples.

In any case, the magnitude order of the biomass value obtained in the French case are in accordance with approximate theoretical values of natural rubber and other chemical substances with bio-based content in tyres. More specifically, the different values of natural rubber content in car and truck tyre have been obtained and are in line with theoretical values.

Sample	Biomass content (%)	Standard deviation
VL1	17	1.69
VL2	18.9	0.36
VL3	17.0	1.69
VL4	18.4	0.01
VL5	20.3	4.00
VL6	18.1	0.04
VL7	17.3	1.00
VL8	19.4	1.21
Average reference values	18.3	

Table 12. Biomass content of passenger car tyres measured by BI (French case).

Sample	Biomass content (%)	Standard deviation
PL1	30.7	0.36
PL2	31.4	1.69
PL3	29.7	0.16
PL4	28.6	2.25
Average reference values	29.1	

Table 13. Biomass content of truck and bus tyres measured by BI (French case).

5. Conclusions

A tyre is a complex product with a biomass content heterogeneously distributed inside it. Furthermore, there is also a huge variability in composition inside the market, by brands and types, each one having a different biomass content. Therefore, to carry out a proper study of biomass content of a batch or a sample representing a significant number of tyres, it is absolutely necessary to make a good selection of the laboratory sample by means of statistical methods to ensure representativeness of the lot. In this chapter, the procedure for managing tyres samples to obtain representative samples by continuous size reduction and quartering has been described.

Furthermore, it should be taken into account that necessary quantities for the biomass content determination are in the order of a few grams or even milligrams, so the sampling step is crucial to obtain proper results.

Several methods have been explored for determining the biomass fraction of tyres, but some of them are not completely reliable and conclusive, mainly for the following reasons:

The results of the thermogravimetric method differed considerably from the known natural rubber content of the reference samples as well as results obtained from the ^{14}C technique that is because the synthetic isoprene cannot be distinguished from natural isoprene. The pyrolysis-GC-FID method is neither considered as a reliable method, mainly for the same reason and because results are affected by temperature and extraction time.

In addition, the presence of textile fibres and stearic acid in the tyre, a well-known source of biomass, cannot be evaluated for both techniques (pyrolysis-GC-MS and TGA),

French and Spanish studies conclude that the ^{14}C techniques are the most reliable for determining the biomass content of end-of-life tyres. Both methods, beta-ionization (BI) and liquid scintillation spectrometry (LSC), lead to results close to the actual biomass content in tyres.

Finally, the reference values of the biomass content of the end-of-life tyres have been established. Average content for passenger car tyres is 18.3% for the French market and 22% for the Spanish market.

In the case of truck and bus tyres, content in both cases are in the range from 29.1% in the French case to 34% in the Spanish case. Apart from errors of different analytical techniques and laboratories, differences found in both studies could be related to different market share in term of sizes and brands in both countries.

In the Spanish case, a reference value has also been established for agro tyres with an average biomass content of 26.4%.

Author details

Leticia Saiz Rodríguez^{1*}, José M. Bermejo Muñoz¹, Adrien Zambon² and Jean P. Faure²

*Address all correspondence to: lsaiz@signus.es

1 Signus Ecovalor S.L, Madrid, Spain

2 Aliapur, Lyon, France

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