

Using used tyres as an alternative source of fuel

Reference values and
characterisation protocols



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Reference document
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In the first part of the present document, there is a presentation of the “reference values” established by Aliapur on the basis of analyses carried out in 2007 and 2008 on several representative samples of the arising of used tyres, with regard to the most relevant physical and chemical parameters for using tyres as fuel: heat output and the fundamental composition of tyres. These reference values are made available to industries that utilise used tyres as fuel to help them calculate and declare their CO₂ emissions in the context of the National Allocation Plan of CO₂ allowances¹.

This work was the opportunity to position used tyres as one of the main other sources of traditional solid fuels.

In addition, in the second part, this work presents the particularities of the characterisation protocol for the tyres and the analyses of the various physical and chemical parameters (and, in particular, the biomass fraction of used tyres).

This document has thus been produced for both industrialists who use used tyres, as well as the Administration, in the context of the dispensation accorded by the MEEDDAT (the French state department for the ecology, energy, sustainable development and land use) on the use of a default value for the biomass fraction for used tyres in the calculation of CO₂ emissions.

¹ A decree dated 31 March 2008 concerning the verification and quantification of emissions declared in the context of the European greenhouse gas emissions trading scheme for the period 2008-2012.

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Introduction and context

In the face of various new regulatory contexts and the importance of sustainable development, the used tyre recycling sector has become organised so as to be able to codify and harmonise its activities and provide homogenous products in terms of quality (format, cut quality and composition).

Standardisation of characterisation methods and specific analyses for used tyres has played a part in changing their status from waste to product.

At the French level, a standardisation committee (CN-PUNR-AFNOR²) focusing on the products made from ELT (end-of-life tyres) has been working since 2005 on establishing experimental standards so as to have common measurement and sampling methods³. With the AFNOR standards that have already been published, France is currently the most advanced European country in terms of standardisation of the products obtained from ELT: French works are proposed as the work basis for defining European standards.

A similar approach to standardisation of common methods for analysing solid recovered fuels is currently under way at the European level (TC 343) and should result in the publication of a proposed standard by the end of 2008.

In this context, Aliapur is highly involved in the works conducted by the committees of the European Committee for Standardization for used tyres: in this context, and in particular in terms of solid recovered fuel, Aliapur has had tested on its products all the methods proposed by the TC343 work group and has been able to show that some of these methods might have limitations when applied to shredded tyres.

→ **The implementation of a characterisation protocol and analysis methods specific to ELT is thus an essential step.**

² 5 groups of experts have been created, including a group on tyre shredding, which works in particular on sampling shredded stock of ELT, the preparations for analysis of the chemical composition of the sample and the analysis methods for the chemical composition, and a liaison group for the technical committee on solid recovered fuels.

³ AFNOR XP T47-751: End-of-Life Tyres (ELT) - Determination of the format of products from primary shredding - Manual method based on the measurement of the largest projected length

AFNOR XP T47-753: End-of-Life Tyres (ELT) - End-of-life tyres (ELT) - Determination of the format of products from primary shredding – Method based on the automated measurement of the largest projected length

Determination of the particle size analysis of granulates issued from End-of-Life Tyres - Method based on the mechanical sieving of product.

AFNOR XP T47-756: End of life tyres (ELT) - Sampling of products from primary shredding - Conveyor scenario

AFNOR XP T47-757: End-of-life tyres (ELT) – Determination of the format of products from primary shredding – Protruding wire evaluation method

Different regulatory requirements imposed on industries that use ELT need specification of the protocol for characterising tyres and conducting physical and chemical analyses. They also need to have reference values at their disposal.

Certain industries, such as cement works and boiler rooms, use ELT as fuel so as to reduce their consumption of traditional fuels and thus also reduce their energy bills. Used tyres have the advantage of presenting not only a high NCV that is similar to that of traditional solid fuels (coke and coal), but also renewable and mineral fractions that should not be neglected.

Since the implementation of the National Allocation Plan of CO₂ allowances in France⁴, industrialists have been subject to new regulatory requirements that impose calculating and declaring their CO₂ emissions (including those associated with the combustion of ELT) every year to the Authorities.

Depending on the level of emissions for these sites, and of the relative importance that tyres can represent in relation to other sources of emissions, industrialists must calculate their CO₂ emissions using the following parameters, determined with a method level⁵ that is more or less high: quantity of fuel, NCV and emission factor (carbon content, taking into account any possible biomass fraction). Depending on the level of emissions on the site and the status of tyres among the other fuels used (major, minor or marginal flow), industrialists must use either default values or specific values obtained from analyses carried out by an ISO 17025:2005 certified laboratory, whilst respecting the requirements in terms of sampling method and frequency of analysis⁶.

A general dispensation was granted by the MEEDDAT for the biomass fraction of ELT⁷ for 2008 and authorises operators to use a default value rather than carry out specific analyses for the biomass fraction, regardless of the category of tyre (major, minor or marginal). This value was established by the MEEDDAT on the basis of the initial data provided by Aliapur in 2007 on the concentration in natural rubber (the MEEDDAT retained 14.6 % of natural rubber for average tyres – see Appendix I).

In accordance with the European Directive, this dispensation must nevertheless be re-evaluated at the national level every year.

→ **Given the new elements provided by the results of studies and analyses conducted on the initiative of Aliapur in 2008, Aliapur considers that it is necessary to provide additional information on this subject.**

⁴ PNAQ established by France for the period 2005-2007 (PNAQ 1), then 2008-2012 (PNAQ 2) following the European Directive known as the Quotas Directive : 2003/87/EC

⁵ The method level defines: on the one hand, the expected precision of the activity variables (that is, the quantities of fuel consumed (a “performance obligation”) and, on the other, the requirements in terms of sampling and measuring emission and oxidation factors and the NCV (an “obligation of means”).

⁶ Excerpt from the decree of 31 March 2008 (annex I, §III-3): “The operator must provide proof that the samples obtained are representative and exempt of bias. The respective value must only be used for the delivery period or the batch of fuel or materials of which it is representative. [...] The sampling procedure and frequency of analysis must make it possible to guarantee that the annual average for the parameter in question be determined with maximum uncertainty that is less than one third of the maximum uncertainty required by the method level approved for the activity data concerning the same flow.” If it is impossible for the operator to meet this requirement, minimal frequency of analysis are provided in the decree.

⁷ Appendix II of the Circular dated 1 July 2008

I. Reference values

The reference values presented in the present document were obtained from the results of analyses carried out in the laboratory on 8 samples of shredded ELT (5 samples from production and 3 samples from loading the barge).

In order to take into account the heterogeneity of the tyres at the microscopic level, it is necessary to either take a large number of samples, or a smaller number but with preparation work. Given the number of characteristics to be analysed (more than 35), the second option was chosen at Aliapur.

The samples were obtained in accordance with standard XP T47-756: *End of life tyres (ELT) - sampling of products from primary shredding - Conveyor scenario.*

They were composed of 3 samples taken

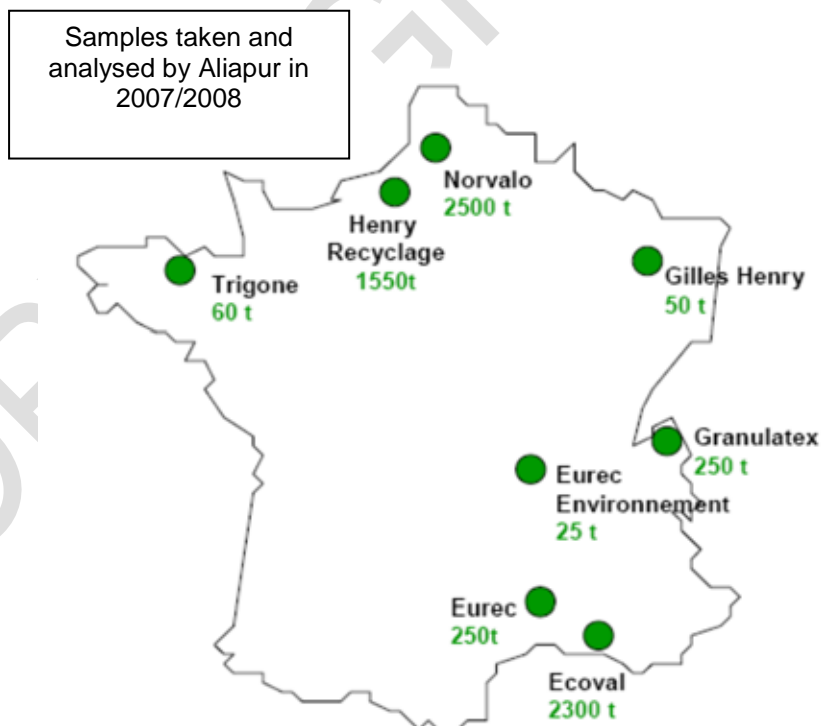
- from the material flow, from under the conveyor belt during production of batches of 20 to 250 tonnes (for samples on the shredding site, representing between 1 day and 2 weeks of production)
- during loading / unloading of the barges of 1,500 to 2,500 tonnes.

The shredded material came from:

- mainly End-of-Life Tyres from Passenger cars (PC)
- mainly End-of-Life Tyres from Trucks.

The localisation of the various zones from which the quantities of samples were obtained is presented on the map below.

Samples taken and analysed by Aliapur in 2007/2008



The results showed that there was good coherence and consistency with the nature of the tyres. The shredded material contained more than 90 % of carbon, iron, hydrogen, oxygen, silica, zinc and sulphur.

A. Spotlight on the key parameters

	Passenger car ELT			Truck ELT		
	Min	Max	Average	Min	Max	Average
NCV (MJ/kg)	29.5	30.6	30.2	26.1	26.7	26.4
Carbon (C)	67.5%	70.1%	69.0%	59.7%	62.6%	61.1%
Biomass fraction (% mass)	17.0%	20.3%	18.3%	28.6%	29.7%	29.1%
Sulphur (S)	1.2%	1.4%	1.3%	1.2%	1.6%	1.4%

The values come from analyses carried out on 8 samples for passenger cars and 2 samples for trucks (the detailed results for each sample are presented in Appendix V).

The results of the analyses carried out on the tyre samples, representative of the generation of ELT in France, showed little variability in terms of NCV, C, C biomass and sulphur parameters.

The truck used tyres have NCV and carbon contents that are lower than those of passenger cars because of the higher proportion of metal in the tyres. Conversely, the content in carbon of biomass origin is greater in the case of used truck tyres.

B. Comparison with other solid fossil fuels

	Passenger car ELT	Truck ELT	Coal	Petroleum coke
NCV (MJ/kg)	30.2	26.4	26	32
Carbon (C)	69%	61%	64-68%	84-97%
Biomass fraction (% mass)	18.3%	29.1%	0%	0%
Sulphur	1.3%	1.4%	1.3%	0.2-6%
EF: t CO ₂ /TJ	59 (x)	43 (x)	90-95*	96*-110
EF: t CO ₂ /t	1.8 (x)	1.1 (x)	2.5	3.1

* Default values for Emission factors (EF) of Coal and coke quoted in the 31 March 2008 decree

** TJ = 10¹² joules (tera joules)

(x) Net emission factors, taking the biomass carbon into account.

Used tyres used as fuel have a high heating value that varies little in relation to the samples taken from the trucks and passenger cars arising, and it is comparable with that of coal and petroleum coke.

In addition, the particularity of ELT is their low sulphur content (around 1.3%, equivalent to that of coal) in comparison with sulphur content for petroleum coke which can vary considerably depending on the origin of the fuel, reaching as much as 6% and thus requiring air pollution control (to reduce the SO₂ emissions so as to respect the emission limit values).

Given the analysis elements for the NCV, carbon content and biomass, the emissions factor for ELT calculated was around 59 t CO₂ / TJ for passenger car used tyres and 43 t CO₂ / TJ for the truck used tyres, or 45% less than that of petroleum coke and coal.

Tyres thus make it possible not only to provide a heat output equivalent to that of petroleum coke and coal, but also make it possible to reduce fossil CO₂ emissions due to combustion significantly because of their biomass fraction (up to 45% of the fuel emissions in case of 100% substitution of coke by used tyres).

Thus, if we take as an example the **production of one tonne of clinker** (at the level of a furnace of average consumption of 3,300 MJ/t of clinker the combustion emissions were as follows depending on the fuel mix:

Fuel mix	Fuel flow	Combustion emissions (kg CO ₂ / t ck)	Fossil CO ₂ emission reduction*
100% petroleum coke	0.1 t coke	314 kg CO ₂ / t ck	
100% coal	0.13 t coal	317 kg CO ₂ / t ck	
100% passenger car tyres	0.11 t passenger car ELT	194 kg CO ₂ / t ck	-38%
100% truck tyres	0.12 t truck ELT	142 kg CO ₂ / t ck	-55%
100% used tyres (70% passenger car + 30% Truck) ⁸	0.11 t tyres	174 kg CO ₂ / t ck	-45%
50% coke + 50% passenger car ELT	0.05 t coke + 0.05 t passenger cars	255 kg CO ₂ / t ck	-19%

* Reduction calculated in relation to the average value for 100% coke or 100% coal

⁸ Distribution of the tyres on the market in 2007, taken from the ADEME report on the 2007 data for tyres (Synthèse Données 2007 pneus – collection Repères): the distribution between passenger car tyres (passenger cars tyres of less than 15 kg) and truck tyres (more than 15 kg) was 70% / 30%.

C. Values for the other elements in the fundamental composition

Used tyres have a carbon content of more than 60%, up to 70% for passenger car tyres. One of the particularities of used tyres is their composition in iron that is also a major element as it can represent up to 27% of the composition of truck tyres. This source of iron is, furthermore, recycled by cement makers (on the condition however that the output remains compatible with the global balance at the clinker and cement level).

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%		
Sulphur (S)	1 to 1.5%	1.2 to 1.6%	1.3%	0.2 to 6%
Minor elements (<1%)				
	Passenger car	Truck	Coal	Petroleum coke
Nitrogen (N)	0.4 to 0.6%	0.3 to 0.4%	1.3 to 1.8%	1.5 to 2%
Calcium (Ca)	0.2 to 0.3%	0.06 to 0.08%	0.18%	Nd
Manganese (Mn)	0.06 to 0.07%	0.1 to 0.2%	0.1%	Nd

The following elements were present at a concentration of < 0.06% (trace elements) (see Appendix IV):

aluminium, arsenic, barium, bromide, chloride, chrome, cobalt, copper, magnesium, molybdenum, nickel, phosphorous, lead, potassium, sodium, titanium.

Nickel in particular was present at a concentration ranging from 0.002 to 0.003%.

The other elements present at concentrations of < 0.001% (at the quantification limit) were: selenium, antimony, beryllium, vanadium and mercury were

The elements present at concentrations of < 0.002% (quantification limit) were: fluorine, cadmium and thallium

II. Characterisation protocol for used tyres

Summary

Aliapur has carried out a range of studies with the BRGM, SGS, CTTM, BETA and the LRCCP, which have shown that it is not always possible to analyse used tyres with the methods designed for other solid recovered fuels.

Aliapur has thus defined and proposed, particularly in the context of the work of the TC343, a protocol and specific analysis methods for characterising tyres that make it possible to:

- let the intrinsic heterogeneity of tyres be expressed during the sampling, sample preparation and test sample stages
- do the preparation and sampling without resulting in either loss, nor addition nor chemical alteration of the material
- analyse the various parameters without bias.

The operating procedure for preparing samples makes it possible to isolate three distinct phases, the presentation of which makes it possible to perform representative analyses (homogenous matter).

It must be monitored strictly so as to know the exact distribution of each phase and to be able to ultimately establish the chemical composition of the sample.

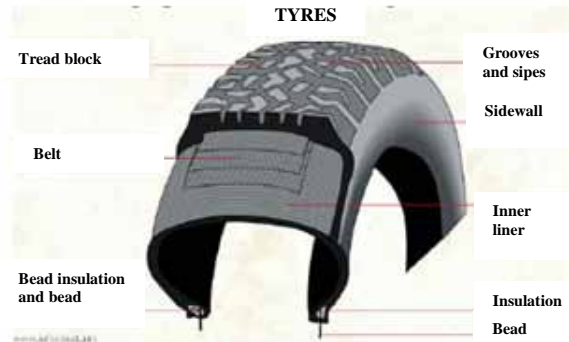
Finally, the analysis methods must be adapted to the characteristics of the different phases.

This operating procedure for sampling and analysis is the procedure that has been used by Aliapur to establish the reference data presented in the first part of this document.

A. Used tyres: a homogenous product in terms of their uses... ...but which are heterogeneous at the microscopic level, requiring precautions in the pre-analysis preparation

The products obtained from recycling are often qualified as heterogeneous. And there is, indeed, an intrinsic heterogeneity to ELT, at the microscopic level, related to their composition.

Tyres are effectively composite materials, essentially made of elastomers, metal wire and textile fibres. These components are, in addition, different depending on the part of the tyre in which they are used. For example, elastomer mixtures are not the same in the various parts of the tyre.



This microscopic heterogeneity is of importance, and must be taken into consideration for the analyses, but does not appear at the scale of industrial use (consumption of around one tonne an hour). This is why the physical and chemical characteristics measured within an arising of ELT do not show any particular heterogeneity.

Certain occasional analyses do not correctly take into account the notions of sampling strategy and preparation of test samples. The results of these analyses have, as a result, obtained very different values for a single product. This nevertheless does not mean that the physical and chemical parameters representative of a tonne of tyres present significant variability. The results obtained under sample, test and analysis conditions respecting good practices with regards to heterogeneous materials show, on the contrary, remarkable stability in the parameters measured (see the results of the batch analyses used to establish the reference values, presented in the Appendix).

The solution for determining, with some precision, the composition in a given quantity of a batch of material from a sample goes through an optimal number of sample takings, to define a statistical approach (either a large number of samples, or a smaller number with pre-analysis preparation work).

Taking a sample from a heterogeneous material is effectively a random process, producing the sampling errors that are listed below and that need to be reduced via preparation work:

- errors of preparation and sampling: the result in particular of the loss or addition of matter, or chemical alteration
- errors of segregation, caused by the heterogeneity of distribution⁹: this error can be virtually cancelled out in cases of homogenisation of the batch by mixing, or by carrying out a maximum number of elementary samples on all of the material by means of quartering, for example
- fundamental sampling errors, related to the heterogeneity of composition¹⁰, and perhaps limited if all the particles have an equal chance of being taken in a sample.

⁹ The heterogeneity of distribution essentially results from spatial, non random distribution of particles within a batch. It depends on the size of the particle groups on which the observations are made, and also on the heterogeneity of the composition of the material studied (see below).

¹⁰ The heterogeneity of composition results from the frequency and physical and chemical particularities of the individual particles in the matter and is exclusively related to the intrinsic properties (chemical composition, size, mass...) of each individual element of the material and is independent of their spatial distribution.

B. The different stages in the sampling protocol: taking and preparing the sample

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1. Simplified sampling protocol diagram

2. Detailed protocol – the constraints and requirements for each stage

- a) **Sampling procedure to obtain a sample that is representative of a batch of ELT**
- b) **Preparing the sample**
- c) **Test sample**

C. The analysis methods specific to used tyres

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D. The particular case of analysing the biomass fraction of tyres

Tyres are in great part composed of elastomers, some of which come from natural rubber (polyisoprene) obtained from the cultivation of rubber. Part of the carbon content of tyres thus comes from the biomass, and the emissions associated with the combustion of this biomass fraction are thus considered to be neutral with regards to the greenhouse effect (CO₂ of biomass origin does not contribute to the greenhouse effect, in accordance with the recommendations of the IPCC and as currently reflected in the EU ETS directive 2003/87/EC, see annex IV).

Several methods have been explored by Aliapur for determining the biomass fraction of tyres. The first approach envisaged by Aliapur was to evaluate how much natural rubber there was in the tyres and thus dose the total concentration in elastomers and then the concentration in natural elastomers. To do this, the pyrolysis-GC-FID method (standard NF ISO 7270-2) used initially involves making up a calibration curve by pyrolysing the samples with known styrene/butadiene/isoprene ratios: samples of known composition were thus analysed by chromatography for their content in each component so as to make up the calibration curve. In the second stage, the sample of unknown composition was pyrolysed and analysed by chromatography under the same conditions and its composition was determined from the calibration curve.

We nevertheless observed several problems during the application of this method.

- extraction time before pyrolysis and pyrolysis temperature could disturb the results
- the presence of brominated butyl could also disturb the results
- determining the styrene/butadiene/isoprene ratio gives relative values, obtained from an estimate made on the basis of nomogram abacus and not measured values
- natural isoprene cannot in any way be distinguished from synthetic isoprene.

In addition, the presence in the tyre of textile fibres of the rayon type and of stearic acid are also sources of biomass and are not evaluated in this case.

→ *Given these limitations, trying to assess the biomass fraction by determining the concentration in natural rubber using this standard cannot be considered to be a reliable method.*

Aliapur thus preferred another approach, directly analysing the carbon concentration of biomass origin (by disregarding the molecule from which the carbon biomass originated), that is, the ASTM D6866-08 method – method B focusing on the biomass carbon¹¹ assay, for this reason considered to be more accurate.

Whilst waiting for finalisation of the method to determine the biomass, which will be standardised at the European level, Aliapur has chosen to use the ASTM D6866-08 method that is recognised in the United States, and has determined the % of carbon biomass at the level of the 12 samples taken in 2007 and 2008 by the BETA laboratory, ISO 17025 certified. This method has in addition been standardised by Aliapur on model mixtures (of known composition).

→ *Aliapur thus recommends using the ASTM method for measuring the carbon14, adapted to all phases (elastomer and textile).*

¹¹ Determining by mass spectrometry the C¹⁴/C¹² ratio producing the “modern carbon” fraction in relation to the “fossil carbon” fraction. Fossil carbon does not contain radioactive carbon as its age is considerably greater than the half-life (5,730 years) of C¹⁴.

III. Appendices

Appendix I: Bibliographical sources

- Préparation et analyse de 7 lots de broyats primaires de PUNR – LRCCP pour le compte d'ALIAPUR – novembre 2007
- Analyses complémentaires de 4 lots de broyats primaires de PUNR – LRCCP pour le compte d'ALIAPUR – avril 2008
- Echantillonnage et caractérisation de granulats de PUNR – BRGM pour le compte d'ALIAPUR – juillet 2006
- Standard Test Methods for Determining Biobased Content of Solid, Liquid and Gaseous Samples Using Radiocarbon Analysis
- Projet XP T47-756 du 31 janvier 2008 – norme expérimentale publiée par AFNOR sur l'échantillonnage et le prélèvement de produits issus de broyage primaire
- Service R&D d'Aliapur 2008 – Caractérisation de broyats de pneus usagés – Composition Élémentaire
- STRATENE – Etude sur les broyats de PUNR en fours Cimentiers – 17 octobre 2006
- Les combustibles utilisés par l'industrie cimentière – Rapport provisoire BRGM/RP – septembre 2008
- Résultats d'analyses de la teneur en carbone biomasse réalisées sur 12 échantillons par le laboratoire BETA accrédité ISO 17025

Appendix II: Excerpt from the circular dated 01 July 2008 from the MEEDDAT – dispensation granted for evaluating the biomass fraction of tyres

Excerpt from the circular dated 01 July 2008 – General dispensation awarded for determining the biomass fraction of used tyres.

The circular specifies that the method to be considered for taking into account this biomass fraction of ELT when calculating CO₂ emissions and the value of the emission factors (t CO₂/T ELT) is:

$$\text{Emissions CO}_2 \text{ non-biomass ELT} = \text{Qty}_{\text{total ELT}} * \text{EF}_{\text{total ELT}} * [1 - 0.146 * (\text{EF}_{\text{biomass ELT}} / \text{EF}_{\text{total ELT}})]$$

Qty_{total ELT} = total mass of tyres (t)

EF_{total ELT} = global emission factor for the tyres (t CO₂/t_{total ELT})

0.146 = mass fraction for natural rubber

EF_{biomass ELT} = emission factor for natural rubber (t CO₂/T_{rubber})

Or

$$\text{Emissions CO}_2 \text{ non-biomass ELT} = \text{Qty}_{\text{total ELT}} * 2.21 * [1 - 0.146 * (3.23 / 2.21)]$$

Appendix III: Detailed analysis methods for the different phases

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Appendix IV: Results of analyses methods on the elementary composition of Passenger car and Truck ELT

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Appendix V: Detailed analysis results for 10 batches of shredded used tyres

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