Physico-chemical properties of Greek End of Life Tyres intended for energy recovery

G. Mavrias[1,*], P. Vounatsos[2], P. Grammelis[2]

[1]Ecoelastika SA, Athens, Marousi, 151 25, Greece
[2]Chemical Process and Energy Resources Institute (ISFTA sector), Centre for Research and Technology-Hellas, Thessaloniki, 57001 Thermi, Greece

Presenting author email: gmavrias@ecoelastika.gr

Abstract
The characteristics and composition of tyres, and consequently of End of Life Tyres (ELT), depend on parameters such as the vehicle type and the climate conditions in which the tyre will be used. ELTs have been under investigation for their characteristics, however, there is not any available literature on the ELT composition produced in Greece, nor for the analysis of each of the components such as textile and rubber crumb. The presented work elaborates on the sampling and analysis of ELT produced and collected in Greece, which are intended for energy recovery. Samples from tyre derived fuel (TDF), textile and rubber of both passenger and truck tyres were collected from two plants, one located in North Greece – Drama Region and one located in South Greece – Attica Region. Sampling was carried out in a three months period following the CEN/TC 343 standards, in order to have an even more homogenous final sample for analysis. The analyses conducted include Proximate, Ultimate, Heating value and biogenic content. Moreover, TDF was analysed for the content in ash and wire, as well as ash composition in major element and minor elements. None of the samples was found to have a moisture over 1% wt and ash content more than 9% wt as received. All of the samples presented Net Calorific Value of more than 26 MJ/kg. An interesting note is that passenger car tyres contain around 35% w.t. dry biomass content, while truck tyres contain around 40% wt. dry biomass content. These facts that can lead to the conclusion that more than 30% of the combustible part of the tyre is renewable while more than 20% w.t. of the tyre is recovered as material through the incorporation in the clinker produced.

Keywords
End of Life Tyres, Physico-chemical properties, energy recovery, thermal valorisation, ultimate analysis, ash analysis

1. Introduction

During the last decade, there is a continuously increasing number of Tyres that are discarded as reaching their end-of life cycle. The methods utilized for treating the used and end-of-life tyres (ELT), lean towards more environmental friendly solutions such as recycling and energy recovery. More specifically ELT management in Europe in 2011 [1] led 1.262 kt for material recovery and 1.231 kt for energy recovery, from which 1.142 kt were recovered in cement kilns while 89kt in other type of plants.
In Greece, thermal recovery accounts for around 50% of ELT treatment, according to the recent data collected and published by the Greek organization ECOELASTIKA which is responsible for ELT collection and management. More specifically, as it is presented in Fig. ***1***, on average 19.000tn of Greek ELT are used annually for energy recovery.

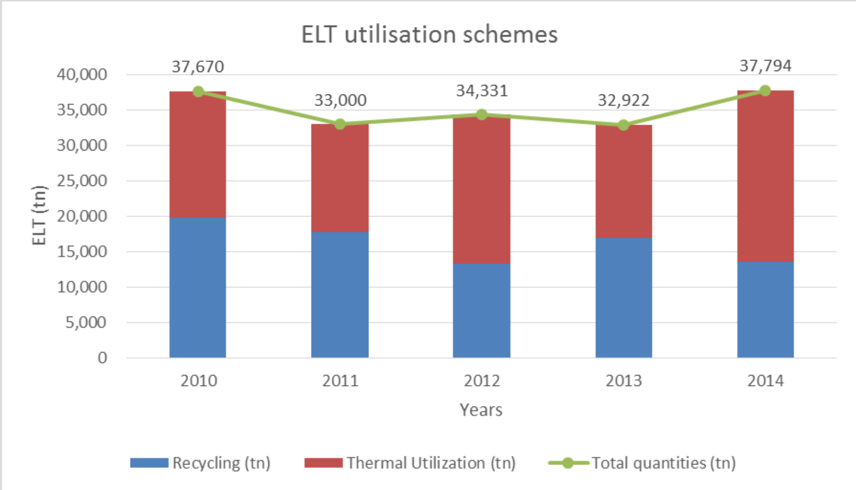

Fig. 1 ELT utilisation schemes and quantities in Greece per type of scheme

Having a high heating value ranging from 28-40 MJ/kg [2], ELTs are mainly used as a substitute of fossil fuels in energy demanding industries such as cement kilns and power plants. For the recovery in cement kilns, Tyres are either used as a whole, cut in half or in the form of Tyre Derived Fuel (TDF) which is chunks of Tyre of certain dimensions and quality. Processing of ELTs takes place in specialized units [3], which through a series of mechanical processes including shredding (TDF production) and granulation followed gravimetric separations produce rubber crumb, textile and wire as is shown in Fig. ***2***.

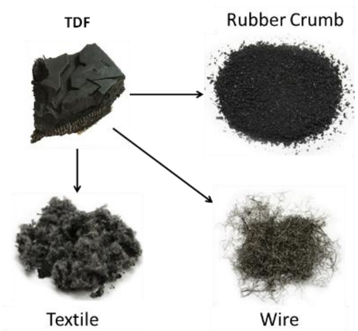

Fig. 2 ELT composition [4]

The characteristics and composition of Tyres (and therefore ELT) vary depending on several parameters, such as: i) the type of the Tyre (passenger car or truck tyre), ii) the producing company, iii) the country in which the tyre is manufactures, iv) the country for which it is produced for, v) Noise production requirements, vi) Speed index etc. [5], [6]. The later years ELTs have been studied in terms of proximate and ultimate analysis [7]-[9] in order to provide a first impression in terms of quality mainly for liquid fuel production through pyrolysis process. However, there is not any available literature on the ELT composition produced in Greece, nor for the analysis of each of the components such as textile and rubber crumb.
The presented work elaborates on the sampling and analysis of ELT produced and collected in Greece, which are intended for energy recovery. The samples were received from two different recycling plants, one located in North Greece – Drama Region and one located in South Greece – Attica Region, in order to have a more representative depiction of the Tyre composition utilized throughout Greece. From the

two aforementioned plants, samples from textile and rubber of both passenger and truck Tyres were gathered, as well as TDF. The samples were collected in a three months period following the European Standards for Solid Recovered Fuels (CEN/TC 343) in order to have an even more homogenous final sample for analysis.
The analyses conducted on TDF as well as rubber crumb and textile, include Proximate, Ultimate, Heating value and biogenic content in order to fully assess the composition of the tyres, combustion characteristics as well as the environmental impact from energy recovery. Moreover, TDF was analysed for the content in ash and wire, as well as ash composition in major element and minor elements. The later analyses were carried out in order to assess the mass and quality of products which would be incorporated in the production of clinker during the thermal recovery in cement kilns.

2. Methods

A brief and concentrated work diagram is presented in Fig 3

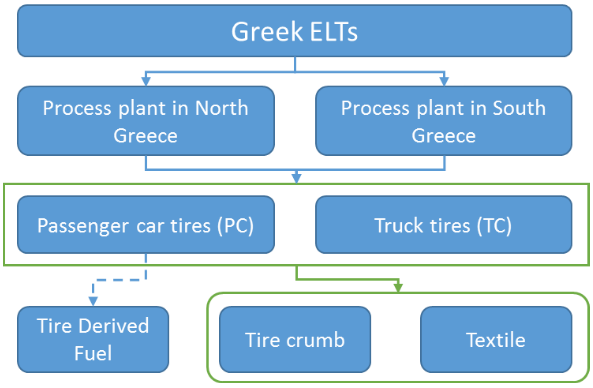

Fig 3 Flowchart of present study

2.1.Sampling procedure

The sampling procedure was designed and implemented according the CEN/TC 343 standard EN 15442:2011 [11]. It was elaborated separately for two sets of analyses due to the different requirements and measuring limitations presented. The first set comprised proximate analysis, ultimate analysis, heating value and biogenic content. During the first set of analyses, the sampling and separation of wire from TDF has taken place because laboratory mills cannot mill/grind the wire included in TDF. Second set was dedicated to ash analysis, wire content of TDF, as well as major and minor elements.
Target of the work elaborated, was to receive results which could be considered representative for all Greece. Therefore, two tyre recycling plants were selected, on located in South Greece and one in North Greece and more specifically near large urban centres such as Athens and Thessaloniki.

A. From South Greece, the recycling plant of ELVAN S.A. was selected, which is located in the industrial area of Aspropyrgos, Attiki. The operation capacity rises to 30.000 tn of ELT per year.
B. From North Greece, the recycling plant of RETIRE SA was selected, which is located in the industrial area of Drama, Region of Eastern Macedonia. The operation capacity rises up to 24.000 tn of ELT per year.

The sampling procedure steps according to the aforementioned standard EN 15442:2011 [11] is presented in the following figure (Fig 4)

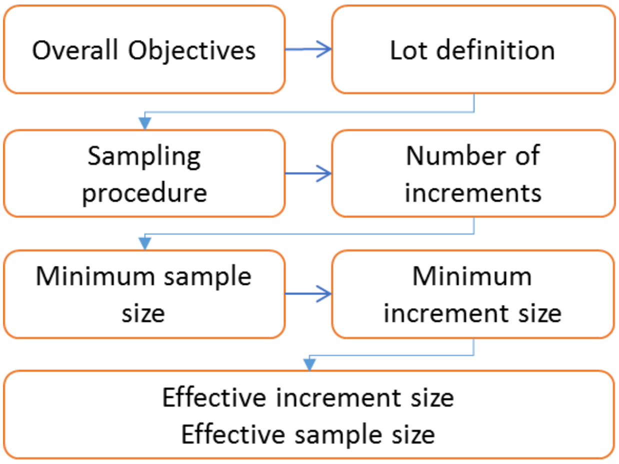

Fig 4 Sampling procedure steps according to EN 15442:2011 [11]

Bellow, the steps for each of the aforementioned recycling plants are presented, regarding the first set of analyses.

ELVAN S.A.

- *Sampling objective:* sampling objective is to gather representative samples for proximate analysis, ultimate analysis, heating value and biogenic content
- *Lot definition and lot size:* Samples were collected during the period of one production day, which cover 20 tn of processed ELT. That was found to be representative taking into consideration the setup of the plant, and the types of ELT it processes. The same procedure was followed for both passenger and truck ELT.
- *Number of increments:* 24 increments from each type of tyre rubber and textile were collected during that day in random time intervals.
- *Sample size:* According to a specific table (D.2) of the EN 15442:2011, the representative sample should be 0.8 kg. In order to be sure regarding the homogeneity of the sample it was decided that the sample size will be 2.5 kg.
- *Increment size:* Increment size was calculated to be 200g
- *Effective sample and increment size:* Increment size was found to be 200g and final sample was found to be 4,8 kg.

RETIRE S.A.

- *Sampling objective:* sampling objective is to gather representative samples for proximate analysis, ultimate analysis, heating value and biogenic content
- *Lot definition and lot size:* During a period of 20 days, in random times in evenly distributed durations, the sampling of 24 increments was carried out from the produced rubber and textile. The same procedure was followed for both passenger and truck ELT.
- *Number of increments:* 24 increments from each type of tyre rubber and textile were during random timings in evenly distributed time periods.
- *Sample size:* According to a specific table (D.2) of the EN 15442:2011, the representative sample was decided to be 2.5 kg.
- *Increment size:* Increment size was calculated to be 200g

- *Effective sample and increment size:* Increment size was found to be 200g and final sample was found to be 4,8 kg.

As far as the second set of analyses is concerned, the same procedure as mentioned above was followed, and the *effective sample size was found to be 36.45kg*, and the *effective increment size was found to be 1.52kg*. In order to have an equally representative sample from Greek ELT, half of the sample was received from the recycling plant of RETIRE SA in North Greece and the rest was received from ELVAN in South Greece.
In the figure bellow (Fig 5) TDF samples from passenger car and truck, are presented. As it is observed, samples derived from truck are thicker than passenger car, have a higher concentration in wire and the wire is bigger in diameter than in passenger car.

Fig 5 Left: Passenger Car TDF, Right: Truck TDF

2.2. Analyses

After collecting the representative sample quantities as presented in the previous paragraph, the sample for analysis was collected after continuous divisions of the sample piles.
Moisture analysis was carried out according to the standard EN 15414-1:2010 [12]. Ash content analysis was carried out following standard EN 15403:2011 [13]. Regarding ultimate analysis (C, H, N, S,), model 2400 CHNS/O Series II of Perkin Elmer was used, with the choice of simultaneous analysis of the elements C, H, N, S. For the determination of the aforementioned elements, standards EN 15407:2011 [14], and EN 15408:2011 [15] were used.
As far as Heating Value is concerned, the samples were analysed according to standard EN 15400:2011 [16], utilizing calorimeter Leco AC-350.
Regarding the second set of analyses, in order to specify ash content and successfully separate wire from the received TDF, a method based on ISO 1171 [17] was followed, which involves several heating steps up to 815^{o}C. After the completion of ashing procedure, the sample was collected including the wire of TDF. The wire was removed using magnets, and ash was collected in order to be analysed in major and minor elements.

For the determination of minor elements, standard EN 15410:2011 [18] was used. The measurement of the minor elements is carried out using the method of Atomic Absorption Spectroscopy with Graphite (GF - AAS) according to the standard EN 15411:2011 [19]. The instrument used is Shimadzu AA-6300 Atomic Absorption Spectrophotometer with GFA-EX7i Graphite Furnace Atomizer.
In Fig 6, the steps of the second set of analyses are presented.

Fig 6 Top Left: sample before ashing, top right: sample after ashing, bottom left: separated wire, bottom right: ash collected

3. Results and Discussion

Following the physico-chemical analyses, the results are presented separately for the two recycling plants in the tables below and for each type of tyre (Table 1, Table 2). The analysis was carried out for each tyre component (rubber, textile) and the TDF composition was calculated by utilizing the average rubber, textile and wire ratio in passenger car and truck tyres as reported by Aliapur [10]. More specifically the ratios used are: passenger car tyres are composed of 80% rubber, 5% textile and 15% wire, while truck tyres are composed of 75% rubber, 0.5% textile and 24.5% wire.

Table 1 North Greece – RETIRE S.A.

	Passenger Car – PC			Truck - TC		
	Rubber	**Textile**	**TDF**	**Rubber**	**Textile**	**TDF**
Moisture (% a.r.)	0.59	2.18	0.58	0.58	1.74	0.44
Ash (% dry)	8.65	5.31	7.19*	7.57	6.18	5.71**
C (% wt dry)	77.98	73.56	66.06	81.56	76.00	61.55
H (% wt dry)	6.73	7.00	5.74	7.28	6.84	5.49
N (% wt dry)	0.78	2.46	0.74	0.59	2.06	0.45

S (% wt dry)	1.43	0.85	1.19	1.24	0.97	0.93
O (% wt dry)	4.43	10.82	4.09	1.76	7.95	1.36
NCV (a.r.)	34.68	27.79	29.13	34.29	29.28	25.86
GCV (dry)	36.40	29.95	30.62	36.02	31.29	27.17
Biogenic content (%wt.)	31.3	53.71	27.73	41.45	52.67	31.35
Biogenic Carbon (%)	22.3	42.83	19.98	32.84	42.66	26.90

* Ash presented does not include 15% derived from wire content
** Ash presented does not include 24.5% derived from wire content

Observing the data obtained from the previous table, there are not notable deviations between the material used for the production of passenger car and truck tyres. The highest difference was observed for Net Calorific Value between the two TDF products. This is attributed to the differences in wire content of the two fuels which equals to about 10% of the fuel weight. The biogenic content presented in the analyses, shows that more than 27% of the fuels under consideration is renewable and it mainly derives from Natural Rubber used during the manufacturing of tyres.
Likewise the data presented in the following table referring to South Greece TDF, present that more than 37% is renewable.

Table 2 South Greece – ELVAN SA

	Passenger Car – PC			**Truck - TC**		
	Rubber	**Textile**	**TDF**	**Rubber**	**Textile**	**TDF**
Moisture (% a.r.)	0.96	1.11	0.82	0.65	1.19	0.49
Ash (% dry)	4.97	9.78	4.47*	5.47	8.91	4.15**
C (% wt dry)	79.62	71.59	67.27	81.47	72.59	61.46
H (% wt dry)	7.24	6.65	6.13	7.39	6.75	5.58
N (% wt dry)	1.83	2.61	1.60	1.79	1.97	1.35
S (% wt dry)	0.89	0	0.71	1.47	0	1.11
O (% wt dry)	5.45	9.37	4.82	2.41	9.78	1.86
NCV (MJ/kg a.r.)	33.06	29.39	27.91	35.03	30.09	26.43
GCV (MJ/kg dry)	35.02	31.16	29.57	36.92	31.95	27.85
Biogenic content (%wt.)	44.54	43.21	37.79	58.34	43.21	43.97
Biogenic Carbon (%)	28.46	33.24	24.43	42.56	33.70	32.09

* Ash presented does not include 15% derived from wire content
** Ash presented does not include 24.5% derived from wire content

Taking into consideration the ratio of tyres collection in South and North Greece, which is 68.03% and 31.97% respectively according to data collected from ECOELASTIKA, the weighted ratio is calculated for the composition characteristics of passenger car and truck TDF, and presented in the following table (Table 3). The column of passenger car without wire refers to the values of TDF-passenger car calculated to 100%, as if the TDF was produced with all wire removed.

Table 3 Average TDF characteristics in Greece compared to literature

	TDF – PC	**TDF – PC without wire**	**TDF - Truck**	**TDF – PC1** Error! Reference source not found.	**TDF – PC2 [22]**	**TDF – PC3 [21]**

Moisture (% a.r.)	0.75	0.88	0.48	0.62	0.84	0.75
Ash (% dry)	5.33*	6.28	4.65**	4.78	9.63	23.37
C (% dry)	66.88	78.69	61.49	83.87	82.52	67.51
H (% dry)	6.00	7.06	5.55	7.09	6.94	5.85
N (% dry)	1.32	1.56	1.06	0.24	0.47	0.25
S (% dry)	0.87	1.02	1.05	1.23	1.7	1.34
O (% dry)	4.59	5.40	1.70	-	-	-
NCV (a.r.)	28.30	33.30	26.25	-	-	-
GCV (dry) MJ/kg	29.91	35.18	27.63	36.02	37.46	31.06
Biogenic content (%wt.)	34.57	-	39.94	-	-	-
Biogenic Carbon (%)	23.00	-	29.77	-	-	-

* Ash presented does not include 15% derived from wire content
** Ash presented does not include 24.5% derived from wire content

Comparing the passenger car values to existing literature **Error! Reference source not found.**, [21], [22], it is observed that in all cases the results do not present significant deviation. Example is that TDF-PC without wire compared to TDF-PC1 and TDF-PC2 which are results without wire present the same quality in terms of ash concentration and heating value. Likewise TDF – PC3 which presents TDF including wire, presents the same trend as TDF 3.
Following the ashing procedure described in paragraph 2.1, the average results regarding wire and ash concentration in passenger car TDF, were found to be 15.42% and 7.44% respectively which is comparable to international literature [10]. Twenty sub-samples analyses are presented in the following table (Table 4).

Table 4 Result from ashing tests

No.	Wire percentage per sample	Ash percentage per sample
1.	20.86%	10.74%
2.	22.31%	6.13%
3.	10.33%	11.20%
4.	8.21%	4.84%
5.	11.82%	6.42%
6.	3.66%	3.54%
7.	13.95%	8.83%
8.	18.24%	4.80%
9.	21.36%	5.77%
10.	16.55%	8.57%
11.	6.87%	5.41%
12.	12.33%	6.70%
13.	14.54%	6.64%
14.	22.12%	7.99%
15.	9.24%	12.54%
16.	18.10%	11.39%
17.	17.76%	12.59%
18.	22.08%	5.06%
19.	15.93%	6.09%
20.	22.03%	3.62%
Average	**15.42%**	**7.44%**

Ash analyses in major elements and minor elements are presented in Table 5 and Table 6 respectively. Major elements are given both as oxide percentages in ash produced, as well as in mg/kg found in TDF.

Table 5 Major elements concentration in ash and fuel

Concentration (%) in ash (dry base)		**Concentration (mg/kg, dry base) in fuel**	
Al_2O_3	10.54 %	Al	4,800
CaO	5.37 %	Ca	3,300
Fe_2O_3	8.97 %	Fe	5,400
K_2O	10.22 %	K	5,300
MgO	8.51 %	Mg	3,200
Na_2O	2.79 %	Na	2,000
P_2O_5	n.d.	P	n.d.
SiO_2	26.65%	Si	17,000
TiO_2	n.d.	Ti	n.d.
SO_3	26.97%	S	9,300
		Total	50,300

* n.d.: not detected –bellow detection limit 0.75 ppm

As observed in the table above, the major oxides which compose TDF ash, are silica, aluminum, potassium, manganese and iron oxide. These five oxides are the ones that are mainly met in ash of most tyres and TDF, and more specifically silica and aluminum oxides which add to more than 50% as this is presented by Singh et al. [23] Minor elements analysis is presented in the following table both as a ppm concentration in and percentage in ash.

Table 6 Heavy metals analysis in passenger car TDF

	Concentration in ppm	**Concentration in % ash**
Antimony (Sb)	n.d.	n.d.
Arsenic (As)	n.d.	n.d.
Cadmium (Cd)	10.48	0.001048
Chromium (Cr)	39.62	0.003962
Cobalt (Co)	1533.41	0.153341
Copper (Cu)	484.22	0.048422
Lead (Pb)	268.73	0.026873
Manganese (Mn)	159.62	0.015962
Mercury (Hg)	n.d.	n.d.
Nickel (Ni)	89.61	0.008961
Thallium (Tl)	n.d.	n.d.
Vanadium (V)	n.d.	n.d.
Zinc (Zn)	183885.51	18.39
Total	186471.20	

* n.d.: not detected –bellow detection limit 0.75 ppm

From the table above, it is observed that five minor elements are below the lowest detection limit of the equipment used which is 0,75ppm. The elements which present the highest concentration are Zinc, Cobalt, Copper and Lead. Zince presents such a high concentration because it is a part of the catalysts which are used during tyre manufacturing. Taking into consideration that average ash concentration in tyre is

7.44%, it is calculated that Zinc concentration in fuel rises up to 1.37% which is in line with Aliapur [10] literature data presenting 1.3-1.5%.
Taking into consideration all of the analyses carried out, it can be seen that during the thermal utilization of TFD, more than 22% can be considered as recycling in cement kilns (ash concentration + wire content) in the case of car tyres and more than 30% in the case of truck tyres. Furthermore, it was found that more than 27% was the biogenic content in both cases, so this lead to the conclusion that more than 28% is renewable and derived from natural rubber.

4. Conclusions

Based on the analyses carried out, it is presented that in all tyre rubber samples both in passenger cars and trucks, present higher NCV than the contained textile. Concerning the analyses of TDF received from south Greece, it was observed that there are not significant deviations between rubber used for car tyres and truck tyres. Similarly, small deviations are presented for textile used in car and truck tyres.
Similarly, regarding the analyses obtained for TDF produced in North Greece, it was observed that there are minor deviations between car and truck tyres. The highest deviation is observed in Net Calorific value and this is mainly based on the difference between Carbon concentration and moisture. Comparing the analyses of car TDF from North and South Greece, the highest deviation is observed in ash concentration which rises up to 2.72%.
Ash and wire content measurements were found to be in line with existing literatures and more specifically content wire measured to be 15.42% compared to 15%, and ash concentration was measured to be between 5-7.5% which is in range of references found providing values from 4 to 9%.
The elements major which present the highest concentration are Zinc, Cobalt, Copper and Lead. Zinc concentration in fuel rises up to 1.37% which is in line with existing literature data presenting 1.3-1.5%.
Taking into consideration all of the analyses carried out, it can be seen that during the thermal utilization of TFD, more than 22% in the case of car tyres in cement kilns can be considered as recycling (ash concentration + wire content) and more than 30% in the case of truck tyres. Furthermore, it was found that more than 27% was the biogenic content in both TDF, so this lead to the conclusion that more than 28% is renewable and derived from natural rubber.

5. Acknowledgements

The authors would like to thankfully acknowledge the contribution of ELVAN S.A. and RETIRE S.A. for their fruitful collaboration during the elaboration of the presented work.

6. References

[1] ETRMA statistics, 2011
[2] M. R. Islam, M. N. Islam, N. N. Mustafi , M. A. Rahim and H. Haniu. Thermal recycling of solid Tyre wastes for alternative liquid fuel: the first commercial step in Bangladesh. Procedia Engineering 56 (2013) 573 – 582
[3] R&D Aliapur, Reference document: Life Cycle Assessment of 9 recovery methods for end-of-life tyres, June 2010
[4] American Tyre Recycling, http://americanTyrerecycling.com
[5] Anne & Russ Evans, The Composition of a Tyre: Typical Components, May 2016
[6] Continental, Tyre Basics: Passenger Car Tyres, 2008

[7] Machin et al, (2017) - Einara Blanco Machin, Daniel Travieso Pedroso, João Andrade de Carvalho Jr., Energetic valorization of waste Tyres, Renewable and Sustainable Energy Reviews 68 (2017) 306–315,
[8] Luo and Feng (2017) - Siyi Luo, Yu Feng. The production of fuel oil and combustible gas by catalytic pyrolysis of waste Tyre using waste heat of blast-furnace slag. Energy Conversion and Management 136 (2017) 27-35,
[9] Ding et al. (2016) - Kuan Ding, Zhaoping Zhong, Bo Zhang, Jia Wang, Addy Min, Roger Ruan. Catalytic pyrolysis of waste Tyre to produce valuable aromatic hydrocarbons: An analytical Py-GC/MS study. Journal of Analytical and Applied Pyrolysis 122 (2016) 55–63
[10] Using used Tyres as an alternative source of fuel – Reference values and characterization protocols, Reference Document, Aliapur, July 2009
[11] EN 15442:2011 "Solid Recovered Fuels – Methods for sampling"
[12] EN 15414-1:2010 "Solid recovered fuels. Determination of moisture content using the oven dry method. Determination of total moisture by a reference method"
[13] EN 15403:2011 "Solid recovered fuels. Determination of ash content"
[14] EN 15407:2011 "Solid recovered fuels. Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content",
[15] EN 15408:2011 "Solid recovered fuels. Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content"
[16] EN 15400:2011 "Solid recovered fuels. Determination of calorific value"
[17] ISO 1171 – Solid mineral fuels – Determination of Ash
[18] EN 15410:2011 "Solid recovered fuels. Methods for the determination of the content of major elements"
[19] EN 15411:2011 "Solid recovered fuels. Methods for the determination of the content of trace elements"
[20] Terry Gray, Tire Derived Fuel Environmental Characteristics and Performance, The First Northeast Regional Scrap Tire Conference Albany, New York June 15, 2004
[21] David Tillman,N. Stanley Harding.Fuels of Opportunity: Characteristics and uses in combustion systems. Elsevier (London) 2004
[22] Mufide Banar, Vildan Akyildiz, Aysun Ozkan, Zerrin Cokaygil, Ozlem Onay, 2012, Characterization of pyrolytic oil obtained from pyrolysis of TDF, Energy Conversion and Management: 62; 33-30
[23] S. Singh, W. Nimmo, P.T. Williams, An experimental study of ash behavior and the potential fate of ZnO/Zn in the Co-combusion of pulverized South African coal and waste tyre rubber, Fuel 111 (2013) 269-279