



Bucaramanga, May 9/2018

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# Characterization of three different solid wastes as energy resources for pyrolysis

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**Abstract.** This work aimed the chemical and thermochemical characterization of three different solid wastes in order to identify promising properties for their further energy valorization by pyrolysis. The chosen materials were: (i) rice husk (RH), (ii) waste tire (WT), and (iii) municipal solid waste (MSW). The characterization techniques used were elemental, proximate, and heating value analyses. In addition, thermogravimetric analyses (TGA) in N<sub>2</sub> atmosphere were also conducted. The obtained results showed that RH has a higher heating value (HHV) of 15.30 MJ/kg and contains less carbon (~41 wt.%) and more oxygen (~38 wt.%) than conventional fossil fuels. The WT has a significant HHV (37.92 MJ/kg) mainly due to their high carbon content (~81 wt.%) and the low oxygen content (~2 wt.%). The MSW, free of metal and glass materials, was mainly composed of volatile matter (~92 wt.%), and showed a HHV of 22.41 MJ/kg. The TG diagrams exhibited different reaction zones which were associated with the decomposition of the main constituents of each sample. This simple but important characterization procedure could be considered as a fundamental tool for the qualification (expected characteristics of the final pyrolysis products) and quantification (maximum conversion efficiency) of the effect of some feedstock properties on the pyrolysis process. In this sense, this work is the starting point for the evaluation of pyrolysis process as an energy valorization method of different wastes.

## 1. Introduction

It is evident the current environmental and social concerns related to the management, valorization and disposal of those materials that have ended their life cycle. The final disposition of these materials, particularly those which present management challenges such as plastics and rubber, has been continuously regulated by a restrictive legislation that makes reuse, recycling and recovery procedures mandatory. These issues have forced the search of proper alternatives and pathways not only to be in line with the current normativity, but also to minimize environmental and public health drawbacks. Moreover, the great dependency on fossil fuels, especially in the transportation and power generation sectors, as well as the environmental impacts associated with their uncontrolled use have motivated some of the main research and development efforts up to date. This has been reflected in the increasing investment on renewable energy projects worldwide, which have been supported through a wide variety of international programs, especially those engaged toward the carbon market, such as the Clean Development Mechanism (CDM) (1), the Verified Carbon Standard (2), and the World Bank BioCarbon Fund (3), among others. In general, there are several factors that have driven the attention toward waste valorization including the environmental damaged case by improperly disposal procedures, non or difficult biodegradability (*i.e.* plastics and rubber), the energy and material recovery potential (*waste to*

energy processes) and the increasing need of recycling hydrocarbons to supply the energy demand for the upcoming years as a consequence of the fossil fuel depletion.

In Colombia, there are 1129 municipalities that produce around 28800 tons of solid wastes per day, with an annual growing rate between 4 and 8% (4). It is estimated that a large fraction of these wastes is disposed inadequately in open dumps, rivers, lakes, and other environmental unsustainable fields, causing a devastating environmental impact. In addition, 110000 tons of waste tires (WTs) are produced each year becoming a serious problem since their very complex structure and composition (*i.e.* vulcanized rubber cured by sulfur, carbon black and silica) make difficult their post-treatment (5). Tires are designed to be extremely resistant to physical, chemical and biological degradation and cannot be treated through simple processes. Moreover, their storage represents a big risk of fire that causes difficulties for their extinction with the subsequent production of highly toxic compounds leading to environmental problems in air, water, and soil, as occurred in: Bogotá (Colombia) in 2014 (6) and Madrid (Spain) in 2015 (7). Roughly speaking, waste management constitutes one of the most challenging problems of daily life in all the countries around the world. Waste management effectiveness depends on several aspects such as the level of technological development, the characteristics of waste, the government support by the establishment of adequate policies, and even the cultural level of the local population (recycling culture) (8).

Despite these drawbacks, municipal solid waste (MSW) and residual biomass have increased their importance as renewable source not only for their potential to produce heat and power using boilers and heaters, but also their ability to be transformed into more versatile fuels such as liquid ones, as well as different types of products for the chemical industry. Currently, biomass and wastes represent around 11 % of the total primary energy supply in the world, estimated to be about 13790 Mtoe for 2015 (9). Although renewable sources are defined as those that can be replenished by nature (hydropower, wind power, solar power, etc.), the Environmental Protection Agency (EPA) has included MSW as a renewable energy resource pointing out that the energy contained in MSW is biogenic, especially when it comes from paper and organic wastes (10). Similarly, WTs could be also considered as a renewable resource since they are produced, in some extent, from natural rubber which is obtained from the *Hevea* tree (11).

Moreover, it is important to highlight that these feedstocks do not threaten food supply and hence, it is not the source of “food or fuel” controversy (12). It has been also established that energy production from residual biomass and wastes will offer to developing countries new income sources by creating new employment opportunities in new bioenergy infrastructures. Thus, this could help to reduce the rural poverty which is one of the Millennium Development Goals (13). In this regard, bioenergy production from residual biomass and wastes seems to be one of the key options for the gradually substitution of fossil fuels (for instance as a counterpart), the mitigation of greenhouse gas emissions and the development of a more sustainable economy model by applying the concept of circular economy. Furthermore, these energy sources can deal with the concern of energy storage to address the problems associated with the intermittent production based on renewable energy such as wind and solar sources.

Power generation from residual biomass and MSWs can follow different conversion routes, known as *waste to energy* processes. These processes include thermochemical (combustion, gasification and pyrolysis) and biochemical (fermentation and bio-digestion) pathways which lead to liquid, solid and gas fractions with high added value in a wide range of applications. Nevertheless, the liquid fraction is particularly more interesting as an energy source because has higher energy density (in volume basis), as compared with gases and solids. Similarly, it can be easily storable, transportable and hence, distributable. In this sense, among all the conversion processes, several authors have highlighted that pyrolysis is much attractive due mainly to its less environmental impact and the possibility to recover liquid and solid compounds with wide potential in the energy and material sectors (14-16). Therefore,

it is considered that the energy contained in any feedstock is recovered in a cleaner way in contrast to other processes such as combustion and gasification. In pyrolysis, lower amounts of nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>2</sub>) are produced due to the inert atmosphere and the lower operating temperatures. Even so, despite these advantages, the selection of any transformation pathway must be based on a detailed understanding of the feedstock physical-chemical properties and the goal fractions to be achieved (liquid, solid or gas).

Therefore, it is important to identify the main characteristics of the feedstock, including residual moisture (RM), volatile matter (VM), fixed carbon (FC), and ash content (proximate analysis), as well as its elemental composition (CHONS). Likewise, thermogravimetric analysis (TGA) provides important and useful information for determining the operational window of these feedstocks under pyrolysis conditions. This characterization is basic but fundamental to define not only proper transformation routes, but also operating conditions. It serves to estimate both maximum process efficiency and expected properties of the resulting pyrolysis products. Taking this into account, this work shows the main chemical and thermochemical properties of three solid wastes to assess their suitability to be considered as energy resources for pyrolysis. These wastes were selected since they are a good representation of the solid wastes generated in Colombia.

## **2. Material and methods**

The chemical and thermochemical analyses used in this work include elemental, proximate and heating value analyses and degradation patterns obtained from TGA. At first glance, this information allows to identify chemical properties, maximum conversion efficiencies and preliminary characteristics of the final pyrolysis products. In addition, TGA helps to define proper operating conditions, especially operation temperatures, in order to reach the maximum release of volatile matter when the feedstock is transformed through pyrolysis. These samples consisted of: (i) rice husk (RH) originally from the department of Tolima (Colombia), (ii) WT, supplied by a Colombian recycling company, and (iii) municipal solid waste (MSW), free of metal and glass materials, generated in one week at Pontificia Bolivariana University (UPB).

### **2.1 Sample preparation**

First, RH sample was ground with a grinding machine to decrease particle size (up to 600 μm, or less). Second, 1.5 kg of a non-specified mixture of milled WT, without both the steel thread and the textile netting, was classified choosing particle sizes under 600 μm. Finally, the MSW sample was obtained from the solid wastes produced in one week at UPB. A mix of plastics, paper/paperboard and organics was selected to carry out all the analyses. These materials are the most abundant combustible fractions of MSW and are considered appropriated for being transformed through pyrolysis. The MSW sample was dried at 105°C for 2 hours in a muffle furnace Terrigeno model D18-Serie 1546, in order to avoid further decomposition and putrefaction. Later on, each material (plastics, paper/paperboard, and organic waste) was ground to decrease particle size.

## **2.2 Methods**

### **2.2.1 Elemental, proximate and heating value analyses**

The standard test methods used to conduct these analyses are shown in Table 1. Likewise, Table 2 reports the standard methods followed to perform the proximate and heating value analysis depending on the feedstock characteristics as well. The RM content was measured using a balance Shimadzu MOC-120H, while ash and VM content were determined gravimetrically by using a Muffle furnace Terrigeno Model D18-Serie 1546.

**Table 1.** Elemental analysis procedure

Parameter	Standard method	Equipment
C, H, N	UNE-EN 15407	Thermo Scientific
O	ASTM D5622-95 (by difference)	Elemental Analyzer
S	Application note 42151 Thermo Scientific	Flash 2000

**Table 2.** Proximate and heating value analyses procedures

Proximate analysis					Heating value
Feedstock	RM	VM	Ash	FC	
RH	UNE-CEN/TS 14774-3 ex	ISO-5623-1974	UNE-CEN/TS14775 ex	By difference	ASTM 240-09
WT	UNE-CEN/TS 14774-3 ex	UNE 32-019-84	UNE 32-004-84	By difference	
MSW	UNE-CEN/TS 14774-3 ex	ISO-5623-1974	UNE-CEN/TS14775 ex	By difference	

### 2.2.2 Thermogravimetric analysis (TGA)

The TGA was conducted in a TA Q50 Thermal Analysis equipment with a weighing precision of  $\pm 0.01$  %. The TGA tests were performed for each waste at three different heating rates (5, 10 and 20°C/min) by using a N<sub>2</sub> volumetric flow of 100 ml/min. These samples were heated from room temperature ( $\sim 25$  °C) to 700 °C and were kept at isothermal conditions for 20 minutes. The particle size used for these tests and all feedstocks was around 300  $\mu\text{m}$  in order to assess only the chemical phenomena. The mass amount was between 14 and 25 mg depending on the material density. With the information collected through these analyses, the conversion grade (X) was determined by means of equation 1.

$$X = \frac{w_o - w_i}{w_o} \cdot 100 \quad (\%) \quad (1)$$

Herein,  $w_o$  is the initial weight of the sample and  $w_i$  is the weight of the sample in each instant of time. TGA and DTG (derivative of TGA) feature important thermochemical parameters such as the initial degradation temperature ( $T_i$ ) and the temperature where the maximum devolatilization rate ( $T_{max}$ ) takes place. These parameters must be taken into account to understand the pyrolysis process of any feedstock. For instance, reactivity can be estimated by analyzing  $T_i$  and  $T_{max}$  in the DTG. Generally speaking, low  $T_i$  values and short periods of time to achieve it, account for more reactive materials since the VM starts being released easily. Likewise, low temperature levels to reach the  $T_{max}$  are also associated with high reactivity. From these parameters, it is possible to find a reactivity indicator ( $R_a$ ) by means of equation 2, which is related to the maximum devolatilization peak in the DTG (17).

$$R_a = \left( \frac{1}{w_i} \right) \left( \frac{dw}{dt} \right)_{\max} \quad (\text{min}^{-1}) \quad (2)$$

Where  $(dw/dt)_{\max}$  is the maximum weight loss rate (mg/min) in the DTG diagram. High  $R_a$  values are linked to high reactivity. This procedure was described by Ghetti (18) to study the reactivity of different coals.

## 3. Results and discussion

### 3.1 Rice husk

RH is an agricultural by-product with low density, which represents approximately 20% of the gross weight of the rice grain (19). The RH represents a production globally around 822 million tons annually (20). Generally speaking, RH is a complex mixture of three polymers: (i) hemicellulose ( $\text{C}_5\text{H}_8\text{O}_4$ )<sub>n</sub>, where n=50–200, (ii) cellulose ( $\text{C}_6\text{H}_{10}\text{O}_5$ )<sub>n</sub>, where n=500–4000, and (iii) lignin (mononuclear aromatic polymers), as well as extractives and ashes. Hemicellulose and cellulose are formed by a polymer chain shorter than the lignin one. From an energy point of view, lignin is considered one of the determining factors along with cellulose for identifying the RH suitability for subsequent processing as an energy

resource (production of bio-char, ethanol, etc.) (21). Indeed, lignin exhibits a high correlation with the higher heating value (HHV) of lignocellulosic feedstocks, as shown in equation 3 (21), where  $Lig$  is the lignin content (wt.% dry basis).

$$HHV = 87.7 (Lig) + 16495 \left( \frac{kJ}{kg} \right) \quad (3)$$

Hemicellulose, cellulose and lignin varied depending on several factors including weather conditions, agronomic handling, type of soil and testing procedures, among others. For RH, hemicellulose ranges from 14 to 28.6 wt.%, while cellulose and lignin varied from 28.6 to 41.5 wt.% and from 20.4 to 33.7 wt.%, respectively (22). In the Colombian case, Marrugo *et al.* (23) found that the RH has a hemicellulose, cellulose and lignin content of 24.50 wt.%, 39.65 wt.% and 35.84 wt.%, respectively (in dry, ash and extractives free basis). Table 4 shows the elemental and proximate analyses, as well as the heating value of the RH sample selected for this work.

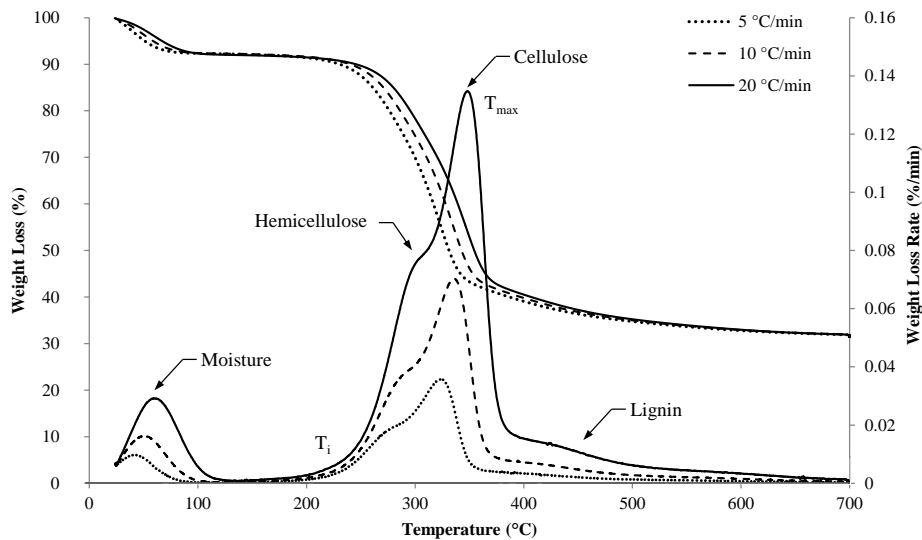
**Table 4.** Elemental, proximate and heating value analyses of RH

Elemental analysis	wt.% (db)	Proximate analysis	wt.% (ar)	wt.% (db)
Carbon	41.13	VM	67.69	71.27
Hydrogen	3.37	RM	5.03	---
Nitrogen	0.33	Ash	16.15	17.00
Oxygen	38.17	FC	11.13	11.72
Sulfur	n.d.	Total	100.00	100.00
Total	100.00	HHV (MJ/kg)	14.53	15.30

n.d.: not detectable

As observed in Table 4, it is noted that RH contains less carbon (41.13 wt.%) and more oxygen (38.17 wt.%) than other fossil fuels such coal and petroleum-based fuels. Also, the HHV is lower than those fossil fuels (15.30 MJ/kg in dry basis). The high oxygen content could be considered as the main drawback when transforming RH by means of pyrolysis. For instance, the liquid fraction resulted from pyrolysis, will have acidic compounds leading to phase separation, repolymerization, coke formation, and insolubility when is blended to conventional fossil liquid fuels (24). Therefore, it will show some difficulties for being used in most of the applications originally developed for conventional fuels. Nonetheless, several techniques such as hydrodeoxygenation and catalytic cracking, blending and emulsification, hydrocracking/steam reforming processes are currently under development in order to improve the quality of this liquid fraction for further implementation in conventional devices like internal combustion engines, boilers, etc. (24). On the other hand, the RH biochar, the solid fraction resulting from RH pyrolysis, has demonstrated a high potential to offset carbon emissions by long term carbon sequestration with additional agricultural benefits such as improvements of soil qualities (fertilizers), and better plant growth (25).

The thermal decomposition of RH depicted in Figure 1 shows three different zones which are linked to moisture, hemicellulose, cellulose and lignin. The first zone is related to the moisture release, which takes place in a temperature range between 25 and 100°C. The second zone corresponds to hemicellulose-cellulose degradation at temperatures between 200 and 400°C. Finally, the third reaction zone, between 400 and 700°C, is mainly associated with lignin decomposition (26). As observed, the degradation rate is no longer significant when temperature reaches 550°C, as most volatiles has already been released remaining the solid fraction (biochar). Moreover,  $T_i$  and  $T_{max}$  are found at ~210°C and ~370°C which are associated with the initial degradation of hemicellulose and the maximum degradation peak of cellulose, respectively. Herein, as the heating rate is increased,  $T_i$  is shifted to lower temperatures, while  $T_{max}$  is shifted to higher temperatures. This phenomenon is explained in detailed later. These results are in accordance to those reported in scientific literature (27).



**Figure 1.** TGA and DTG of RH

Commonly, the behavior of lignocellulosic biomasses during pyrolysis has been referred to the performance of its natural components (hemicellulose, cellulose and lignin). In this sense, it is well-known the slow conversion of lignin, between 160-900°C, contrary to the faster decomposition of hemicellulose (220-315°C) and cellulose (315-400°C) (28). However, these components may interact in different and complex manners along the process which suggests that the final pyrolysis products cannot be associated with the single composition and behavior of each constituent. In other words, when lignocellulosic biomasses are fed into a pyrolysis process, the interactions between these components show a significant influence on the formation of different chemical compounds contained in the liquid, the solid and the gaseous fraction (29).

### 3.2 Waste tire

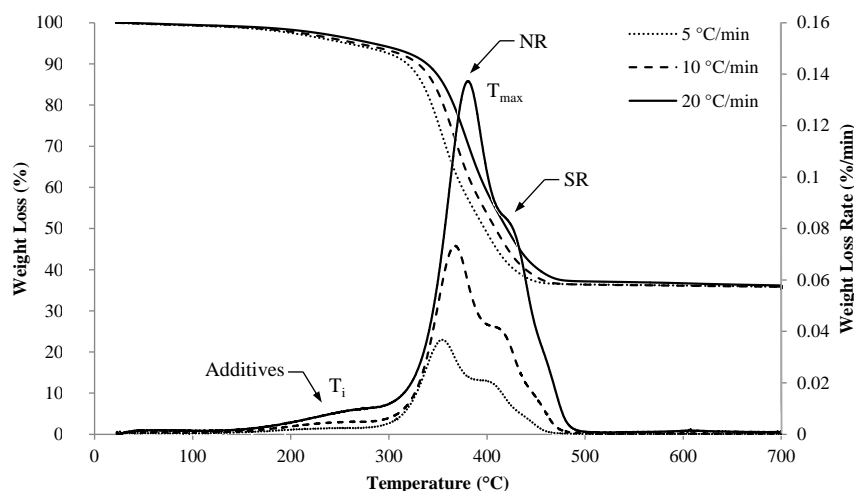
Tires are made of rubber (both synthetic and natural rubber) (60-65 wt.%), carbon black (CB) (25-35 wt.%) and some accelerators and fillers which are added during the manufacturing process. Natural rubber (NR) comes from the *Hevea* tree, while synthetic rubber (butyl rubber (BR) and styrene-butadiene (SBR) copolymer) is generally derived from petroleum-based products. CB, an amorphous carbon of quasi-graphitic structure, is produced mainly by partial combustion of fossil hydrocarbons. Finally, fillers and accelerators consist of organic and inorganic compounds (30). This composition changes depending on brand, age and type of tire (passenger car tire (PCT) or truck tire (TT)). Table 5 points out both the elemental and proximate analyses, as well as the heating value of the WT sample selected for this work.

**Table 5.** Elemental, proximate and heating value analyses of WTs

Elemental analysis	wt.% (db)	Proximate analysis	wt.% (ar)	wt.% (db)
Carbon	81.49	VM	60.66	60.96
Hydrogen	8.21	RM	0.50	---
Nitrogen	< 0.10	Ash	6.48	6.51
Oxygen	1.74	FC	32.35	32.51
Sulfur	2.05	Total	100.00	100.00
Total	100.00	HHV (MJ/kg)	37.73	37.92

As expected, WT have a significant HHV of 37.92 MJ/kg (in dry basis) which is greater than that of coal (bituminous coal which range from 24.5 to 32.6 MJ/kg (17)). This is due to the higher content of carbon (81.49 wt.%). Likewise, the low amount of oxygen (1.74 wt.%) and moisture (0.5 wt.%) lead to

the formation of a high-quality liquid fraction when this feedstock is pyrolyzed, with almost neutral pH, stability, and moderated viscosity and density, among others. Although it can exhibit up to 1 wt.% of sulfur, which hinders its direct application as an alternative fuel (31), this liquid fraction is considered as a potential source in the petrochemical market (32). Several upgrading techniques are currently being studied to improve these properties (33). Similarly, the CB added during the manufacturing tire process is also recuperated after pyrolysis. The CB as well as the inorganic compounds are trapped in the solid fraction (34). Among others, this carbonaceous material can be used for activated carbon production (34), or as solid fuel (HHV ~30 MJ/kg). However, the most attractive application is as substitute of commercial CB, after being upgraded/refined (35).



**Figure 2.** TGA and DTG of WT

The TGA and DTG for WTs also present three different zones related to the degradation of rubber compounds (NR, SBR and BR), as can be noticed in Figure 2. The first zone (200-300°C) is related to the tire rubber additives decomposition; the second zone (310-450°C) (highest peak) corresponds to the NR decomposition; and finally, the third zone (400-500°C) is linked to the synthetic rubber (BR and SBR) degradation (36). Furthermore,  $T_i$  is reached at ~230 °C and is associated with the additives devolatilization, while  $T_{max}$  is obtained at ~370°C and is linked to the NR degradation. On the other hand, as the heating rate increases, the weight loss profile is shifted to higher temperature, as reported elsewhere (37). This means that the degradation rate increases as the heating rate is increased. Likewise, the temperature at which the maximum devolatilization begins and ends is also affected. This phenomenon is attributed to the combined effects of the heat transfer and the changes of devolatilization kinetics of each component (38), resulting in delayed decomposition in terms of temperature. Finally, it is worth to note that pyrolysis reactions start at 200 °C and finish at 480 °C, approximately. Therefore, lower temperatures than 500°C could lead to the incomplete conversion of the WT, especially at high particle sizes.

### 3.3 Municipal solid waste

As commented before, the MSW used in this work is a mixture of plastics, paper/paperboard and organic matter. The plastic waste consisted of plastic bottles (from water, soda, oil, juice, etc.), as well as plastic bags and food packages, among others. It considers a mixture of polyethylene (PE) (low density (LDPE) and high density (HDPE)), polypropylene (PP), and polystyrene (PS). The polymeric structure of both LDPE and HDPE is essentially a long chain of aliphatic hydrocarbons. The difference in density is due to the chain branching (39, 40). In contrast, PP has a different structure than both LDPE and HDPE given the presence of a methyl group ( $\text{CH}_3$ ), while PS is made of styrene monomer and contains a benzene ring ( $\text{C}_6\text{H}_6$ ) (40). On the other hand, paper/paperboard waste comes from newspaper,



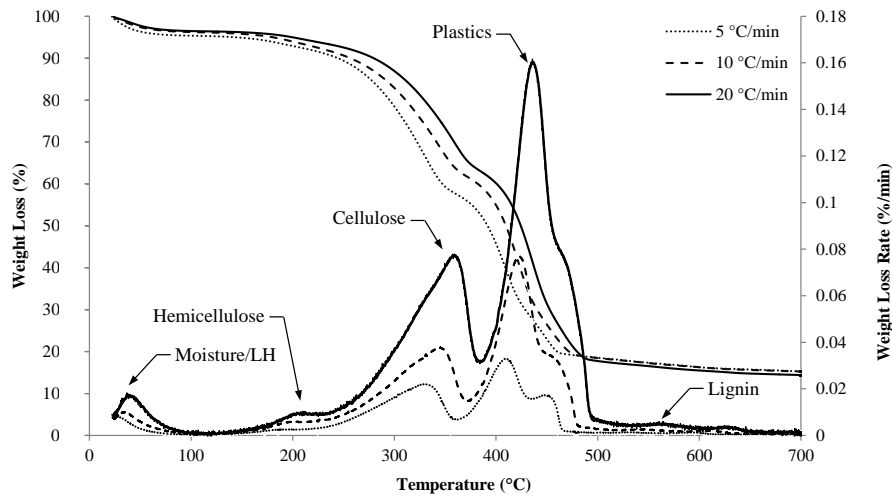
boxes, glossy paper, cardboard, etc. The common element of these materials is pulp obtained from wood. Wood is composed by cellulose (40-45 wt.%), the skeletal polysaccharide; hemicellulose (27-39 wt.%) which form the matrix; and lignin (21-30 wt.%), the encrusting substance that binds the cells together (40). Additionally, wood contains many low molecular-weight organic compounds (2-5 wt.%) and small amount of mineral matter (0-3 wt.%). Finally, the organic waste is a mix of different fruit peels and vegetable wastes. All they are mainly lignocellulosic materials and the content of cellulose, hemicellulose and lignin depends on their specific nature. Table 6 shows the elemental and proximate analyses, as well as the heating value of the MSW. It is important to point out that the RM reported in Table 6 is the final moisture once the sample was dried and stabilized to avoid putrefaction and decomposition (initially a moisture content around 80 wt.%).

**Table 6.** Elemental, proximate and heating analyses of the MSW

Elemental analysis	wt.% (db)	Proximate analysis	wt.% (ar)	wt.% (db)
Carbon	55.67	VM	87.69	92.45
Hydrogen	6.73	RM	5.15	---
Nitrogen	< 0.10	Ash	2.28	2.40
Oxygen	35.20	FC	4.88	5.14
Sulfur	< 0.10	Total	100.00	100.00
Total	100.00	HHV (MJ/kg)	21.26	22.41

The properties of the lignocellulosic fraction (paper/paperboard and organic wastes) are quite different in contrast to plastics. This fraction usually presents a FC content between 10-20 wt.%, while the VM ranges between 20-30 wt.% (41). However, plastics contain up to 90 wt.% of VM since they come from petroleum-based products (42). This fact explains the high VM in the MSW (92.45 wt.% in dry basis) as well as the HHV (22.41 MJ/kg in dry basis) due to the high share of plastics (up to 50 wt.%) into the MSW selected in this work. Similar to RH, the main drawback of the MSW sample for being transformed by means of pyrolysis is the high oxygen content (35.2 wt.%).

On the other hand, Figure 3 shows the TGA and DTG of the MSW. Similar to the results obtained for RH and WTs, different zones can be identified. However, as the sample is a complex mixture of different components, the identification of each compound, as made for the other samples, represents a difficult task. However, Sorum *et al.* (40) studied the plastics and paper behavior separately by using TGA/DTG in order to have a better understanding of this phenomenon. They found that the major weight loss of cellulosic matter (paper) occurred at 250-400 °C, with a maximum devolatilization point between 355 and 371 °C. These results were expected taking into account the negligible presence of lignin in the feedstock analyzed by authors which reduces the degradation time. On the other hand, the degradation of plastics (PS, PE and PP) presented a slight weight loss within a narrow temperature range from 80 to 100 °C. Then, the major devolatilization took place at temperatures of 350 and 500 °C with a maximum peak between 413 and 479 °C. Similarly, Miranda *et al.* (43) analyzed the thermal decomposition of sweet orange dry peel by using TGA/DTG at different heating rates (1, 5, 10, 20, and 40 °C/min). They found four stages of weight loss and four peaks at 47 °C, 223 °C, 346 °C, and 479 °C, which were associated with degradation of water soluble components, hemicellulose, cellulose and lignin, respectively. According to these results, it can be inferred that the first peak in Figure 3, between 25 and 100 °C, can be attributed to the release of moisture and some light hydrocarbons (LH) (coming from plastics which degrade in a narrow temperature range of 80-100 °C). The second and third peak can be related to degradation of hemicellulose/cellulosic compounds (paper, organic waste). The fourth peak is linked to the maximum weight loss rate of plastics; while the fifth peak is associated with the lignin degradation.



**Figure 3.** TGA and DTG of MSW

Finally, Table 7 gathers the  $T_i$ , the  $T_{max}$  and the devolatilization velocity associated with the highest peak ( $R_a$ ) for all the samples. Likewise, Table 7 reports the (C+H)/O and VM/FC ratios, which are considered a chemical criterion to evaluate the reactivity, especially in the case of gasification and/or combustion applications (17). According to Ghetti (18), feedstock with high oxidation grade, which means low (C+H)/O ratio, are more reactive during combustion and gasification. Similarly, and under oxidations conditions, the higher the VM/FC ratio, the higher the devolatilization rates and also a more reactive feedstock (17). In the case of pyrolysis process, it is difficult to determine the reactivity from these relations because more complex kinetic phenomena are involved. Even so, the VM/FC ratio provides the theoretical process efficiency in terms of volatiles and solid fraction yields.

**Table 7.** Reactivity analysis

Feedstock	Heating rate (°C/min)	$T_i$ (°C)	$T_{max}$ (°C)	(C+H)/O	VM/FC	$R_a$ (min <sup>-1</sup> )
RH	5	210	321	1.26	6.08	0.036
	10	208	334			0.070
	20	205	347			0.134
WT	5	300	348	29.31	1.86	0.037
	10	294	362			0.074
	20	212	375			0.138
MSW	5	267	407	1.94	17.96	0.034
	10	246	422			0.079
	20	194	435			0.162

As observed RH and MSW are more reactive for combustion and/or gasification applications in contrast to WTs due to their lower oxidizing grade (lower (C+H)/O ratio). However, RH and MSW tend to release more VM than WT due to their higher ratios of VM/FC, which could be benefit for pyrolysis for obtaining more liquid and gas fractions. In terms of degradation temperature and velocity ( $R_a$ ), it can be inferred that these values are strongly influenced by the heating rate. Therefore, it is seen that higher heating rates lead to higher devolatilization velocities and  $T_{max}$ , but lower  $T_i$ .

#### 4. Conclusions

RH, WT and MSW were analyzed by elemental, proximate and heating value analyses. WT has the greater HHV (37.92 MJ/kg in dry basis), followed by MSW (22.41 MJ/kg in dry basis) and RH (15.30 MJ/kg in dry basis). Also, WT can be regarded as a promising feedstock for pyrolysis mainly due to the low oxygen (~2 wt.%) but high carbon (~81 wt.%) that promote the formation of a high-quality liquid fraction to be used as a fuel. Contrary, RH and MSW are characterized for a high oxygen content (~38 and ~35 wt.%, respectively) which lead to the formation of oxygenated compounds in the liquid fraction

after pyrolysis. Hence, a low pH and high instability are expected. However, they can serve as precursors for interesting and value-added chemical compounds. From the TGA, it was observed that 550°C is enough to conduct the pyrolysis process for all these feedstock. Higher temperatures do not improve the devolatilization process because at this temperature the pyrolysis has been already completed (in the case of WT) or is no longer significant (in the case of RH and MSW). In addition, DTG showed different degradation zones for all the components of the WT (NR, BR and SBR) and the RH (hemicellulose, cellulose and lignin). However, for the MSW this identification is more complicated since the sample is complex mixture of different components (plastics, hemicellulose, cellulose and lignin). On the other hand, RH and MSW tend to release more VM than WT due to the higher ratios of VM/FC (~ 6 and ~18 respectively).

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