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Proiect POSDRU/88/1.5/S/61178 – *Competitivitate și performanță în cercetare prin programe doctorale de calitate (ProDOC)*



## UNIVERSITATEA POLITEHNICA DIN BUCUREȘTI

Facultatea de Energetică

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Faculty of Engineering

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# TEZĂ DE DOCTORAT

*ANALIZĂ CRITICĂ A PROCESELOR DE PIROLIZĂ ȘI GAZEIFICARE  
APPLICATE FRAȚIILOR DE DEȘEURI CU POTENȚIAL ENERGETIC  
CRESCUT*

*CRITICAL ANALYSIS OF PYROLYSIS AND GASIFICATION APPLIED TO  
WASTE FRACTIONS WITH GROWING ENERGETIC CONTENT*

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Politehnica University of Bucharest



University of Trento

# PhD THESIS

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## LIST OF SYMBOLS AND ACRONYMS

ASS	Air System Separation
ATTW	Advance Thermal Treatment of Waste
BS	Ballistic Separator
DOE	U.S. Department of Energy
ECSS	Eddy-Current Separation System
FC	Fixed Carbon
HHV	High Heating Value
HHV	High Heating Value
HSLT	High Speed, Low Torque hammer mills
IGCC	Integrated Gasification Combined Cycle
IMSWMS	Integrated Municipal Solid Waste Management System
ISWMP	Integrated Solid Waste Management Plan
LCA	Life Cycle Assessment
LHV	Low Heating Value
LSHT	Low Speed, High Torque shear shredder.
MBT	Mechanical-Biological Treatment
MS	Magnetic Separation
MSW	Municipal Solid Waste
MW	Molecular weight
NVS	Non-Volatile Solids
PCW	Paper and Cardboard Waste
PP	Polypropylene
PS	Polystyrene
PSW	Plastic Solid Waste
RDF	Refuse Derived Fuel
RH	Relative Humidity
RMSW	Refused Municipal Solid Waste
SC	Selective Collection
SDF	Solid Derived Fuel
SRF	Solid Recovered Fuel
SWOT	Strengths, Weaknesses/Limitations, Opportunities, and Threats
T.E.P	Tons of Equivalent Petroleum
UNEP	United Nations Environmental Programme
VS	Volatile Solids
WtE	Waste to Energy

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*Let your imagination take shape*

## CHAPTER 1

### 1. INTRODUCTION

The research **aim** is to establish the optimum energy efficiency conversion line using thermal-chemical processes with application for a decentralized integrated scenario models with material and energy recovery from Municipal Solid Waste (MSW). The research, in particular, **focuses** on the experimental and theoretical characterization of the light combustible packaging waste patterns conversion process, which can be considered as contribution for future development of an integrated plant for energy production. The research will conclude with a novel model based on advanced waste pre-treatment leading to an original set of conversion chain configurations to a sustainable Integrated Municipal Solid Waste System (IMSWS).

The research **objectives** are:

- contribute to the knowledge on cellulosic and polymeric wastes transformations during pyrolysis and gasification processes;
- optimize the light packaging waste mixture gasification process in order to provide high quality syngas and energy efficiencies;
- develop an IMSWS focused on: feasibility assessment study, sensitive analysis, technological and environmental benefits.

#### 1.1. Trends in Municipal Waste Management

The growth of living standard had led to the drastic increasing in waste generation. According to the statistics, it's estimated that EU-27 produces annually over 250 million tonnes of municipal solid waste, ranging from 316 kg per capita in the Czech Republic to 831 kg per capita in Denmark [1].

Besides the demography, climate, socio-economic and industrial development, the variation rates are affected by the lack of information between environmental policy-makers, manufactures and stakeholders.

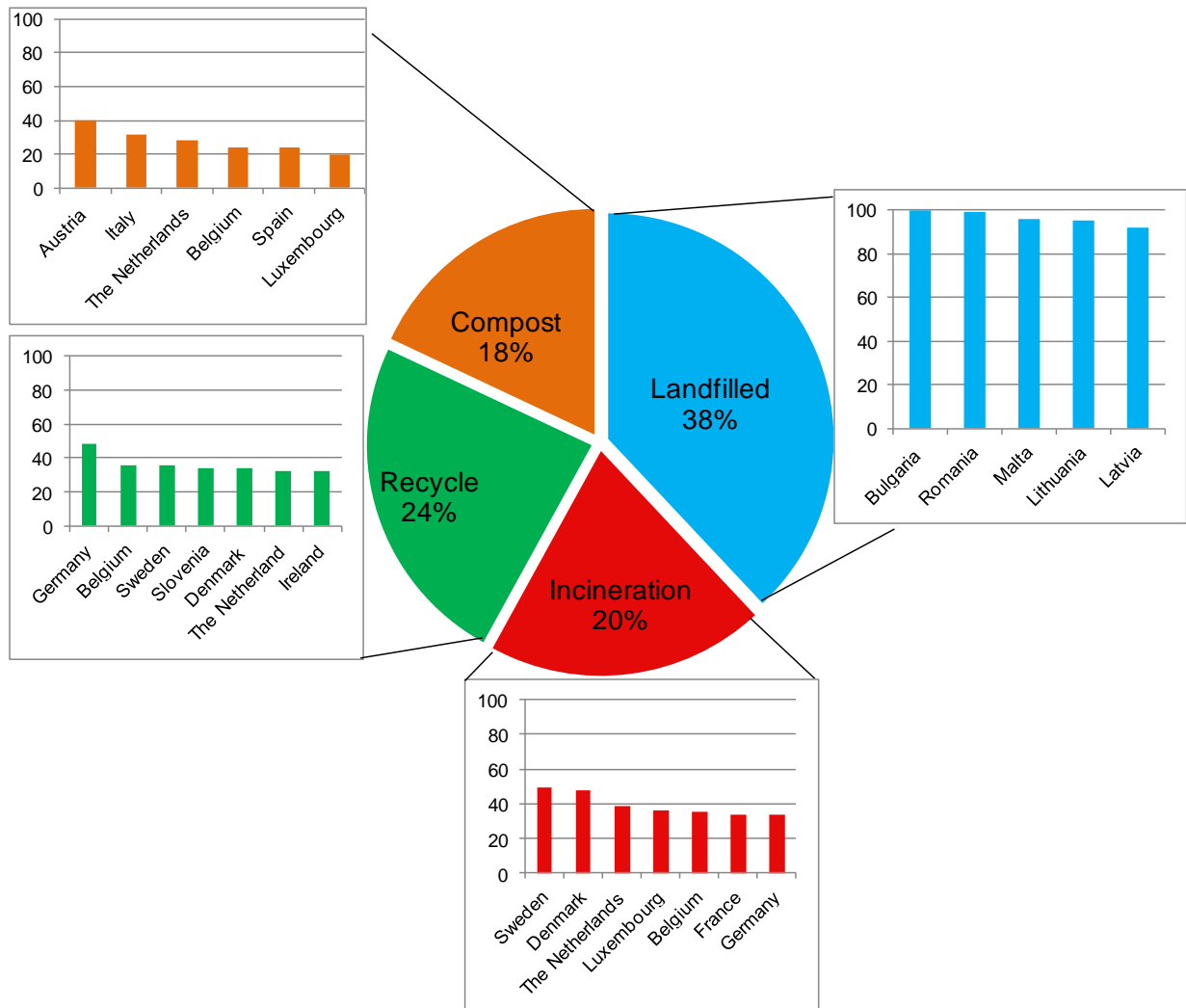
After decades of experience, the design and implementation of an Integrated Municipal Waste Management System (IMSWS) is still challenging. The complexity of a sustainable strategy mainly comes from: the high various sources of wastes, the quantitative and qualitative characteristics, the technological restrictions, but mostly from human factor concepts BANANA (Built Absolutely Nothing Anywhere Near Anyone), LULU (Locally Unwanted Land Use), NIMBY (Not in My Back Yard), NOPE (Not On Planet Earth), or NOTE (Not Over There Either). In long term vision, the eco-efficiency of any Integrated Municipal Solid Waste Management System (IMSWMS) has to have 3 dimensions: sustainability, society and economy.

##### 1.1.1. Current status and issues of MSW treatment

Looking over the enhancement hierarchy of waste management, in the first place, waste preventing is the most sustainable option. Practice shows that in a consumer's society, such as European Union, the waste volume has grown with 11.5% in 12 years and might with 45% by 2020 [2].

By legislation, this issue is covered by the Sixth Environment Action Programme (2002–2012) which has as overall goal on the decoupling of resource use and waste generation from the rate of the economic growth. Because of its slightly progresses the commission proposes to continue it by 2020.

In 2009 the municipal waste European average was 513 kg per capita from which: 38% was landfilled, 20% incinerated, 24% recycled and the remaining of 18% composted as shown in Figure 1.1.



**Figure 1.1. Current EU status in Municipal Solid Waste Treatment**

The largest amount of waste fraction from the MSW composition is the biodegradable waste, followed by paper and cardboard with 38%, plastics with 30% and an overall annual packaging waste increase of 4%. In 2009, the packaging waste averagely generated by citizen was estimated to 163 kg/inh/year in EU-27 [2]. The packaging waste composition in Romania and EU-27 is presented in Figure 1.2.

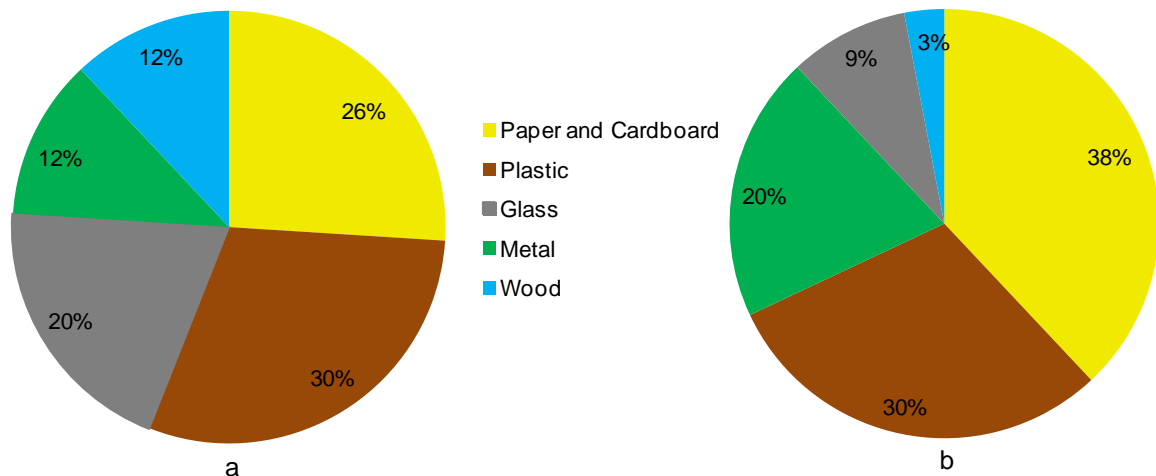


Figure 1.2. Packaging waste composition in Romania (a) and EU-27 (b) in 2009

The **reuse option** is closely related to a number of issues such as urban lifestyles, resource consumption patterns, jobs, income levels and cultural factors. Still is also becoming more financially attractive in terms of: post-consumer materials separation, re-processing and re-manufacturing. A new concept of reusability is gaining momentum within the industrial level – refurbishment. Refurbishment is when a product is returned to the original manufacturer, is tested, restored to its original condition and is resold [3].

**Recycling** involves costly sorting and treatments during which pollutants present in waste may be transferred to the environment or incorporated into new products. In Europe (Fig. 1.1), the strongest growth in the last decade, has been shown by Ireland in first place, which quadrupled its non-wood recycling rate from 15% to 60% , followed by Italy with growth from 29% to 62% in second place and the UK third (30% to 60%)[4]. For the optimization of Selective Collection (SC), users play an important role. The lack of professional standards for waste management and the need to educate the citizens strongly influence the sorting quality. This problem can be avoided through eco-activities and household collection campaigns. If separation is not done by consumers it employs a wide range of technologies, space limitation and costs. A series of tools have been discussed (Zotos et al., 2009; Cosmi et al., 2001), focusing on the fact that the local authorities should play a key role in supporting the changes towards sustainable development [5,6].

As the literature shows [7], increasing recycling rates from 15% to 50% increases cost by a factor 3, while environmental impact remain broadly similar. In terms of plastics, combining 15% mechanical recycling with 85% energy recovery offers the most eco-efficient recovery scenario.

Previous studies regarding the Life Cycle Assessment (LCA) of packaging waste recovery, reveal that recycling is a convenient energetic measure due the energy savings made by the production of second raw materials in comparison with virgin ones. In percentage terms, the production of paper paste and pulps shows a 99% energy saving, closely followed by aluminium with 94%, plastics with 91% and glass with 41%. In other words, the recycling of aluminium materials permits a 187.834 MJ<sub>eq</sub> saving for each ton of raw material produced and plastics with 72.573 MJ<sub>eq</sub>/t [8].

Nowadays, in Romania SC has not been adequately developed yet. Nevertheless, in some regions, the authorities have adopted different pilot strategies in order to improve the waste management system [9]. Generally, SC regards the materials that can be economically valorized, such as packaging one.

According to the Romanian plastic/cellulosic stock exchange, in 2011, the prices of recycled PET flakes varies between 550-600 \$/tonne in comparison with cellulosic 120-140 €/tonne. Yet, the waste recycle market isn't stable due to the economical trends. For example, the global crises had an important impact on the stock waste market that drop from 86 €/tonne cellulosic material recycled in 2008 at 2 € /tonne in 2009[10]. Conform the National Environmental Protection Agency (ANMP, 2009), in 2007, from the total quantity of packaging placed on the Romanian market (1,287,018 tonnes), only 37% was recovered and 31% recycled [11].

Presently the *recovery* is desired in terms of thermal disposal, especially incineration with energy recovery, a viable form of waste-to-energy (WTE) valorisation often used in industrialized nation.

In the last decade, the Waste to Energy (WtE) global capacities doubled up to 350 million annual tonnes. In the next five years, it can be expected a further growth at almost 420 million annual tonnes of waste treated. For EU-27, it's clear that the countries with no energy recovery facilities (Romania, Bulgaria, Cyprus, Greece and Malta) also achieve relatively low recycling rates because their waste management infrastructure in general is at an early stage of development. In Europe there are 467 municipal solid waste incineration plants with a total capacity of 49.7 Mt/y [12]. As presented in Figure 1.1, they are most used in Sweden with 49%, followed closely by Denmark with 48%, the Netherlands 39%, Luxembourg 36% and Belgium 35% respect to the methods used for waste disposal.

In spite all that, the current status of waste management shows that landfill is the preferred option in the EU and many other industrialized countries, even though it can cause leaching of contaminants into soil and groundwater. According to Eurostat (Figure 1.1), in 2010 Bulgaria landfilled 100% of its treated waste, followed by Romania with 99%, Malta with 96%, Lithuania with 95% and Latvia with 92%.

Today, in Romania, about 95%-99% of MSW goes to the landfill without pre-treatment. However, Romania has obtained a transition period (until 2017) for the closure of the old landfills (open dumps). At the moment, in Romania, a thermal/incineration plant for MSW valorization doesn't exist. At national level, it is possible to send some MSW fractions, together with other raw materials that has a high quantity of combustible materials, for co-combustion in cement factories.

### **1.1.2. Basic waste management legislation in European Union**

The policymakers are mainly focused on environmental and economical strategies. The last trends in the European Union directives on waste management are based on strict targets that imposed the recycling of materials, energy generation and waste treatment before disposal.

Since the 1<sup>st</sup> of January 2007 Romania has been one of the EU-27 countries that had to implement and comply with all the European Directives regarding waste management: waste reduction, recycling, reuse and energy recovery. Since 1993, Romania has created a national data base regarding MSW and industrial waste generation and management. Data have been reported to EUROSTAT and to the EEA (through EIONET) [13]. The waste management plans are elaborated by the Local and Regional Environmental Protection Agencies under the coordination of the National Environmental Protection Agency in conformity with Romanian Law no 27/2007 on waste.

In 1999, Directive 99/31/EC includes the keys of waste landfilling through measures, processes and guidelines that could avoid or reduce the irreversible environmental impact starting at local level (surface and underground water, soil and atmosphere) and global level (primarily by greenhouse effect and human health). Pursuant to Article 5(1) of the Directive, Member States must set up a national strategy for the implementation of the reduction of biodegradable waste going to landfills with 50% by 2013 and by 35% by 2016, taking into account the production of 1995.

In 2004, Directive 2004/12/EC (European Commission, 2004) updated Directive 94/62/EC and redefine targets for packaging and packaging waste recovery and recycling. In these context it is foreseen a recovery degree of useful materials from waste packaging for recycling or incineration with energy recovery of 60% for paper or cardboard, 22.5% for plastics, 60% for glass, 50% for metals and 15% for wood and an overall valorisation of 50% of MSW by 2020.

Directive 2005/20/EC imposes some later deadlines for wastes valorisation until 2015 for certain Member States such as: the Czech Republic, Estonia, Cyprus, Latvia, Lithuania, Hungary, Malta, Poland, Slovenia, Slovakia, Romania and Bulgaria.

The primary concern regarding waste thermo-chemical treatments are the emission values and their impact on the environment as a whole. The European Union and the United States have defined all the best available technologies (plasma, pyrolysis and gasification) as forms of incineration. The Waste Incineration Directive 2000/76/EC is designed to impose limits on greenhouse gas emissions for both prevention and reduction. Thus WtE Plants are environmentally sound energy recovery operations and complementary to the recycling targets.

### **1.1.3. Integrated Solid Waste Management Plan**

The MSW management is an important part of urban infrastructure that ensures the environmental protection and human health. Currently the wide range of attractive MSW treatments, offers a multitude of possibilities and combinations of processes and technologies that lead to different designs and solutions for waste management plans. The United Nations Environmental Programme (UNEP) had compiled four sets of guidelines on Integrated Solid Waste Management (ISWM): quantification and characterization of solid waste streams from different sources, assessment of solid waste management systems, target setting and identification of stakeholders' issues and guidance manual for preparation of ISWMP of a city. All these guidelines lead to the most important characteristics of any system – sustainable development [14]. Some studies show that reducing waste generation in the first place is the most sustainable option. One of the most important stakeholders is a local community that has to modify the behaviour patterns through eco-activities. The efficiency of MSW selective collection has an important role in the characteristics of Residual Municipal Solid Waste (RMSW), therefore also on the thermal treatment technology [15]. If separation is not done by consumers it employs a wide range of technologies, space limitation and costs. The separation process requires shredder, special drums, conveyor belts and trammels to divide the waste stream into the different material fractions. Nevertheless with all process handpicking it is essential for the separation of certain wastes.

#### 1.1.4. Selection criteria of waste with growing energetic content

In this context the waste disposal as renewable source has become a global necessity in terms of sustainable and long-lasting environmental protection. Due to the high various sources of wastes, the quantitative and qualitative characteristics of the final product might change by: heterogeneity in form and density, moisture matter, biodegradable content and porosity distribution which are not uniform but are randomly distributed over the entire waste yield.

In **the first part** of the research the selection of the light packaging waste as study material was made due its consisted quantity in the MSW stream, its energetic potential and the increasing interest regarding its treatment in WtE alternative plants. The selection criteria were the basis of the primary questions raised at the beginning of the study:

1. Are the light packaging waste physical-chemical characterization data presented in literature similar with plastics, paper and cardboard waste stream coming from the SC of different countries, especially Romanian as main case study?
2. What process parameters can be improved to optimize the pyrolysis and gasification processes of light packaging waste?
3. Which are the technological considerations that had to be studied in order to obtain WtE maximum conversion and low environmental impact from pyrolysis and gasification processes of light packaging waste?

An experimental study on physical-chemical characterization, pyrolysis and gasification processes on light packaging waste fractions complete the first part of the research.

**The second part** of the research was developed by considering: the experimental data obtained in the first part of the research, the same EU legislation but different national waste management strategies and different MSW compositions. Several IMSW scenario models were developed for South- Eastern and Central Europe-like regions.

The following criteria served as the basis in the case studies selection and waste treatments:

1. Nature and MSW flow
2. MSW heterogeneity respect to SC optimization
3. Energy potential of the products
4. Non-volatile solid content
5. Best available technologies on waste advance mechanical sorting and advanced thermal treatment.
6. Efficiency of the waste treatment process and their applicability at large scale
7. Type of co-generation plant.

**The final goal** of the IMSW scenario models proposed represents a good example of future waste management models with practical applicability. The latter offers a sustainable IMSWS of life cycle recovery (material and energetic) with positive environmental impact by using the best available technologies suitable for commercial scale practice.

## **1.2. Overview of Waste to Energy alternative processes**

An overview of advanced thermal treatments is presented in the sub-chapter for pyrolysis and gasification processes in terms of: state of the art review, process stages, waste thermo-chemical conversion, process outline, operating parameters, process efficiency, reactors types, and technological, operational, environmental and a brief economical comparison of both processes respect to incineration.

### **1.2.1. State of the art**

In the last years, much effort has been focused to develop environmentally friendly technologies that use waste feedstock as alternative to fossil fuels. These types of products have two major advantages for power generation sector: reduction of specific primary energy consumption which has a direct effect on air pollution and reduce energy resource demand in accordance with rapid reduction of fossil fuel reserves. Even if the waste sources have a high energetic potential, the power sector is reluctant to major structure modifications because of: waste availability and homogeneity, technological and economical block that have to be overcome before alternative energy can replace even a small portion of the power provided by fossil fuel. Currently Romania doesn't have a developed technology with full recovery of waste. For example, this country does not excel in the selective collection system [16]. In these times, the poor amount of sorting/removing equipment of waste mixture reduces the exploitation of household wastes in short and medium terms. In the long term it is necessary to conduct an analysis to determine the opportunity to acquire existing technologies and use these types of wastes, considering the fact that this practice is widely applied in the countries of Northern and Western Europe. European countries apply this technology in the energetic field, because it represents an economic benefit as fuel and disposal solution.

Even though the combustion process has benefits from the technological simplicity point of view, the waste thermal disposal poses potentially serious air pollution problems due to the release of harmful gases such as dioxins and hydrogen chloride (chlorine content), airborne particles (high treatment temperature) and carbon dioxide [17]. Unlike fossil-fired power plants, MSW incinerators have significantly lower energy efficiencies (13–24%) mainly due to lower steam temperatures to prevent severe boiler corrosion, fouling and slagging (fireside problems) and high air excess (up to 1.8). In energy efficiencies this result is typically about 15% [18]. Only a plant got 30%.

In the last years, pyrolysis and gasification technologies have emerged to address these issues and improve not only the energy output, but also the greenhouse emissions. These modern technologies offer an alternative process that devolatilizes solid or liquid hydrocarbons and convert them in by-products as energy carriers, offering both upstream (feedstock) and downstream (product) flexibility. The U.S. Department of Energy's (DOE) 2010 have compiled information about waste-to-energy facilities using pyrolysis and gasification technology either in construction, operation or proposed for operation. Currently, there are more than 45 operating plants which are using the pyrolysis process for waste treatment or integrated with other thermo-chemical conversion technologies, especially gasification. Most of them are in Japan, twelve treating biomass, industrial waste and sewage sludge. Also countries like Germany, USA and UK have operating plants which use pyrolysis as a first stage pre-treatment process for municipal and hospital waste to energy conversion [19]. At the moment, most of the operating facilities treat between 8,000-225,000 tonnes/year of biomass, domestic waste, industrial waste, medical

waste, MSW. The pyrolysis/gasification power generation plant with simple cycle has an energy performance of 11-20%, less efficient in comparison with modern combustion.

Although some of the new technologies are called ‘gasification’, in fact they are ‘gasification-combustion’ processes, Integrated Gasification Combined Cycle (IGCC) power plant, where the calorific value of the MSW is recovered in the form of steam (as in conventional WtE processes). The technological suppliers claim that this option permits the supply of fuel gas into a CC gas turbine increasing the technological performances of pyro-gasification plant at 24-30% making it more energetic efficient than incineration. Special attention will be given to the Advanced Thermal Treatment (ATT) efficiencies in the gasification section due various data claimed by researchers, technology providers and applicability to real scale. The quality of synthesis gas derived from MSW depends on the unique characteristics of the feedstock, gas cleanup for impurities, chlorine content and tars formation at high temperature and pressure, which could cause problems in downstream processes and economic exploitation.

Plasma gasification technology represents the latest development in WtE industry, with only 3 plants in Japan are intended to operate on MSW [12]. Literature is controversial [20] and shows that experiences with plasma gasification technology is still only theoretical and small-scale, no more than 300 tonnes/day MSW, when it comes to commercial industrial application.

In conclusion from the above mention, the current information about the industrial status of the existing Advance Thermal Treatment of Waste (ATTW) leaves signs for interpretation given the fact that most of MSW pyro-gasification or IGCC plants are operable on biomass or biodegradable matter. Primarily the challenges of a MSW gasification plant commercialization, comes from the non-uniformity, heterogeneity, size and moisture of the feedstock. The latter characteristics generally dictate scale for the gasification reactor. In addition, the processing costs of pre-treatment, conversion of MSW into Solid Recovered Fuel (SRF) and advanced flue gas cleaning might affect the overall economic balance. The indicative for capital and operating costs for 100,000 tonnes of waste/year using the combustion process is 55 million Euro, respective 3,765,000 Euro/year, while for pyrolysis and gasification is significant higher with 73.2 million Euro initial investments and 6,700,000 Euro/year for operation and maintenance [21].

## 1.2.2. Pyrolysis

*Pyrolysis is the degradation of macromolecular materials with heat alone in the absence of oxygen.* In practice, it is not possible to achieve a completely oxygen-free atmosphere; present pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, **nominal oxidation** will occur. Therefore thermal desorption will occur if volatile or semivolatile materials are present in the waste [22].

### 1.2.2.1. Pyrolysis principles and conversion line

The pyrolysis process brings a fresh view in the waste conversion technology that has the ability to produce: gases (rich with low cut refinery products and hydrocarbons), tars (waxes and liquids with very high calorific value) and char (carbon black and/or activated carbon).

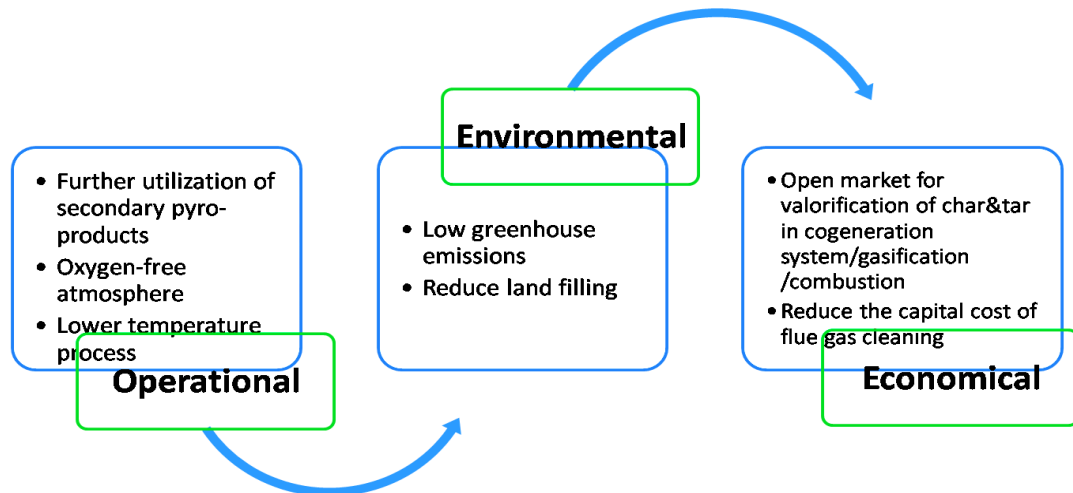


Figure 1.3. Pyrolysis process advantages

Pyrolysis typically takes place under pressure at **operating temperatures** above **350 °C(800 °F)**. There are two main types of pyrolysis treatments:

- *Slow pyrolysis (torrefaction, carbonization)* occurs at lower process temperature and longer vapour residence (5-30 min). The slow pyrolysis favours the production of charcoal due to the thermal slow decomposition and low volatile matter release.
- *Fast pyrolysis* occurs at high temperature and longer residence time. The latter parameters increase the waste conversion into gas, moderate temperature and short the vapour residence time (2 s) optimizing the formation of liquids products.

Table 1.1 presents the operating parameters and products resulted from different pyrolysis processes.

Table 1.1. Pyrolysis technology variants [23]

Pyrolysis technology		Residence time	Heating rate	Tmax(°C)	Product
Carbonisation		Hours	Very low	400	Charcoal
Slow		5-30 min	low	600	Charcoal Pyrolysis oil Gas
Fast		0.5-5 s	Fairly high	650	Pyrolysis oil
Flash	Liquid	< 1 s	High	<650	Pyrolysis oil
	Gas	< 1 s	High	>650	Chemicals Fuel gas
Ultra		< 0.5 s	Very High	1000	Chemicals Fuel gas
Vacuum		2-30 s	Medium	400	Pyrolysis oil
Hydropyrolysis		< 10 s	High	< 500	Pyrolysis oil chemicals
Methanopyrolysis		< 10 s	High	> 700	Chemicals

**Pyrolysis** plants for waste treatment usually include the following **basic process stages**:

1. Preparation and grinding: the grinder improves and standardizes the quality of the waste presented for processing, and as such promotes heat transfer.
2. Drying (depends on process): a separate drying step improves the LHV of the raw process gases and increases efficiency of gas-solid reactions within the reactor.
3. Pyrolysis of waste: besides the pyrolysis gas, a solid carbon-containing residue is generated which contains mineral and metallic compounds.
4. Secondary treatment of pyrolysis gas and pyrolysis coke: condensation of the gases for the extraction of energetically usable oil mixtures and/or incineration/gasification of the gas and coke for the destruction of organic compounds and simultaneous utilization of energy. Pyrolysis of organic materials produces combustible gases, including carbon monoxide, hydrogen and methane, and other hydrocarbons. Particulate removal equipment such as fabric filters or wet scrubbers are also required. The heating value of pyrolysis gas typically lies between 5 and 15 MJ/m<sup>3</sup> based on MSW and between 15 and 30 MJ/m<sup>3</sup> based on SRF [24].

Figure 1.4. [25] shows the summarized mechanism of MSW pyrolysis process in a fixed bed reactor using calcined dolomite as catalysts.

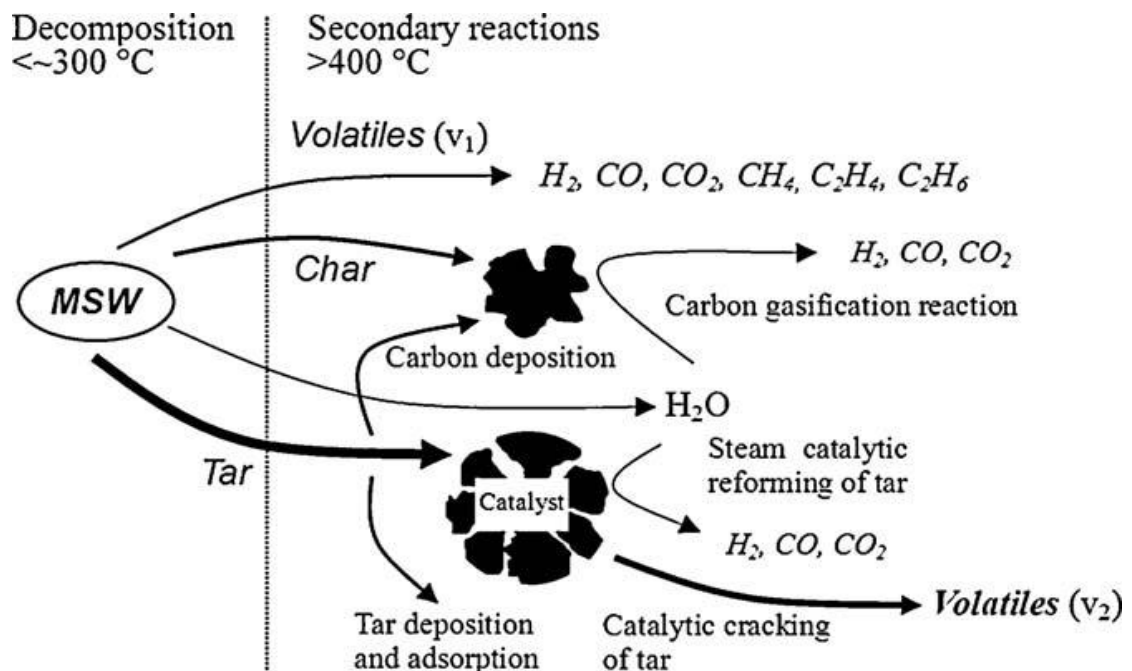


Figure 1.4. Schematic of catalytic pyrolysis of MSW in a fixed-bed reactor using calcined dolomite as catalysts

**Mechanism of catalytic pyrolysis of MSW [25]**

**A.** As in any thermal process, the primary step is the **decomposition** or thermal cracking of the material. This is a thermo chemical breakdown of MSW with production of water, tar, char and volatiles. At this step temperature is the most important parameter influencing the product yields distribution. In this case the process temperature depends on the waste/material melting point. The decomposition could occur at temperatures round 300 °C, and can last until a temperature of 700 °C or even higher depending on type of material. As the temperature increases, the moisture present in the sample evaporates, then thermal degradation and devolatilization of dried portion of the particles took place, and the volatile species gradually evolved out from the particles surface and underwent further pyrolysis.

**B.** Then, the second step secondary reactions of **tar cracking** occur at higher temperatures (>400 °C). The main secondary reactions of tar cracking and shifting include decarboxylation, decarbonylation, dehydrogenation, cyclization, aromatization, and polymerizing reactions, which were given in order of increasing pyrolysis severity (e.g., increasing temperature). Part of vapours (mainly heavy oil fraction) were absorbed by the active surface of the catalyst, and then cracked to light vapours. The light vapours then underwent series reactions such as deoxygenating, cracking to form H<sub>2</sub>O, CO<sub>2</sub>, CO, alkanes, alkenes and aromatic hydrocarbons. These reactions would result in a decrease of tar vapours and increases of gas and water yields. When all of the volatile species were removed from the solid, a residue of char is left.

The pyrolysis process could be described by the following reactions, in particular for water contribution in the process:



The reactions (Eqs. (1.1), (1.2), (1.3) and (1.4)) are endothermic. Therefore, those reactions were strengthened at the higher temperature of 750–900 °C. The main equations responsible for H<sub>2</sub> and CO increase are:

- Boudouard reactions describe in Equation 1.1
- Carbon gasification reaction Equation 1.2
- Reverse water–gas shift reaction Equation 1.3
- Cracking reactions of tar Equation 1.4

Summarizing up, depending on the type of feedstock used, after the conversion processes in non-oxidant atmosphere and purification of the solid, liquid and gaseous products, combustible materials are obtained in from of:

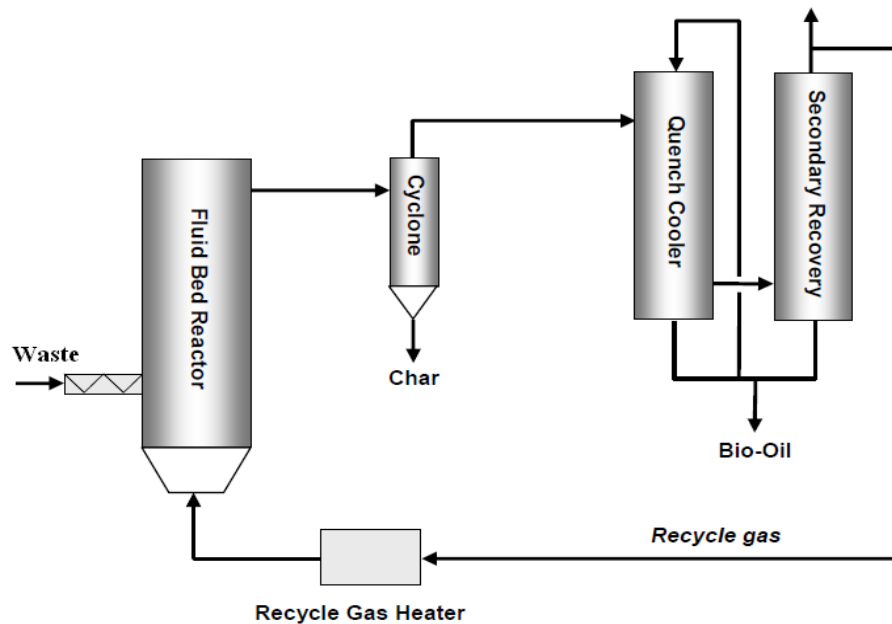
- **pyrolysis gases** (CO<sub>2</sub>, CO, H<sub>2</sub>, hydrocarbons etc.) with a calorific value of that ranges 7-30 MJ/Nm<sup>3</sup>, low in nitrogen oxides.
- **pyrolysis oil** (heavy oil), **wax or tar** with a energetic potential from 20 up to 32 MJ/kg; it may contain sulfur and chlorine and needs to be cleaned before firing;
- **pyrolysis coke** (carbon and inorganic products) with 15-22 MJ/kg inorganic fraction is eliminated as slag and stored in a controlled warehouse.

### 1.2.2.2. Pyrolysis reactors

Conventional thermal treatment methods, such as rotary kiln, rotary hearth furnace, or fluidized bed furnace, are used for waste pyrolysis.

#### ➤ **BUBBLING FLUID BEDS**

Bubbling fluid bed (BFB) is a well study and applied technology. The reactor designs (Figure 1.5.), they are characterized as proving high heat transfer rates in conjunction with uniform bed temperatures , both being necessary attributes for fast pyrolysis [26].



**Figure 1.5. Process Schematic for a Bubbling Fluidized Bed Pyrolysis Design**

BFB reactors represent an appropriate technology for waste conversion into fuels because [27] :

- Simple in construction and operation
- Good temperature control
- Very efficient heat transfer to biomass particles due to high solids density
- Easy scaling
- Well-understood technology
- Good and consistent performance with high liquid yields that can range from 70 up to 75 wt.% for wood feedstock on a dry feed basis
  - Heating can be achieved in a variety of ways as shown in Figure 1.6.
  - Residence time of solids and vapours is controlled by the fluidizing gas flow rate and is higher for char than for vapours
    - Char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures so rapid and effective char separation/elutriation is important
      - Small biomass particle sizes up to 3 mm are needed to achieve high biomass heating rates
      - Good char separation is important—usually achieved by ejection and entrainment followed by separation in one or more cyclones
      - Heat transfer to bed at large scale has to be considered carefully due to scale-up limitations.

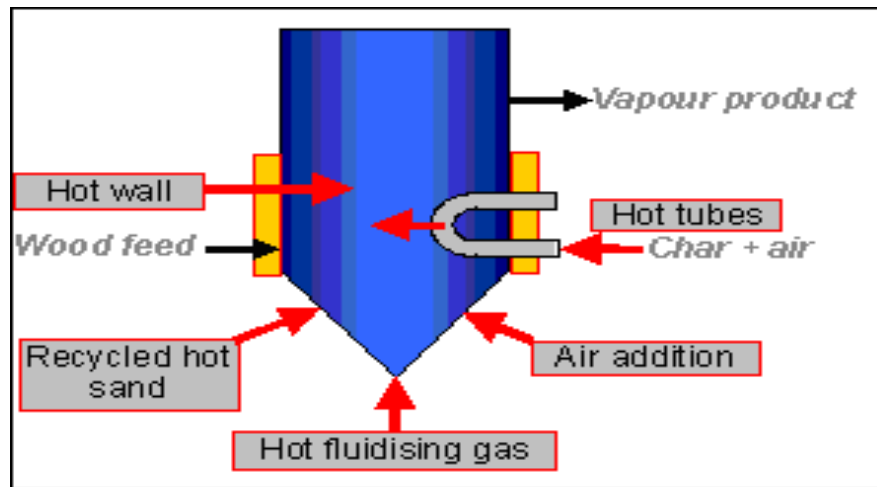


Figure 1.6. Methods of heat transfer to a pyrolysis reactor [29]

➤ **CIRCULATING FLUID BED (CFB)**

Circulating fluid bed (CFB) and transported bed reactor systems have many of the features of bubbling beds described above, except that the residence time of the char is almost the same as for vapours and gas, and the char is more attired due to the higher gas velocities [28].

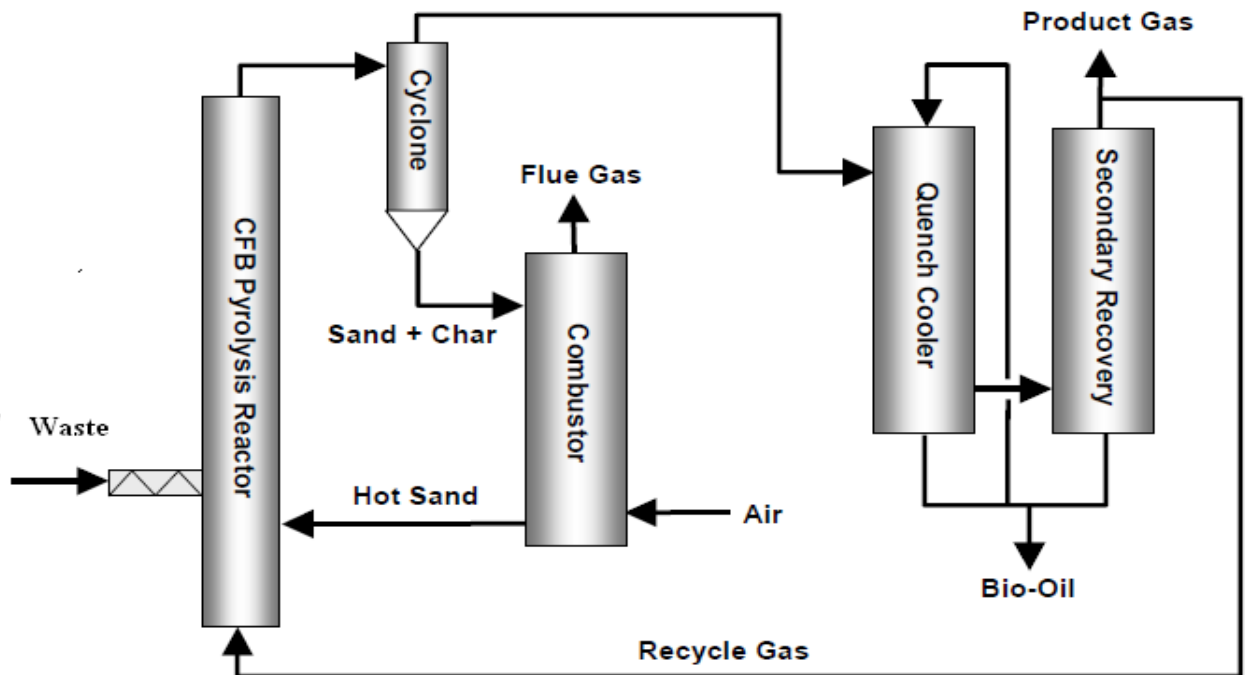


Figure 1.7. Schematic circulating fluid bed process [26]

➤ **ABLATIVE PYROLYSIS**

Ablative pyrolysis is a different WtE concept in comparison with fast pyrolysis. The vortex reactor was developed by National Renewable Energy Laboratory in order to exploit this phenomenon presented in Figure 1.8.

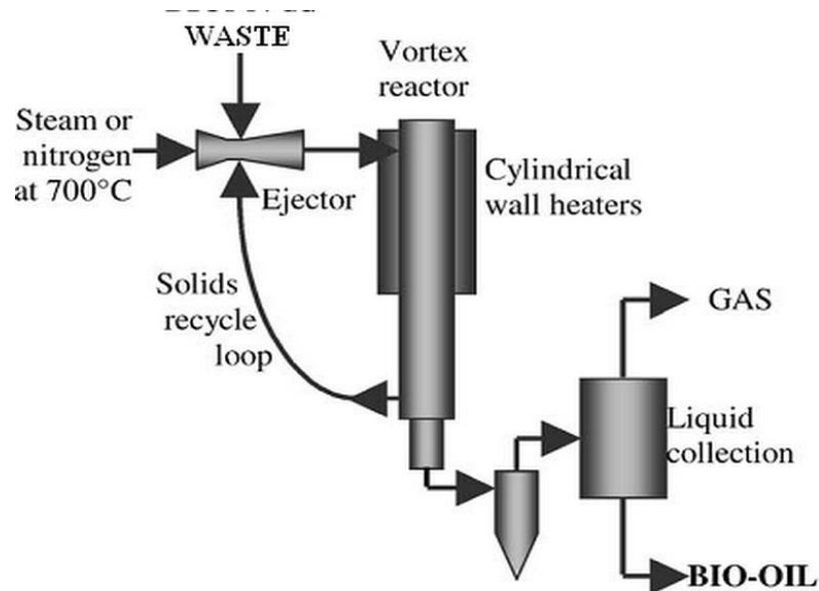


Figure 1.8. NREL Vortex ablative reactor [29]

In ablative pyrolysis heat is transferred from the hot reactor wall (less 600°C) to the material that is in contact with it under pressure. At this point unidirectional forces occur on the heated material due to the high pressure action achieved through centrifugal force or mechanically. The latter stage of the process is quickly followed by the vapours formation and collection of the pyrolysis gases. In comparison with other types of reactors, where the rate of heat transfer within the material surface is the main process parameter, in ablative pyrolysis the material is highly influenced also by the pressure. Therefore the heat transfer is no limited by the size of the waste feedstock.

The process in fact is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing waste as in other reactors. However the process is surface area controlled so scaling is more costly and the reactor is mechanically driven so is thus more complex [29].

***1.2.2.3. Literature review on light packaging waste pyrolysis***

Because of the plastics, paper and cardboard studied in this research, here below a comparative analysis is made by type of light packaging waste fraction.

➤ **PYROLYSIS OF PLASTICS**

Pyrolysis of different types of plastics has been studied over the last decades. A comprehensive review of the results is presented by Scheirs and Kaminsky (2006) [30].

The **mechanism of thermal degradation of waste plastics** is very complex and includes, amongst others, the following reactions: chain fission, radical recombination, carbon–hydrogen

bond fission, hydrogen abstraction, mild-chain  $\beta$ -scission, radical addition, etc. [31]. During the process free radicals are generated which propagate chain reactions resulting in cracking polymers into a broad mixture of hydrocarbons existing in a liquid (tar/wax/oil) and gaseous (pyrolysis gas) phase. Several factors mainly influence the thermal-degradation process such as: residence time, temperature and the type of pyrolysis agent. As the residence time and temperature increases, the composition of the products shifts towards compounds which are more thermodynamically stable [32].

At maximum rate, the devolatilisation time of **PE starts at 365°C** indicating its low stability. The decomposition of **HDPE and LDPE starts at 430°C** and exhibits a **maximum** rate of pyrolysis at **495°C**, whilst is followed from the evolution of paraffines and olefins [33].

The **PET maximum** degradation rate occurs at **450°C**.

In conclusion the thermal stability of the plastic waste studies can underline starting from the lowered one: **HPDE>LDPE>PP>PET** [34].

Previous studies conducted on polymers waste by Adrados et. al. (2012)[35] have indicated that **500°C** is the **optimum temperature** for the **treatment of polymeric waste by pyrolysis** because at lower temperatures, complete decomposition of organic matter is not achieved, and at higher temperatures, there is an increase in the gas yield at the expense of the liquid yield. From **the experiments conducted in the current research**, it can be noted that in this case the agglutination rate will increase, therefore in mixture with other products (specially inhomogeneous waste) **may cause technical problems**. Still for achieving high yield of olefin from pyrolysis process the operating temperature must range between 600°C and 800°C [36]. It can be concluded that lower temperatures (>400°C) increase the liquid product generation such as tar/oil/wax, although higher temperature enhance the production of by-products based on aromatics, acetylene, hydrogen, methane and soot.

The thermo-gravimetric analysis (TGA) of PS,PP,PET,ABS,PET led by Encinar and González (2008) [31] in **nitrogen atmosphere and in isothermal conditions** (400°C-500°C) with a heating rate ranging between 5-20 K/min revealed that:

- the bigger fraction is composed **of liquid/wax**, named **tar** (95–30%);
- in the second place are the **gases**, named **pyrolysis gases** (65–2%). The gas fraction consisted of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, CO and CO<sub>2</sub>
- the **solid** fraction (named **char**), whose yield is ever lower to the 10%.

In this context pyrolysis becomes more attractive due to the formation of valuable aromatics such as styrene, toluene and ethyl-benzene even thou the extraction of this compounds is not easy. If they are subject to a thermal treatment in non-oxidant atmosphere, all polymers are composed of hydrocarbons (C<sub>1</sub>-C<sub>6</sub>) together with small quantities of CO, CO<sub>2</sub> and H<sub>2</sub>. The hydrocarbons from the pyrolysis of plastics cannot be used directly as fuel: it is necessary to carry out a fractional distillation of the oil obtained from the process, separating the components that are useful for this purpose. Refining the oil is obtained benzene, toluene and other aromatic hydrocarbons.

### ➤ **PYROLYSIS OF PAPER AND CARDBOARD**

The most predominant material in paper is wood. Wood consists of three major components: cellulose (40-45%), hemicelluloses (27-39%) which form the matrix, and lignin (21-30%) the encrusting substance that binds the cells together [37].

The **pyrolysis of cellulose** was been studied on more than a century.

The **cellulose and lignocelluloses pyrolysis** can be divided in **four individual stages**:

1. moisture evolution,
2. hemicelluloses decomposition,
3. cellulose decomposition and
4. lignin decomposition.

A recent literature review was made by L     (2012) [38], about cellulose pyrolysis kinetics on the existence and role of intermediate active cellulose. On the basis of data obtained by Thermal Gravimetric Analysis (TGA), differential thermal analysis (DTA) and mass spectrometric thermal analysis (MTA), in 1965 the general kinetics on pyrolysis of pure cellulose scheme was proposed [39]. Its **decomposition** would occur according to two competitive **reactions** occurring directly from **cellulose**:

- the first one (200  C –273  C ) is a slightly endothermic reaction of dehydration followed by an exothermal process producing char and light gaseous species.
- the second one (273  C –340  C or up to 400  C[37], cellulose is postulated to be transformed into an intermediate and unstable compound (1,4-anhydro-\_-d-glucopyranose) which rearranges. The authors underline the strong influence of inorganic salts which can be explained by such a mechanism. The maximum rate of weight losses is between 355-371  C. In combination with hemicelluloses materials (e.g. cardboard ) the catalytic effect might appear due to the presence of inorganic species such as ash and residues from the sulphate production process, that can lead to the decomposition of cellulose to occur at lower temperatures [37].

After the fully decomposition of the material the stabilization of char, tar and pyrolysis gas occurs. It is well known that the pyrolysis gas mainly contains H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, trace amounts of larger gaseous organics and water vapour.

### ➤ **PYROLYSIS OF TETRA-PACK**

The pyrolysis curve of tetra pack presents two distinct weight loss steps located in the temperature regions of 200–400   C similar of paper and the second one at 450–550  C for plastics. Thus, tetra pack begins to decompose at a low temperature (270   C) and reaches the maximum pyrolysis rate at 370   C, close to the corresponding temperature of cardboard (373   C).

## **1.2.3. Gasification**

Gasification, or ‘‘indirect combustion’’ is the conversion of solid waste to a gaseous fuel by heating in a gasification medium such as steam or air or oxygen (amount lower than that required for the stoichiometric combustion).

There are two main types of gasification:

- ***direct gasification or auto thermal gasification*** where part of the fuel is combusted to provide the heat needed to gasify the rest, as in the case of air gasification.
- ***indirect gasification or allothermal gasification*** where the heat energy is provided by an external supply as in the case of plasma torch utilization.

A better representation of the gasification process in connection with the above description is presented in Figure 1.9. [40].

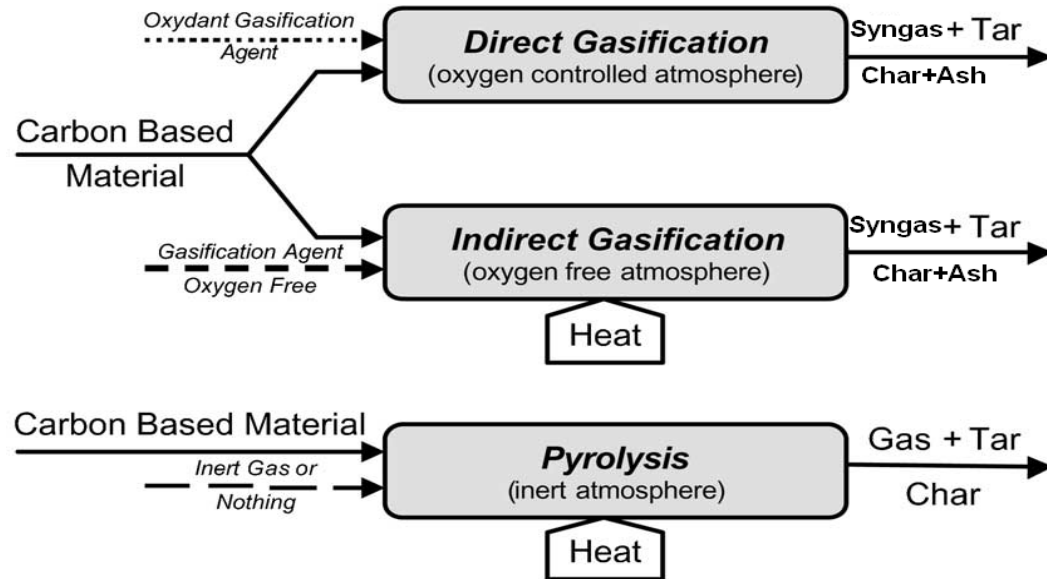


Figure 1.9. Gasification process

Depending on the temperature the gasification process converts the feedstock input into three major fractions:

- combustible **gas** named (“producer gas” or “syngas”);
- **liquid** fraction (tars and oils);
- **char**, consisting of almost pure carbon plus inert material originally present in the feedstock.

The combustible gas contains  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , trace amounts of higher hydrocarbons, inert gases present in the gasification agent, various contaminants such as small char particles, ash and tars [41]. One of the eco-friendly concepts that gasification treatment presents is given by the low temperature process that limits the formation of the dioxins and large quantities of  $\text{SO}_x$  and  $\text{NO}_x$ . As a result, the volume of flue gas is low, requiring smaller and less expensive gas cleaning equipment. At this stage, gasification generates a fuel gas that can be integrated with combined cycle turbines, reciprocating engines and potentially, with fuel cells that convert fuel energy to electricity more than twice as efficiently as conventional steam boilers [42]. The key of an efficient WTE gasification system is to overcome the problems associated with the main contaminants released and formed in the process: tar, alkaline, heavy metals and halogen.

### 1.2.3.1. Gasification principles and conversion line

The chemical process of solid waste gasification is quite complex and includes several endothermic and exothermic steps as Figure 1.10 [43] shows.

Depending on the type of waste, the feedstock to be gasified passes through a conversion chain:

- **heating and drying**, that occurs at temperatures up to about  $160^\circ\text{C}$ : it is a combination of events that involve liquid water, steam and porous solid phase through which liquid and steam migrate.

▪ **pyrolysis** (or devolatilization) is given by the thermal decomposition of the feedstock into light gases ( $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $H_2O$ ,  $NH_3$ ), to condensable vapours (containing tars) and solid carbon (char). This phase is an endothermic process that occurs at temperatures above  $500^\circ C$  involving thermal cracking reactions and heat and mass transfer. The product obtained is characterized by a 75%-90% mass fraction of volatile matter in the form of steam plus gaseous and condensable hydrocarbons. The by-products formation in the devolatilization stage (light gases, condensable vapours and char) mainly depends on the original composition and structure of the waste but also on operation conditions such as: heating rate, temperature, pressure and reactor type.

▪ **thermal cracking** of the vapour fraction to gas and char

▪ **gasification of the char** by steam (steam gasification) or by air/oxygen (partial oxidation) **partial oxidation** of fuel gas, vapour and char

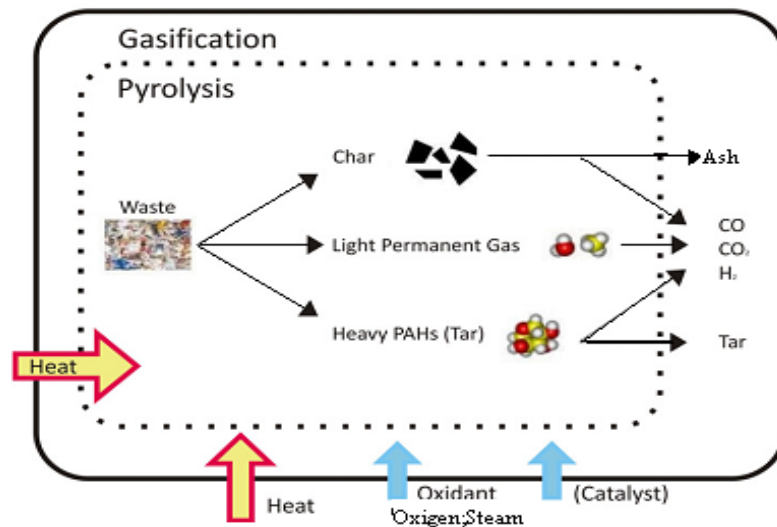


Figure 1.10. Schematic representation of pyrolysis, gasification and combustion stages

Three type of syngas gas qualities (Table 1.2) can be produced from gasification by varying the gasifying agent, the method of operation and the process operating conditions [44].

Table 1.2. Syngas heating value type of gasifying agent

	Heating value [ $MJ/Nm^3$ ]	Agent
Low heating value	4–6	air and steam/air
Medium heating value	12–18	oxygen and steam
High heating value	40	hydrogen and hydrogenation

In general a gasification reactor can be divided into 4 different conversion zones according to the values of the process operating parameters:

▪ **drying zone**, receives the energy by heat transfer from other zones of the reactor. The rate of the drying depends on the process temperature, gasifying agent velocity, moisture content of the drying gas, size and surface of the feedstock material etc. Once the fuel is fed into the reactor in

the drying zone, the internal temperature of the material shifts from 25°C up to 160°C. No chemical reaction takes place in this zone.

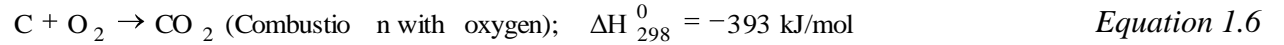
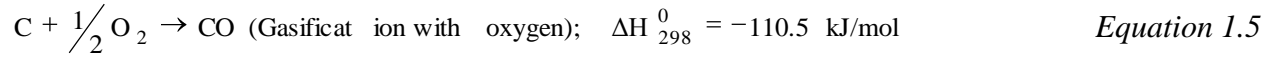
▪ **pyrolysis zone, (or devolatilization zone)** is the first area where chemical reactions begin to occur. In the pyrolysis zone the temperature increase quickly due to the temperature difference between the dried material and hot gases. The rapid transfer in this zone leads to the volume reduction of the material causing it physical-chemical changes.

▪ **reduction zone,**

▪ **oxidation zone** is characterized by heterogeneous chemical reaction of combustion and partial oxidation. The O<sub>2</sub> content decreases from 21% to 0% and CO<sub>2</sub> decreases significantly when air is used as gasifying agent. The oxidation zone has the highest temperature due to the exothermic nature of the reactions.

The position of these zones in the gasifier depends on the reactor type, the combustible feedstock and gasifying agent motion. The areas differ mainly from the multitude of the reaction that occurs in time and different temperatures of the process.

Major reactions involved in the gasification process are combustion (reaction with O<sub>2</sub>), Boudouard reaction (reaction with CO<sub>2</sub>) and steam gasification (reaction with steam) [45]. The main gasification reactions and there enthalpy are described in equations from 1.5 to 1.8.

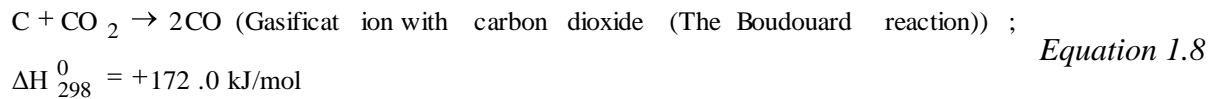


These two reactions (Eq. 1.5 and 1.6 ) are exothermic and can provide the heat necessary for the endothermic reactions occurring in the drying, pyrolysis and reduction zones (i.e. autothermal process).

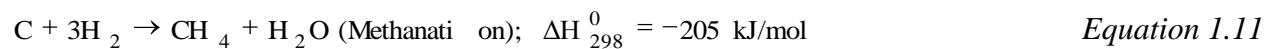
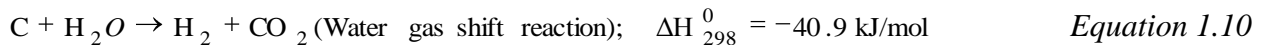
The water steam introduced as gasifying agent or generated by the drying and pyrolysis of the waste reacts with the solid carbon according to the heterogeneous reversible water gas reaction (Eq. 1.7)



This equation together with Boudouard reaction (Eq. 1.8) are the most important endothermic reduction reactions that increase the gas volume of CO<sub>2</sub> and H<sub>2</sub> at higher temperatures and lower pressures.



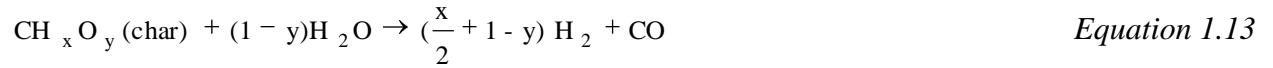
Some of the minor reactions normally associated with the gasification process are:



The light hydrocarbon and char reaction generalized reaction, formed in the devolatilization stage is:



The char is further gasified in the rest of the process as per the overall reaction given below:



Gasification processes are operated either at atmospheric pressure or at an elevated pressure in the presence of steam, air/oxygen. Equilibrium considerations suggest slower decomposition of steam and CO<sub>2</sub> with increasing pressure. However, pressure up to 2.94 MPa does not exert any significant impact on the composition of syngas. Most of the commercial or near commercial gasifiers operate at elevated pressures (~2.94 MPa) [46].

### **Role of the main gasification process parameters**

The *main parameters* playing a role in the waste conversion are: the operating temperature, pressure, residence time in the reactor, the amount of gasifying agent (ER and SC parameters), gas velocity, syngas heating value, syngas flow rate, syngas production, process efficiency, fuel consumption.

In the following a *comprehensive overview* will be made on the main *process parameters*:

#### **➤ Operation temperature and pressure**

Combustible gas H<sub>2</sub> and CO concentration increased with increases in temperature, while CO<sub>2</sub> and CH<sub>4</sub> decrease. Char yield decreased with increases in temperature. The water fraction decrease with temperature due the endothermic water-gasification reduction reaction. In Figure 1.11 (right) the effect of temperature and pressure on equilibrium gas composition in oxygen gasification of coal is presented [47]. The gasification temperature effect on synthesis product distribution obtained from MSW gasification is presented in Figure 1.11 (left) [48].

It can be concluded that CO and CH<sub>4</sub> reach to their maximum as result of the exothermicity of their formation and the endothermicity of their conversion. Low pressure favours the CO and H<sub>2</sub> formation event at high temperatures.

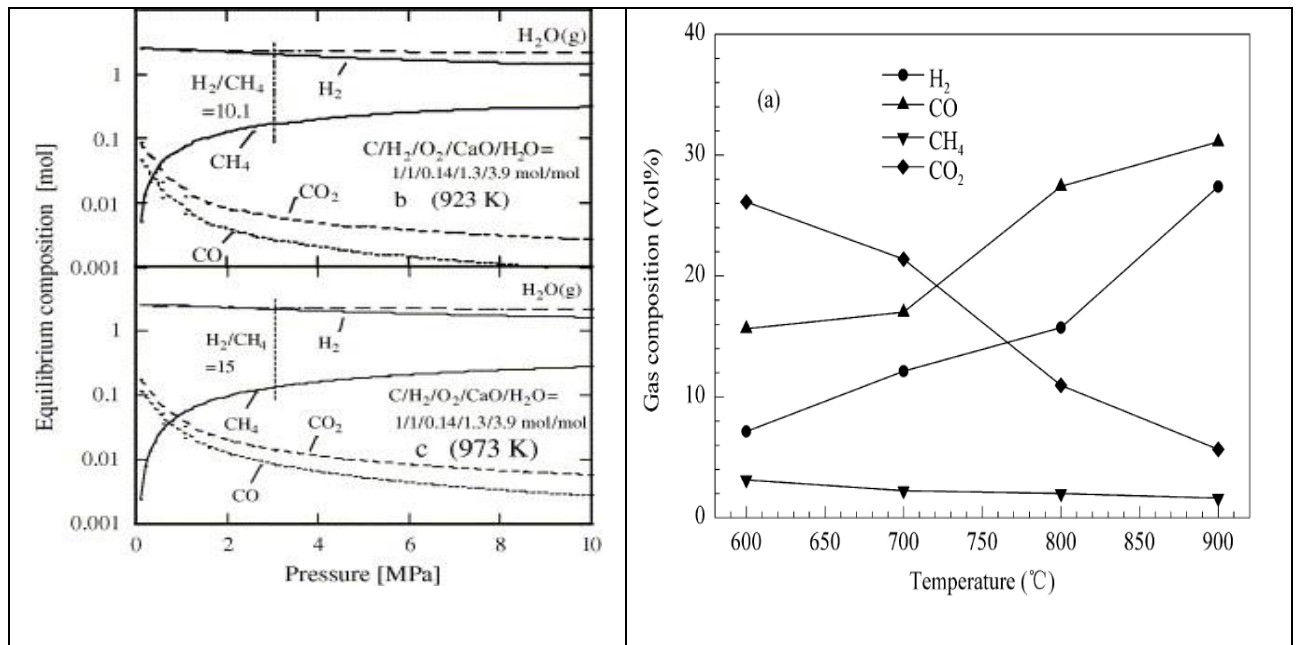


Figure 1.11. Gas equilibrium composition at various pressures (right) and effect of gasification temperature on synthesis product distribution obtained from MSW gasification (left) [48]

#### ➤ *Residence time of gases and waste inside the reactor*

This parameter is largely defined by reactor type and design, and for a fixed gasifier design can be varied to a limited extent: for instance, in a fluidized bed, by varying the superficial gas velocity and, in a moving grate, by increasing the velocity of the grate elements [43].

Zhao et.al. 2010, presented the evolutionary behaviour of syngas chemical composition (volume fraction of H<sub>2</sub>, CO, and CH<sub>4</sub>) from municipal solid waste gasification with hot blast furnace slag with several gasifying agents of steam, air, and N<sub>2</sub> (Fig. 1.12). The major chemical species determined here were: H<sub>2</sub>, CO, CH<sub>4</sub>, and CO<sub>2</sub>. The amount of chemical species is given by the gasifying agent type and residence time in the gasifier. The steam registers the highest gaseous yield, because of the increase in forward reaction in water gas reaction ( $C + H_2O(g) \leftrightarrow CO + H_2$ ), water gas shift reaction ( $CO + H_2O \leftrightarrow CO_2 + H_2$ ), steam-hydrocarbons reforming reaction ( $C_xH_y + mH_2O \leftrightarrow CO + (m + y/2)H_2$ ) and steam-tar reforming reactions.

The time corresponding to the maximum volume fraction of major chemical species determined is different. H<sub>2</sub> volume fraction shows a peak at 30 s, CO 20 s, and CH<sub>4</sub> and CO<sub>2</sub> volume fractions show maximums at the same time (10 s). This is due to the methane oxidation reaction, carbon dioxide-carbon reduction reaction, water gas reaction, and cracking reaction of tar.

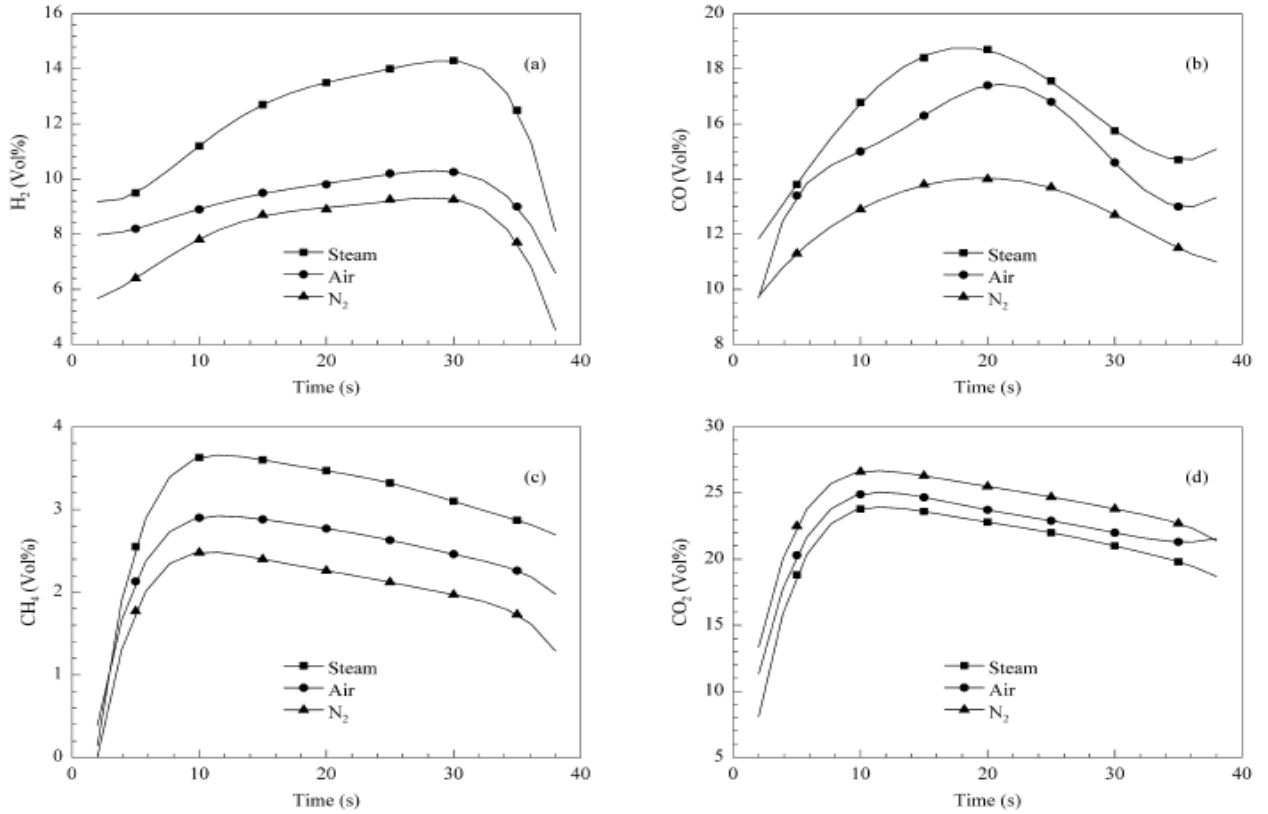


Figure 1.12. Evolutionary behaviour of major chemical species determined in volume fraction for different gasifying agents (650 °C, MSW 20 g). (a)  $H_2$ , (b)  $CO$ , (c)  $CH_4$ , (d)  $CO_2$  [48]

#### ➤ Amount of gasifying agent

The amount of gasifying agent is defined as fraction of gasifying agent ratio used in the gasification process and stoichiometric amount of the same agent ratio for complete combustion of the material; it is named Equivalence Ratio (ER) for partial oxidation and Steam to Carbon ratio (SC) for steam gasification. Equivalence ratio (ER), i.e. the ratio between the oxygen content in the oxidant supply and that required for complete stoichiometric combustion. It is likely the most important operating parameter in gasification-based WtE units, since it strongly affects the gas composition (including tar content) and its chemical energy. Values close to zero correspond to pyrolysis conditions while values equal or greater than one indicate combustion conditions as Figure 1.13 shows [43]. The steam to Carbon ratio (SC) quantifies a corresponding factor in the steam reforming process, i.e. the ratio between the supplied steam and the carbon fraction presented in the feedstock. Combustible gases from the syngas produced are increasing depending on the gasifying agent used in the process taking into account the next argument:  $N_2 < \text{air} < \text{steam}$ . The combustible components and the heating value of the produced gas decreased with decreases in the equivalence ratio. For example, a ER zero value corresponds to pyrolysis, while stoichiometric combustions is defined  $ER=1$  [43].

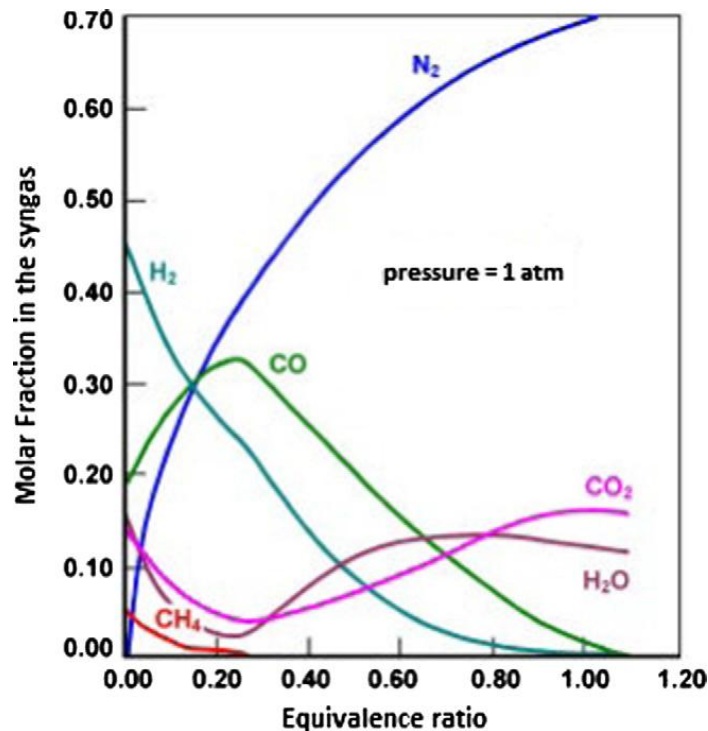


Figure 1.13. Syngas composition at the chemical equilibrium as a function of equivalence ratio, for the gasification of wood at 1 atm [43]

The unconverted char remains at lower ER values with higher tar content. Part of syngas goes by through an oxidation process at higher ER values with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  formation. The latter stage reduce the syngas heating value that could cause incomplete combustion in the combustion chamber that is usually downstream of the gasifier.

#### ➤ *Gas velocity*

The gas velocity (also named ‘‘superficial velocity’’) dictates the gas, tar and char production rates, the gas calorific value, fuel consumption rate and conversion efficiency. This parameter is defined as the gas flow rate on the cross-sectional reactor area. The low rates of the superficial velocity can cause slow pyrolysis process conditions, emphasizing the tar content in syngas and also residual char yields.

#### ➤ *Efficiency and fuel consumption*

This last parameter is in direct connection with the quantitative and qualitative properties of the syngas production. The syngas calorific value by type of gasifying agent was presented in the previous subsection. The feedstock input influences the overall performance of the process. Usually the overall efficiency values can range between 70-80%. The initial fuel consumption in terms of feedstock input quantity, feedstock pre-treatment (if necessary), energy consumption for starting and maintaining the gasification process, flue gas treatment for syngas production are important for the evaluation of the overall process efficiency. This quantity measured directly, or by mass balance is usually expressed as unit mass per time ( $\text{kg}_{\text{waste}}/\text{h}$ ) or per generated energy ( $\text{kg}_{\text{waste}}/\text{kWh}_{\text{el}}$ ) with typical values ranging between 1 and  $1.3 \text{ kg}_{\text{waste}}/\text{kWh}_{\text{el}}$ .

### 1.2.3.2. Gasification reactors

On the report of Rauch, 2003 [49] the gasifiers' classification can be made with different criteria:

According to the *gasification agent*:

- air-blown gasifiers;
- oxygen gasifiers;
- steam gasifiers;

According to the *heat for gasification*:

- autothermal or direct gasifiers: heat is provided by partial combustion of the fuel;
- allothermal or indirect gasifiers: heat is supplied from an external source thorough heat exchangers or indirect processes, i.e. separation of gasification and combustion zone.

According to the *process pressure*:

- atmospheric;
- pressurized.

According to the *reactor design it can be mention*:

- fixed bed;
- fluidized bed;
- entrained flow;
- rotary kiln gasifier

#### ➤ FIXED BED GASIFICATION

The fixed bed gasifier has been the traditional process used for gasification, in solids move either counter current (updraft) or concurrent (downdraft) to the flow of a gas as reaction takes place, and the solids are **converted to gases**. **The operation temperatures** are around 1000°C.

In the *updraft gasifier*, feed is introduced at the top and the air at the bottom of the unit via a grate (Figure 1.14 left). Therefore the flow of the fuel and gases are counter current to each in the updraft gasifier. Immediately above the grate the solid char temperature reaches about 1000 °C. Ash falls through the grate at the bottom and the hot gases pass upwards and are reduced. Higher up the gasifier again, the biomass is pyrolysed and in the top zone, the feed is dried, cooling the gases to around 200–300°C. In the pyrolysis zone, where the volatile compounds are released, considerable quantities of tar are formed which condenses partly on the waste higher up and partly leaves the gasifier with the product gas. The temperature in the gasification zone is controlled by adding steam to the air used for gasification, or by humidifying the air. Due to the low temperature of the gas leaving the gasifier, the overall energy efficiency of the process is high but so also is the tar content of the gas. The filtering effect of the feed helps to produce a gas with a low particulate content [44].

In a *downdraft reactor* (Figure 1.14 right), co-current, the carbonaceous material is fed in from the top, the air is introduced at the sides above the grate while the combustible gas is withdrawn under the grate. As a consequence of the downdraft configuration, pyrolysis vapours allow an effective tar thermal cracking. However, the internal heat exchange is not as efficient as in the updraft gasifier because the gases leave the gasifier unit at temperatures about 900–1000 °C [44]. Nippon Steel claims power generation from about 400 kWh/t<sub>MSW</sub> (when MSW is co-gasified with

bottom ash discharged from other MSW incinerators and with combustible and incombustible residues from recycling centres) to about 670 kWh/t<sub>MSW</sub> (when only MSW is gasified), depending on the feedstock properties (LHV and ash content, which causes higher sensible heat of melt) and boiler system [50].

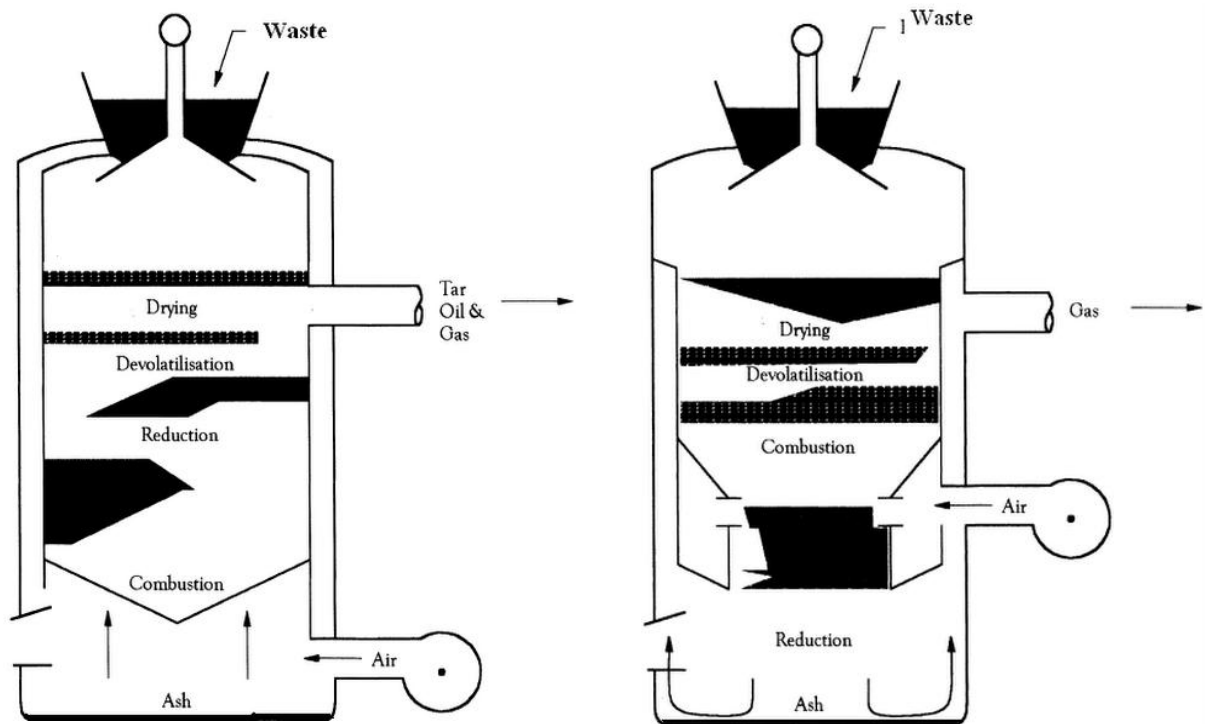


Figure 1.14. Updraft gasifier (left) and Downdraft gasifier (right) [44]

The *cross-draft* gasifiers are well suited for the use of charcoal. Charcoal gasification results in very high temperature, above 1500°C, in the oxidation zone which can lead to material problems. Start up time (5-10 minutes) is much faster than that of downdraft and updraft units. An advantage of the system consists in the very small scale operation units (10 kW).

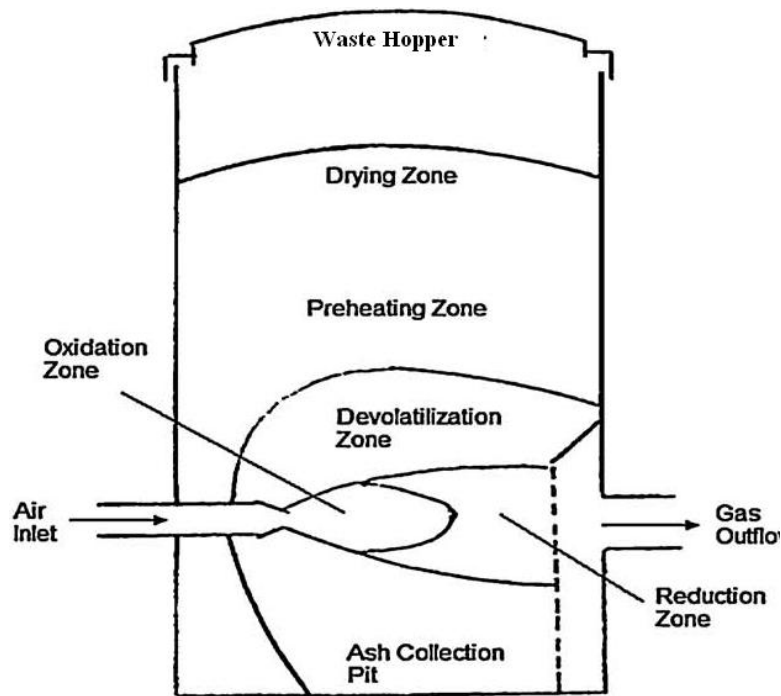


Figure 1.15. Cross-draft gasifier

### ➤ **FLUIDISED BED**

Fluidization is the term applied to the process whereby a fixed bed of fine solids, typically silica sand, is transformed into a liquid-like state by contact with an upward flowing gas (gasification agent) [51]. Fluidized bed reactors can be classified by configuration and the velocity of the gasifying agent, e.g., bubbling, circulating, spouted, and swirling fluidized beds.

The efficiency of a fluidized bed gasifier is about five times that of a fixed bed, with a value around  $2000 \text{ kg}/(\text{m}^2 \text{ h})$ . Fluidized bed reactors are gasifier types without different reaction zones. They have an isothermal bed operating at temperatures usually around  $700\text{--}900^\circ\text{C}$ , lower than maximum fixed bed gasifiers temperatures. The *bubbling fluidized bed (BFB)* and *circulating fluidized bed (CFB)* gasifiers are schematically presented in Figure 1.16. In a BFB reactor, the velocity of the upward flowing gasification agent is around  $1\text{--}3 \text{ m/s}$  and the expansion of the inert bed regards only the lower part of the gasifier. Bed sand and char do not come out of the reactor because of the low velocity. The velocity of the upward flowing gasification agent in a CFB reactor is around  $5\text{--}10 \text{ m/s}$ . Consequently, the expanded bed occupies the entire reactor and a fraction of sand and char is carried out of the reactor together with the gas stream [40]. This fraction is captured and recycled in the reactor using an air cyclone that intercepts the gas stream.

CFB gasifiers of biomass and refuse-derived fuel are proposed for instance by Metso Power that is completing a  $160\text{MW}_{\text{fuel}}$  unit at Lahti, in Finland, fired with household waste (origin sorted), industrial waste, demolition wood and waste wood from industry, that started in operation in 2012 [43].

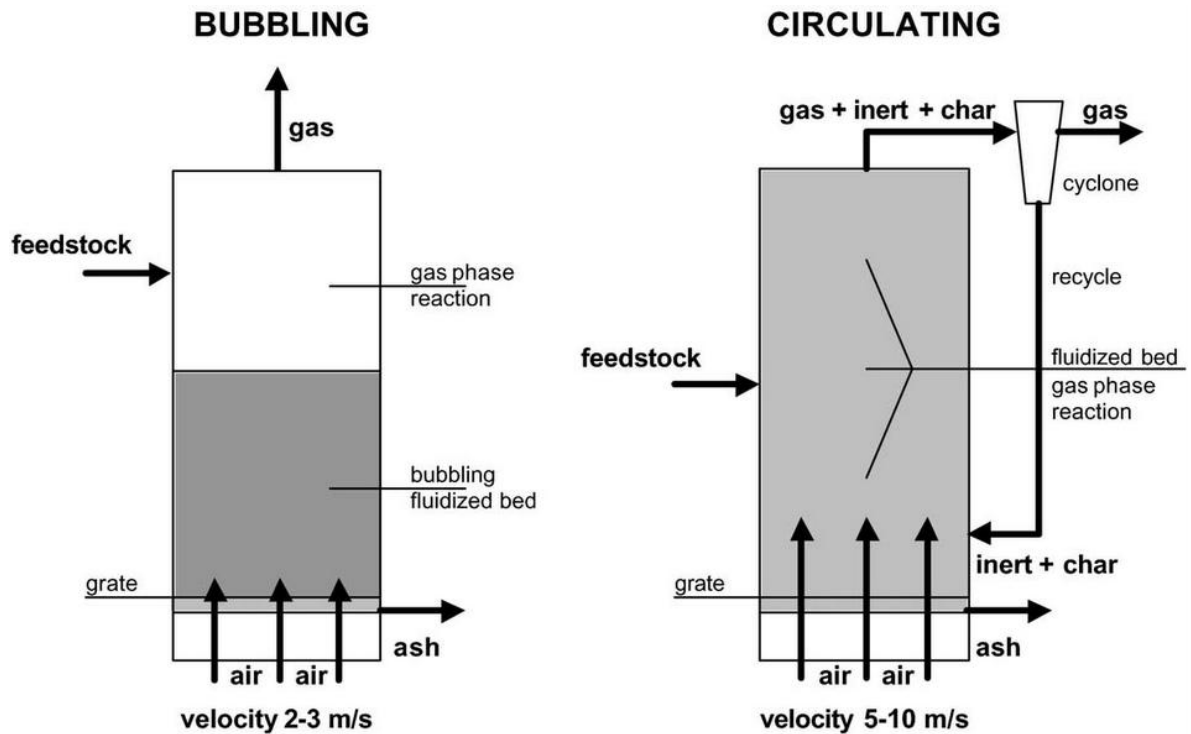


Figure 1.16. Bubbling Fluidized bed (BFB) (left) and Circulating Fluidized bed (CFB) (right) gasifiers

### ➤ ENTRAINED FLOW GASIFIERS (EFG)

These types of reactors are operating at high temperature (approximately 25 bars) where the bed is characterized by the absence of inert materials. In this terms they can treat coal, mixed materials waste (such as polymers), refinery residues etc. The feedstock to be size reduced before entering into the reactor. It can be fed directly in the gasification chamber making the high-pressure feeding almost inexpensive. The operating temperatures range between 1200°C -1500°C with short residence time (1s) that leads to fast conversion of the feedstock into syngas.

The turbulent flame position at the top of the gasifier burns some of the fuel, proving large amount of syngas. There are usually used at large scales (greater than 100 MW<sub>th</sub>). As gasifying agent pure oxygen or air is used because of it high conversion temperatures operation conditions that eventually can cause problems of materials selection and ash melting. The ash melts onto the gasifier walls, and is discharged as molten slag into the quench chamber for cooling: metals present are encapsulated in the cooled slag. The overall process efficiency reaches up to 100%.

### ➤ ROTARY KILN GASIFIER [43]

This reactor is largely used in several applications, from the industrial waste incineration to the cement production. The rotary kiln concept accomplishes two objectives simultaneously: moving solids into and out of a high-temperature reaction zone and mixing the solids during reaction. A kiln is typically comprised of a steel cylindrical shell lined with abrasion-resistant refractory to prevent overheating of the metal as presented in Figure 1.17. It is generally inclined slightly toward the discharge end (about 0.03 m/m), and the movement of the solids being processed is controlled by the speed of rotation (about 1.5 rpm). Rotary kilns are used as first stage of a two-step process in the Mitsui Recycling 21 process. The waste is gasified at 450°C in a gasification drum and converted into gas and char with other residue of metals, ash and debris. After separation and recovery of aluminum, iron and other residue, the exit stream is fed into a

high temperature combustion chamber and burnt at 1300 °C and low excess air ratio (about 1.2), where ash also fed into is melted and slag. The waste is gasified with high temperature air obtained in a high temperature air heater, and then no additional external fuel is needed. The recovery of iron, aluminum and slag, which can be sold, leads to a very high waste volume reduction ratio, which can reach 1/200 of the original waste volume.

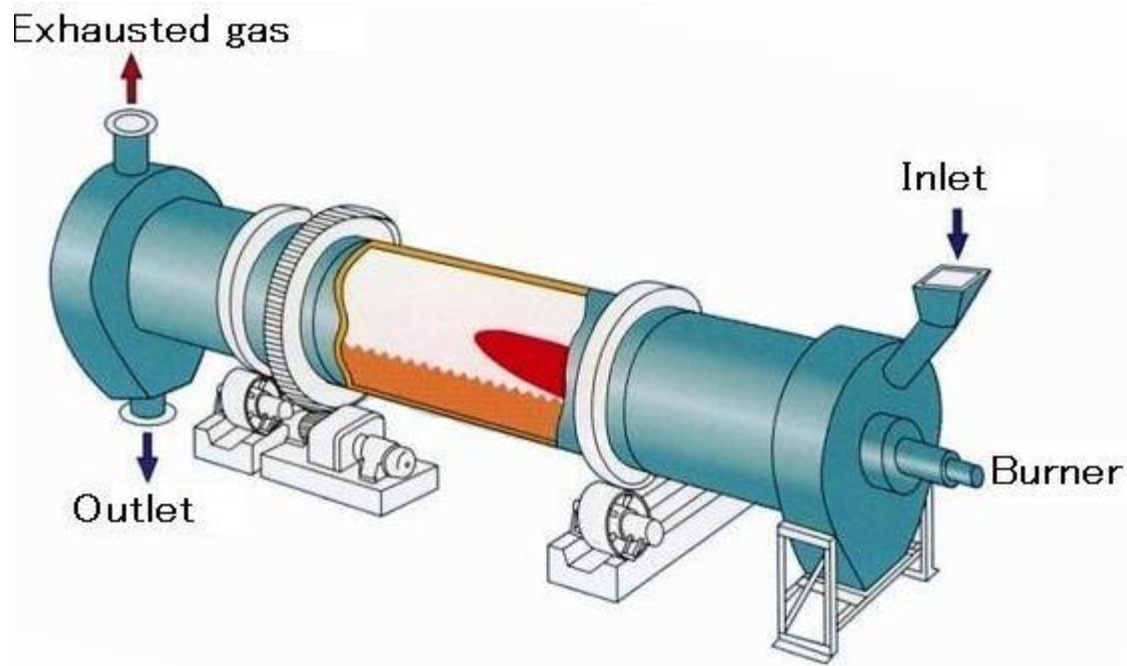


Figure 1.17. Rotary kiln gasifier [52]

#### ➤ MOVING GRATE GASIFIERS

Mechanical grates are the most utilized reactor type for combustion-based WtE units. This constant-flow grate feeds the refuse continuously from the refuse feed chute to the incinerator furnace, provides movement of the refuse bed and ash residue toward the discharge end of the grate, and does some stoking and mixing of the burning material on the grates. The grate furnace has been recently proposed for gasification process by Energos (which has several plants in operation in Norway, Germany and United Kingdom) to improve the fuel flexibility of MSW gasifiers. The thermal conversion takes place in two stages: the primary chamber for gasification of the waste (typically at an equivalence ratio of 0.5) and the secondary chamber for high temperature oxidation of the syngas produced in the primary chamber. The gasification unit is equipped with a horizontal oil-cooled grate that is divided into several separate sections, each with a separate primary air supply, and a water-cooled guillotine installed at the inlet of the gasification unit to control the thickness of the fuel bed. The oxidation in the secondary chamber is facilitated by multiple injections of air and recycled flue-gas.

### 1.2.3.3. *Literature review on light packaging waste gasification*

There is a growing interest in the application of thermo-chemical WtE alternative processes especially for MSW fractions.

The plastics and especially biomass waste gasification has been wide study at in lab-scale reactors specially in fluidized bed gasifier.

As Grimshaw and Lago, 2010 and Hankalin et al., 2011 reported that 0.5 value can be used in particular for wet fuels in moving grate gasifiers and fluidized bed gasifiers [53,54]. Other studies have shown that small ER reduce the conversion of lignocellulosic biomass gasification decreasing the process efficiency [55]. The **optimum** value for **ER** in **biomass** gasification ranges between **0.2-0.4** which differs to various operating parameters and it's dependent on the producer gas subsequent application [56]. For example if the temperatures are lower than 850°C, tar yield is high and ER should be increased to 0.3-0.4 in order to overcome this situation.

In Lv et. al studies [55] the **ER** variation ranges between **0.19-0.27** for **lignocellulosic** biomass gasification. It was observed that ER ratio could be divided in two stages 0.19–0.23 as first stage and 0.23–0.27 as second one. In the first stage the LHV of the gas increases from the 8.82 to 8.84 MJ/m<sup>3</sup> due to the increase of gas yield from 2.13 to 2.37 m<sup>3</sup>/kg. In the second stage due to the gas decrease the LHV decrease also. This can be explained by the oxidation reactions which also decreased the concentration of CO, CH<sub>4</sub> and C<sub>n</sub>H<sub>m</sub> and increased the CO<sub>2</sub> concentration. In this case the optimum ER parameter was chosen.

In Narvaez et. al. [56] the ER varied between 0.25-0.45. By **increasing the ER** the H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> is reduced. In biomass gasification process a maximum concentration of H<sub>2</sub> was obtained at ER of 0.26. The tar content decreased also by increasing the ER at 0.45. They reported a LHV of 5.2–7 MJ/m<sup>3</sup> at ER of 0.25 and 3.5–4.5 MJ/m<sup>3</sup> at ER of 0.45.

Mansaray et al.[57] also obtained lower heating value of the produced gas from biomass at high ER which was enabled due to the promotion of the oxidation reaction and dilution of the produced gas with N<sub>2</sub>. In their report the ER was increased from 0.25 to 0.35, the concentration of CO<sub>2</sub> and N<sub>2</sub> also increased while the concentration of the combustible gases gradually decreased. Over more the **tar yield** decreases from 14.6 kg/h to 7.0 kg/h as consequence of the large oxygen amount that can react with volatiles in the pyrolysis zone. They also realized that the gas yield increased from 1.3 to 1.98 m<sup>3</sup>/kg<sub>lignocellulosics</sub> as the ER was raised from 0.25 to 0.35.

Kim et. al.[58] observed some remarkable differences in the biomass and mixed plastic air gasification. In the plastic mixture experiment with **increasing ER**, the variation in the **H<sub>2</sub>** concentration is not significant, but shows a **small decrease**, from 14.18 vol.% to 12.56 vol.%. In the case of biomass gasification in the same gasifier, the decrease in the H<sub>2</sub> concentration was relatively strong at a higher ER. The small decrease in H<sub>2</sub> concentration in the plastic gasification may have been caused by the generation of tar being much higher during the plastic gasification compared to that during biomass gasification and; therefore, tar adsorption and cracking, which leads to H<sub>2</sub> production, take place more sufficiently and actively, even at a higher ER than that of the biomass gasification.

It has been reported that the gasification of paper waste in a fluidized bed gasifier at 650°C with an ER of 0.2 reach up to **syngas flow rate** ( $Q_{\text{syngas}}$ ) of 0.84 Nm<sup>3</sup>/kg<sub>paper waste</sub>. In the same study plastic waste reaches up to  $Q_{\text{syngas}}$  of 3.1 Nm<sup>3</sup>/kg<sub>plastics</sub> at 700°C and ER of 0.2[59].

In the present study the ER of 0.2-0.3 was chosen as an optimum parameter for the packaging waste mixture used in the air gasification process in a lab-scale rotary reactor.

Ahmed et al. [60] reported results on the gasification of PE and wood chips in terms of syngas yield, hydrogen yield, total hydrocarbons yield, energy yield and apparent thermal efficiency have been shown from PE–WC blends as compared to expected weighed average yields from the individual components at 900°C using steam as gasifying agent.

According to Di Gregorio and Zaccariello, 2012 the energetic, environmental and economic performances of the Packaging Derived Fuel (PDF) to energy gasification based plant (bubbling fluidized bed air blown gasifier ) for a nominal capacity of 500 kW<sub>e</sub> is reported in Table 1.3 [61].

**Table 1.3. Synthesis of Energetic, Environmental and Economic performances for the PDF-to- energy**

	<b>Power production</b>	<b>Combined heat and power</b>	<b>District heating</b>
<i>Energetic performance</i>			
Total energy conversion efficiency, %	23.8	78.2	78.2
Specific PDF conversion rate, kWh/kg <sub>fuel</sub>	0.97	3.20	3.20
<i>Environmental performance</i>			
Waste export, kg/kg <sub>fuel</sub>			
Liquid	0.035	0.035	0.035
Solid	0.033	0.033	0.033
Gas	7.96	7.96	7.96
<i>Economic performance</i>			
Total plant costs, k €/kW <sub>e</sub>	4.86	5.04	7.44
Operating costs, (k €/y)/kW <sub>e</sub>	0.53	0.54	0.63
Average cash flow (k €/y)/kW <sub>e</sub>	0.35	1.5	1.56
Internal rate of return,%	0.5	29.8	18.9

The previous research highlights the main **benefits** given by gasification over combustion such as:

- gasification-based plants in the power configuration (i.e. first cleaning and then burning the syngas) involve reduced environmental loads compared to those combustion-based because of the reducing reaction atmosphere.
- the latter observation implies very low exhaust gas rates compared to those from combustion plants which must be operated with an air excess between 50 and 70%.
- the substoichiometric oxygen flow rates fed in the gasification reactors promotes the partial oxidation of the carbon content of the fuel and, therefore, a low CO<sub>2</sub> emission.
- utilizing the fluidized bed reactor and applying the tar recycling solution, the only solid waste stream to be disposed is that of ash residues collected at the cyclone, representing only the 2.3% of the original waste (PDF).

## CHAPTER 2

### 2. PHYSICAL-CHEMICAL CHARACTERIZATION OF LIGHT PACKAGING WASTE

#### 2.1. Light packaging waste physical-chemical characterization: a literature review

In the current sub-chapter, valuable up-to-date literature information will highlight the physicochemical properties that contribute to the knowledge on cellulose, lignocellulose and polymers WtE transformation chain. The final goal of these comprehensive study is to determinate the optimal polyolefins and lignocellulosic packaging waste mixture parameters for engineering purpose development in conventional WtE plants. In this study six representatives' commercial plastic solid waste (PSW), paper and cardboard waste (PCW) were chosen due the significant quantities in the MSW streams: newspaper, cardboard, Tetra Pack(R), high density polyethylene (HDPE), PP (polypropylene) and PET (polyethylene terephthalate).

The study was conducted due to technological necessities, by breaking barriers which trend to delay the widespread of conventional industrial waste energy recovery plants. One of them is a constant remaining problem regarding the quantitative and qualitative waste characteristics influenced by: heterogeneity, size, form, moisture matter, density, porosity, biodegradable content and change of purity level by the end of its life cycle. The latter characteristics dictate the primary WtE process parameters in terms of: temperature, primary agent by type of process ( $N_2$ , air, oxygen or steam), thermal degradation associated with retention time, heating value and ash content. To all these it can be added the effect of reaction conditions, the mechanism of reaction and process kinetics.

These data are compared with the experimental results obtained during the research.

##### 2.1.1. Paper and Cardboard

Typically paper consists on organic and inorganic materials. The organic portion includes cellulose, hemi-cellulose, lignin and/or various compound of lignin (from 70% up to 100%). The inorganic portion is mainly made of filling and loading materials such as calcium carbonate, clay, titanium oxide etc. (0-30%).

On the **molecular level**, cellulose, the primary and most stable component of paper fibers has properties imposed by its structure, which creates amorphous and crystalline regions in fibrils. The amorphous regions are random, flexible, and water accessible while the crystalline regions are ordered, rigid, inert, and relatively impermeable to water [62].

The **density** of paper ranges from  $250 \text{ kg/m}^3$  for tissue paper to  $1,500 \text{ kg/m}^3$  for some special paper. Printing paper is about  $800 \text{ kg/m}^3$  [63].

**Dimensional stability** of paper can be improved by avoiding fiber to absorb moisture. This dimensional instability of paper arises ultimately from the moisture sensitivity and swelling of the cell wall [64]. Considering the type of paper, the dimension of paper varies with moisture content, therefore the use of paper can be by expansion or contraction. It has been observed that cellulosic fibres swell in diameter from 15 to 20%, passing from the dry condition to the fibre saturation point.

**Friction** is the resisting force (kinetic/static) that occurs between two paper or paperboard surfaces in contact when the surfaces are brought to slide against each other. This is valued thorough the coefficient of friction, which is the ratio of the frictional force, to a force acting perpendicular to the two surfaces. Measurement of the coefficient of friction has applications in packaging where a high coefficient will indicate that containers such as sacks, bags and paperboard containers will resist sliding in unit loads or on packaging lines [27].

Almost all grade of paper has some percentage of **moisture**. Moisture in paper varies from 2 - 10% depending on relative humidity, type of pulp used, degree of refining and chemical used as Table 2.1 shows. Most physical properties of paper undergo change as a result of variations in moisture content. Water has the effect of plasticizing the cellulose fiber and of relaxing and weakening the inter-fiber bonding. The electrical resistance and the dielectric constant of paper both vary with moisture content. The absorption and reflectance of certain bands of infrared and microwave radiation by paper are affected by its moisture content. The amount of water present in a sheet of paper is usually expressed as a percent. The amount of water plays an important role in calendaring, printing and converting process. Moisture control is also significant to the economic aspect of paper making. Water comes free. Poor moisture control can adversely affect many paper properties[65].

**Table 2.1. Typical paper moisture values**

<b>Grade</b>	<b>Percentage [%]</b>
Newsprint	7.5-9.5
Office/Business Paper	4-4.5
Printing paper	6-7
Tissue	2-7
Accepted trade tolerance+/- 10%	

**Temperature and humidity** are two other important parameters that are related with moisture. This effect conditions on the physical properties determinates the buildup of static of the paper subjected to pressure and friction. With the increase of dryness the paper becomes more static. Furthermore the cellulosic fibers are hygroscopic, in other terms, there are capable of absorbing water from the surrounding atmosphere. In this context, the amount of water depends on the humidity and temperature of the air in contact with the paper.

The **pH** value of paper might indicate atmospheric pollutants (e.g. SO<sub>2</sub>) or residual acidic/alkaline chemicals existence in the pulp (e.g. lignon in the wood pulp).

**Permanence** is paper conversation property in time (up to several hundred years). The types of paper which have high long permanence are acid-free with alkaline reserve (e.g. the pure cellulose fiber).

The most fiber-based papers have a varying degree of **porosity**. This parameter represents a critical factor that can indicate the absorption rate of the material, influencing the moisture content and not only. Paper is a highly porous material and contains as such as 70% air.

For paper WtE conversion, besides the characteristics mention above, we can't disregard the size, colour and opaque grade that might influence the gaseous species properties during the thermo-chemical process.

### 2.1.2. Plastics

Plastics are polymers ready to be thermally decomposed. It is well known that plastics are mostly derived from crude oil and are more thermally stable than the cellulosic materials. The physical properties of polymers depend not only on the kind of material but also on the molar mass, the molar-mass distribution, the kind of branching, the degree of branching, the crystallinity (amorphous or crystalline), the tacticity, the end groups, any superstructure, and any other kind of molecular architecture. Furthermore, the properties of polymers are influenced if they are mixed with other polymers (polymer blends), with fibers (glass fibers, carbon fibers, or metal fibers), or with other fillers (cellulose, inorganic materials, or organic materials)[66].

The three type of materials studied in the current research PE, PP and PET are specific from the polyolefins family. They are produced from olefin (alkene) monomers because the olefins contain a reactive double bond. The starting material, ethylene, is called the monomer and the final product consisting of many thousands of bound ethylene units is called the polymer[67]. It's estimated that polyolefins represent 40% of total plastics production in Western Europe, which is 55 million tons year<sup>-1</sup> [68]. This group of thermoplastic polymers, such as HDPE, LDPE, PE and PP is characterized by having similar physical and chemical properties, that limits the separation process by fraction and increasing its costs. The polymeric structure of both LDPE and HDPE is essentially a long chain of aliphatic hydrocarbons. PP has a slightly different structure than LDPE and HDPE with a metyl group (CH<sub>3</sub>) in the repeating unit [37].

- **PE (C<sub>2</sub>H<sub>4</sub>)** is a type of polyolefin with a density of 0.94–0.96 g/cm<sup>3</sup>. Because of its versatility (large range of density, molecular weight (MW) and MW distribution, and chemical inertness), LDPE remains a popular plastics in use today. Its melting point temperature varies in range from 126 up to 135°C. The heat capacity cp might come to 2.1–2.7 kJ\*kg/K. [69].

- **PP (C<sub>3</sub>H<sub>6</sub>)**-is a type of polymer with a density of 0.886 - 1.70 g/cm<sup>3</sup>. A major advantage is Polypropylene's higher temperature resistance 173°C.

- **PET (C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>)**- has benefits from processing characteristics and high strength and rigidity for a broad range of applications: extreme low water absorption, resistance to chemical attack and high environmental stress crack resistance, heat ageing resistance (melting temperature 255°C ), good colour stability. As physical property we can mention the 1.37 g/cm<sup>3</sup>. The moisture absorption at saturation in air of 23 °C is 50% RH (relative humidity).

A combination of paper and plastics was studied using tetra pack® packaging waste. The components of **Tetra pack®** are: kraft paper (about 70% in weight, wt), low-density polyethylene (LDPE, about 25 wt %), and aluminium foil (about wt 5%). For this reason their degradation is correlated to the decomposition of lignocelluloses and plastic fractions.

## 2.2 Aim of the physical-chemical experimental research

Some of the impediments to establish the optimal parameters for a WtE large scale plant are: waste feed flow that should be representative for local or regional area, the environment process reproduction that can provide the same accuracy results, the use or treatment of secondary products and pollutants emission.

The most common wastes analyses are: Elemental Analyzer, Calorimetric Bomb and Thermo-Gravimetric Analysis. One of the main drawbacks of this test is provided by the quantity of the sample ranging from micro quantities (a few milligrams) to bulky and dense materials. Therefore a representative sample mixture from MSW is almost excluded from the discussion. Beside that argument the materials can be analyzed by fraction obtaining valuable information on: ultimate and proximate composition, heating value and thermal degradation, the effect of reaction conditions, the mechanisms of reactions and the pyrolysis kinetics.

In worldwide scientific research, former analyses were made on packaging waste most of them have been performed on materials with a purity of up to 99%. In this context, the physical and chemical properties of the material which can be acquired during the landfilling process are not taken into account. From this point of view, the laboratory tests were made on wastes taken directly from a Romanian landfill sites or from selective collection, for more accurate results and applicability on industrial waste energy recovery plants. All the samples were washed and dried before being subject to tests. For a higher accuracy of the tests certain analysis standards can be found. Most of the codes are referring to coal and coke analysis which can be a starting point for MSW analysis [70].

In the present research, the aim of the chemical and kinetic experimental characterization is to offer a preview on range selection of the input data for the display process by making a direct comparison with the data that can be found in literature.

## 2.3 Material and methods

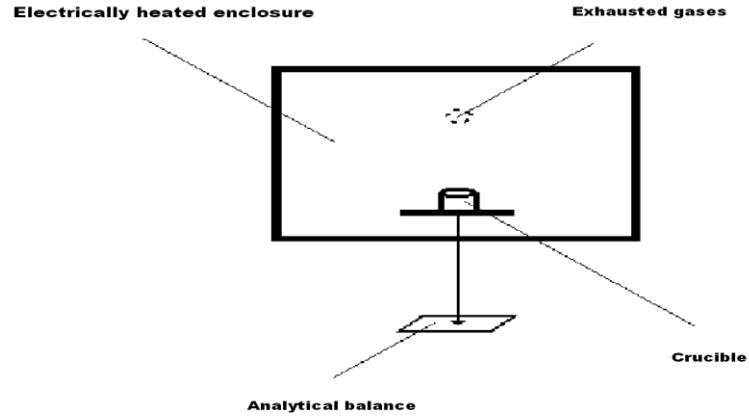
### 2.3.1. Proximate analysis

First the thermo-chemical characterization was made for each waste component separately due to high heterogeneity of the product and small quantity analyzed. A lab scale electric furnace was used for the determination of proximate analysis.

The volatile matters, inert and fixed carbon content were determinate in dry basis for newspaper, cardboard, Tetra Pack, HDPE, PP and PET. The data will offer a first insight on the energetic characteristics and kinetic behaviour of the packaging waste fractions studied.

#### 2.3.1.1. Calcination furnace

The primary analysis for volatile matter, fixed carbon and inert fraction determination was made using the Nabertherm electric furnace, type L9/11/SW with the following components (shown in Figure 2.1): carriage, precision balance, swing gates door and rated operating temperature of 1100°C. It's also equipped with a multilayered insulation that consists from high quality refractory materials for reducing heat loss. The temperature are measured with a thermocouple NiCr-Ni long life that be found inside the furnace. Some indications from D3173-85 ASTM-standard were considered.



**Figure 2.1 Electric furnace scheme**

The higher safety operation class of the instrument is given by a control device that offers security against most types of operating errors. Environmental conditions for optimal operation are a temperature of 5-40 ° C and humidity up to 95% without any condensation. The amount of air allowed inside can be adjusted with a lever located on the right side of the oven door. All command and control operations for the oven is made from a device command and control type P320MB1, which allows programming the oven temperature variation for the five ramps and four levels of temperature and can thus simultaneously set four different temperatures, each corresponding a residence time of the oven at that temperature and heating times between two temperatures. The device has a digital screen that displays the current temperature indicated by thermocouple (located in the furnace room) and a series of status indicators of the process.

In order to obtain the volatile matter fraction, the samples were subject to a pyrolysis process with an average temperature of 800°C for 40 minutes of dried material. The difference in weight between before and after heating gave the volatile solids content (%) of the sample.

$$\text{Volatile Solids (VS)} = \frac{\text{Loss in weight}}{\text{Net dry weight}} \times 100 \quad [\%] \quad \text{Equation 2.1}$$

The fixed carbon and inert (non-combustible) fraction were determined in a combustion process at 1000°C, for about 1 hour [71].

$$\text{Inert} = \frac{\text{Loss in weight}}{\text{Net dry weight}} \times 100 \quad [\%] \quad \text{Equation 2.2}$$

$$\text{Fixed carbon (FC)} = 100 - \text{Volatile Solids} - \text{Inert} \quad [\%] \quad \text{Equation 2.3}$$

## 2.3.2. Ultimate analysis

### 2.3.2.1. Elemental Analyzer

The elemental composition of the material studied was performed in an Euro EA Elemental Analyzer 3000 (with 0.3% accuracy). As Figure 2.2 shows, the EA 3000 series is based on the principal of dynamic flash combustion using chromatography separation of the resultant gaseous species ( $N_2$ ,  $CO_2$ ,  $H_2O$  and  $SO_2$ ) and TCD detection. The carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) concentration elements were determinate after the combustion of the sample, using Helium as gas flow carrier. The analytical process was made automated using the Callidus Software. The D3174- 82 ASTM standard was used. The parameters used in the analysis were: the carrier flow 80 ml/min, the carrier pressure 80 kPa at a temperature of 980°C for front furnance and 115°C for gas-chromatography oven.

Due to the low weight of the sample, 0.7 – 2 mg, the mixture of the materials is difficult and unfeasible. For this reason the experiments were carry out on each packaging waste fraction.

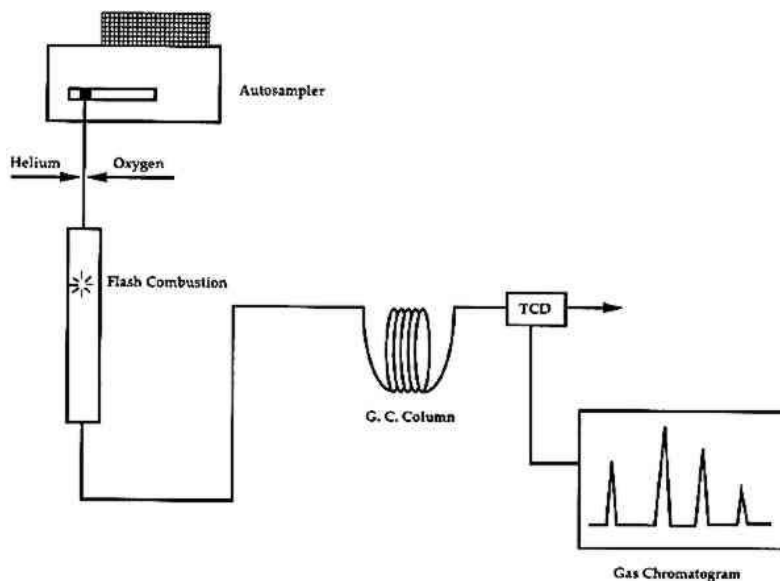


Figure 2.2. Elemental Analyzer EA 3000[72]

### 2.3.2.2. Scanning Electron Microscopy (LV-SEM) [73]

The goal of the current investigation was to determine the chemical composition of selected packaging materials coming from different countries and compare these measurements with the data obtained through Carbon-Hydrogen-Nitrogen-Sulphur-Oxygen (CHNS-O) elemental analyzer, which is conventionally used to characterize waste materials. A second objective of the study was to observe the morphology and microstructure of the surface of the samples and locate eventual elemental impurities detected through the chemical analysis. The capabilities of the experimental approach are discussed in connection with their application to the study of waste sample materials and in comparison with alternative experimental methods such as Elemental

Analysis (EA). These data provide a more accurate evaluation of packaging waste life cycle assessment and its environmental impact.

### **Low Vacuum Scanning Electron Microscopy (LV-SEM) - Energy Dispersive X-ray Spectroscopy (EDXS) analysis of packaging samples**

In the present experiments, the raw packaging material (used as reference) and packaging waste sample analyzed are representative for the MSW flow in England, Italy and Romania. The paper and cardboard, Polypropylene (PP) and Polyethylene terephthalate (PET) waste samples were provided from the countries mentioned above. In order to detect the possible changes during packaging materials life cycle, pure sample (reference sample) of plastics were analyzed.

SEM observations were carried out using a low-vacuum (LV) instrument equipped with an EDXS system. Low vacuum conditions were used during SEM observations (LVSEM). The pressure in the specimen chamber was kept at 0.5 Torr by introducing a controlled amount of water vapour. The presence of the gas in the chamber reduces the accumulation of charge on the surface of the samples and allows their imaging without coating their surfaces with gold or carbon even if, as the analysed packaging materials, are nonconductive. This guarantees a better chemical analysis by EDXS, as there is no contribution from the coating material and moreover allows the preservation of the specimen that remains available, unchanged, for possible further analysis. In the case of paper-based materials this also guarantees to keep the original moisture content in the material [74]. The selection of the operational parameters of the scanning electron microscope was driven by the fact that the samples to be analyzed are organic and thus electron beam sensitive [75] and composed of low atomic number elements that scatter weakly the electrons producing low image contrast [76]. Although, in the present work the low vacuum mode was employed, and thus the charge accumulation on the surface was reduced, radiation damages of the sample were observed after the accomplishment of EDXS analysis or when the beam was focused on a small area. As already observed by Rothbard [8] for paper materials, it was found that operating the instrument at 10 kV is more appropriate for these sensitive samples than 20kV accelerating voltage that is conventionally used in our laboratory for other inorganic samples. In fact, lowering the primary beam accelerating voltage reduces the beam current at the sample and, thus, should lower the chances of damage. As a consequence, the results of the EDXS analysis will be related to an interaction volume closer to the surface because the beam will penetrate less in the sample. The samples were mounted on a SEM stub using a conductive tape and the images of their surface were recorded using the Gaseous Secondary Electron (GSE) and the Backscattered Secondary Electron (BSE) detectors at different magnifications. The GSE detector is able to capture the low energy secondary electrons produced by the inelastic interaction of the beam with the material at a depth of 50-500 Å in the sample and, thus, provides high resolution images which highlight the morphology of the surface; the BSE detector collects the high energy backscattered electron produced by the elastic scattering between the electrons and the material in deeper areas of the sample and whose emission is dependent on the atomic number and thus it allows the detection of differences in composition among the various areas of the sample. EDXS spectra were acquired with a counting time of 100 seconds and, through the software that controls the analysis (GENESIS, 2001), setting up a region of interest (ROI) in the range of energies where the x-ray photons of the sulphur characteristic K line are detected: from 2.250 keV to 2.360 keV. To detect differences in the composition of packaging waste materials coming from different countries, the measurements were acquired under identical conditions, in order to have similar background counts. The EDXS spectra of the matrix of the samples were acquired placing the microscope in the scan mode, thus the x-rays collected were from the entire field of view. The EDXS spectra of the particles deposited on the surfaces of the samples and on

the inclusions were acquired placing the microscope in the spot mode which allows the collection of the x-rays only from that spot.

Special attention was given to the detection of sulphur in the materials, as it would cause unwanted effects during their incineration in waste treatment plants [77].

### 2.3.3. Energy potential

The determination of heating value of the materials used in the research will give an insight of the amount of fuel output and energy that could be recovered. Generally, the heating value of a fuel may be reported on two bases, the higher heating value or gross calorific value and the lower heating value or net calorific value. The higher heating value (HHV) refers to the heat released from the fuel combustion with the original and generated water in a condensed state, while the lower heating value (LHV) is based on gaseous water as the product [78].

In the first part of this section, the direct combustion of the samples was made in order to determine the energetic potential of the materials. The calorimeter system C 200 was used for the High Heating Value (HHV) estimation of the samples.

Secondly, using the proximate and ultimate analysis data, several prediction models are used for HHV and Low Heating Value (LHV) estimation.

#### 2.3.3.1. Calorimetry

The heating value of light packaging waste was determined experimentally with calorimeter system C 200 using the ASTM D2015 standard method. The C200 (Figure 2.3) is a compact low cost combustion calorimeter used to determine calorific values of liquid and solid samples by employing an adiabatic bomb calorimeter which measures the enthalpy change between reactants and products. It is easy to use due to its Keypad and a clear display. Another great feature is its size. The “IKA-Cube” with its dimensions of 400 x 400 x 400 mm (16 x 16 x 16 inches) fits in almost every niche. The unit is highly operator maintenance friendly. The external power supply of the unit complies with all global voltages from 100 - 240V AC, 50/60 Hz. The Calorimeter itself is powered with low operating voltage 24 V DC. Calorific value measurements can be made in accordance with DIN, ISO, and ASTM. Details about the Standards can be found in the Standards Section of this Guidebook. There are 4 different measurement modes available. Depending on the purpose the user can choose the best mode for each individual application.

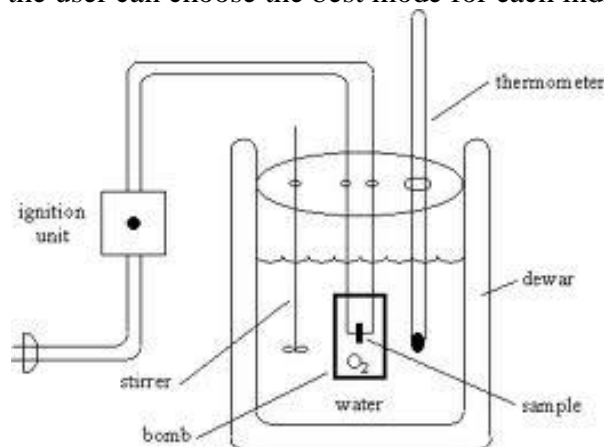


Figure 2.3. Calorimeter device C 200[79]

The calorimeter bomb, after the sample charge, is saturated with 30 bar of pure oxygen. The weight sample will not exceed 20 mg. The high heating value (HHV) of the samples was estimated with accuracy of 99.85%. Low heating value (LHV) was obtained by subtracting the heat of vaporization of the water vapour from the HHV.

### 2.3.3.2. Prediction of heating value from proximate and ultimate analysis

Even though the calorimeter is easy to use and relatively accurate, it might not always be accessible to researchers. The determination of heating value is possible using empirical correlations based on the ultimate and proximate analyses data. One of the earliest and most popular correlations used in nowadays is the Dulong's correlation first introduced in the late 1800s and based on data from ultimate analysis of coal. Up to now, based on elemental analysis data, alternative formula are applied for MSW calorific value determination. Other researchers had developed empirical models based on proximate analyses data obtained from co-cracking of petroleum vacuum residue with coal, plastics and biomass [80].

Still there are impediments when it comes to a fully commingled waste stream heating value determination. Major difficulties are faced in obtaining accurate results, particularly for elemental compositions of different waste types, in developing countries. Elemental composition of the waste is the most crucial parameter for determining thermal energy [81].

The empirical formulas used in the current study for **HHV** determination are presented in Table 2.2 (Equation 2.4,2.5,2.6,2.7). These models have been created based on data from the physical composition, proximate analysis and elemental analysis of the fuel or refuse which have limitations and are as follows [82]:

- when a model is created, the basis used, such as the weight, in percentage or in fraction, on an ash free or moisture free basis or both, is not defined in the equation, causing inaccurate usage;
- A review also shows that sometimes the same model is reproduced based on different units causing confusion, i.e. Btu/lb, kJ/kg, kcal/kg, etc;
- Another study clearly states that the models created, performs best in the country/locality in which it is created, while producing over or under prediction when used internationally.

**Table 2.2. Heating value models equation used in the current study**

Name	Equation	Units	Remarks	Application
Dulong	$HHV = 144.5C + 609.6H - 76.2O + 40S + 10N$	Btu/lb	Modified (wt%)	MSW/Coal
Scheurer-Kestner	$HHV = 81(C - 3 \times O/4) + 342.5H + 22.5S + 57 \times 3 \times O/4 - 6(9H + W)$	kcal/kg	(wt%)	MSW
Goutal	$PCS = 147.6FC + K * WV$	Btu/lb	(wt%)	Refuse

\*where : W-wt% water, dry basis; K is a constant that varies with the value of volatile matter

Each type of formula developed is relying on different properties of the material studied. For example in the Dulong and Scheurer-Kestner equation the constant coefficients were assessed by taking into account :

- empirical formulas
- the amount of combustible elements Carbon , Hydrogen and Oxygen
- the anhydrous stage of the material

- molar heat (isobaric)
- heat capacity
- heat of reaction component / product)
- unit expressed
- stoichiometric relationships (Van Krevlen diagram)

The constant coefficients in Goutal equation were developed based on :

- empirical formulas
- the anhydrous stage of the material
- size, shape, resistance to abrasion, material density
- melting temperature
- molar heat (isobaric)
- heat capacity
- enthalpy (component / product)
- ash-free material
- unit expressed
- the K constant is varied with the Volatile Matter content and it can be expressed as :

$$K = \frac{VM}{1.8} [\%] \quad \text{Equation 2.8}$$

**Lower heating value (LHV)** is obtained by a correction factor, calculated according to the Equation 2.9:

$$LHV = HHV - 5.83 \times W \times 4.1868 \quad [kJ/kg] \quad \text{Equation 2.9}$$

\*where: W –material water vapour source; HHV – is given in kcal/kg

$$W = W_t + 9 \times H \quad (\%) \quad \text{Equation 2.10}$$

\*where: W- total moisture content; H - hydrogen fraction, dry basis

To achieve a higher accuracy a comparison between the calorimetric bomb and empirical formulas was made. For a better comparison of the methods paper, cardboard, PP, PE and PET mixture (Mix 1:1) samples were considered. In this punctual work, the influence of moisture growth on HHV was studied. The moisture content was increased with 10% after each experimental procedure. The maximum moisture considered was associated with MSW one, up to 60%. The experimental HHVs reported were compared with Scheurer-Kestner empirical formula results.

## 2.4 Results and discussion

### 2.4.1. Primary analysis of light packaging waste

#### 2.4.1.1. Results and discussion on proximate analysis

The proximate analysis data are relevant in determining what quantity of packaging waste is suitable for thermo-chemical processes. This quantity is the volatile matter component of the waste. Also the analysis offers a preview on the mass balance of the system. The weight

percentages (wt.%) of moisture, volatile matter (VM), fixed carbon (FC) and ash of a packaging waste fractions coming from waste selective collection are presented in Table 2.3.

**Table 2.3. Proximate analysis of samples**

Sample	Proximate analysis [wt%]			
	V.M.	F.C.	Ash	Total
Newspaper	88.4	3.5	8.1	100
Cardboard	87.5	6.6	5.9	100
Tetra pack	90.6	1.3	8.1	100
PP	99.13	0.27	0.60	100
HDPE	99.74	0.06	0.20	100

The cellulosic ash content varies between 5.9 and 8.1 % in comparison with plastic waste where the ash is under 1 %.

One of the key points of the combustion analysis is that both types of materials can be used in mixtures, therefore the quantity of by-products that may require a subsequent storage will be low. The percentage volatile solid is a major consideration with respect to the volume of the paper, cardboard and plastics waste and hence its WtE plants design. So the concentration of the volatile solids provides an indication of the temperature rate and gaseous species produced during the thermo-chemical process and helps in determining the solid-retention time in the batch reactor.

#### **2.4.1.2. Results and discussion on Elemental Analysis**

Depending on the type of packaging waste fraction analyzed, the Elemental Analysis reveals the high energetic potential of each product. This is explained by the high content of carbon and hydrogen from the analysis shown in Table 2.4.

**Table 2.4. Elemental analysis of light packaging waste**

Sample	Ultimate analysis [wt%]					Total
	C	H	N	S	O	
Newspaper	47	7	2	1	43	100
Cardboard	48	8	2	1	41	100
Tetra pack	54.6	5.3	2.8	-	37.3	100
PP	85.5	12.5	1.2	0.1	0.7	100
HDPE	84.70	14.47	0.11	0.12	0.60	100

As expected, according to elemental analysis the chemical composition and the quality of the materials is different even from similar products reported by previous works in the field.

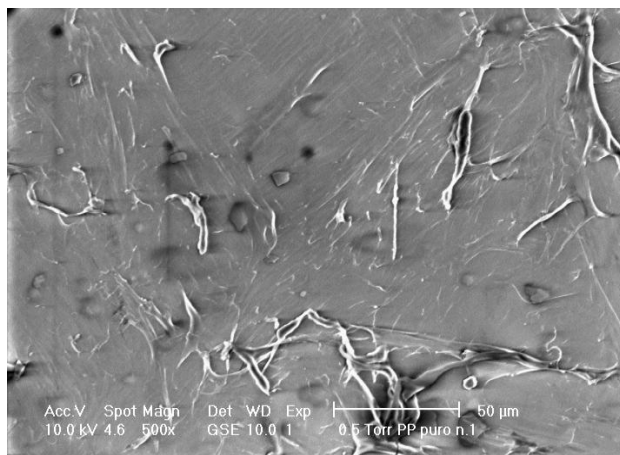
The ultimate analysis points out the carbon content with 40% higher at polyolefines products, in comparison with lignocellulosic materials. Considering that Tetra-Pack has in its composition 25% plastic film, the carbon matter is about 10% higher compared with paper and cardboard. Another interesting aspect that should not be neglected is the sulfur content, which is approximately 1% for paper and 0.12% for plastics. As the literature shows [83,84] the sulfur presence in plastics and paper materials will not exceed 0.37 % respectively 1.47%. Further studies will be dedicated to this discussion in order to determine if new different substances that might

come from the life cycle use change the chemical composition of both paper and plastics materials.

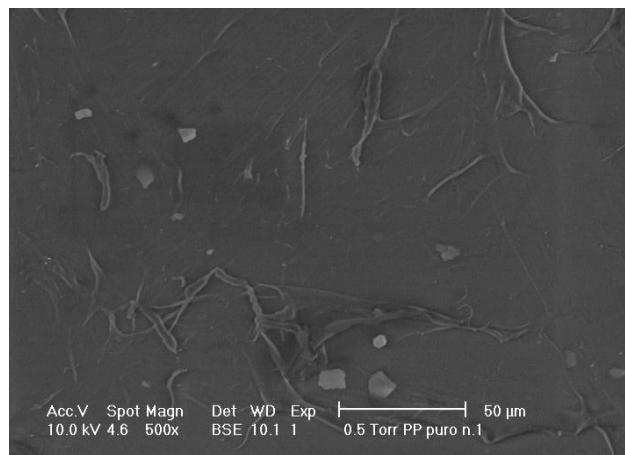
The C/N (%) and C/H (%) ratio for paper and cardboard is similar to hemicelluloses, cellulose and lignin that are the three main components in this type of waste. The C/N and C/H ratio doubled at the polyolefinic polymers in comparison with cellulosic ones due to its crude oil origins. The possibility to obtain rich aromatic hydrocarbons makes plastic waste pyrolysis more attractive, even though the separation process from a fully commingling stream is still challenging. The combination of paper and plastics, Tetrapack product reveal a higher C/N in comparison with lignocellulosic waste.

#### ***2.4.1.3. Results and discussion on Scanning Electron Microscopy analysis***

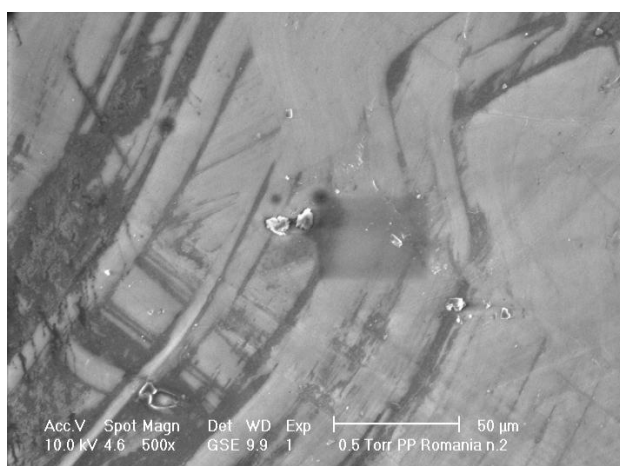
Polypropylene (PP) film is the second most used flexible packaging material [85] and with polyethylene and polystyrene is one of the preferred plastics for chemical recycling because the products of its pyrolysis have properties comparable with petrochemical feedstock [86]. For what concerns the PP samples analysed in this study, it was observed that both the reference one (Fig. 2.5 and 2.5) and the one coming from Romania (Fig. 2.6) have scratched surfaces with deposited irregularly shaped particles. Acquiring the images with the BSE detector the particles look in both samples brighter than the matrix (Fig. 2.8 and 2.9), thereby they should be composed by elements with higher atomic number than the matrix. On the surface of the reference PP also some fibre-shaped/branch-shaped particles were observed. Acquiring the images of these two samples with the BSE detector it appears that they are quite homogeneous in composition as no areas with strong differences in the hues of gray are highlighted (Fig. 2.4).



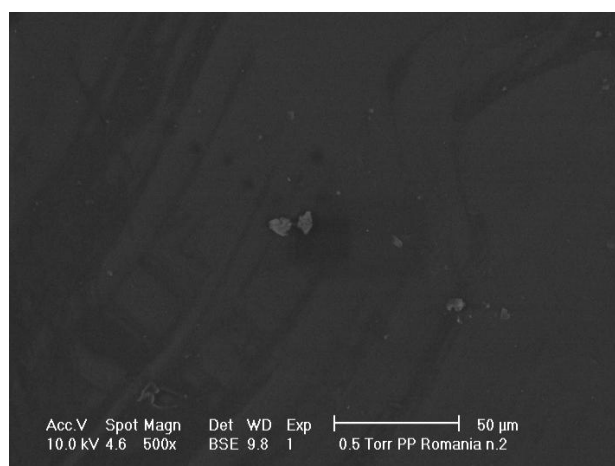
**Figure 2.4. SEM image of reference PP acquired using the GSE detector**



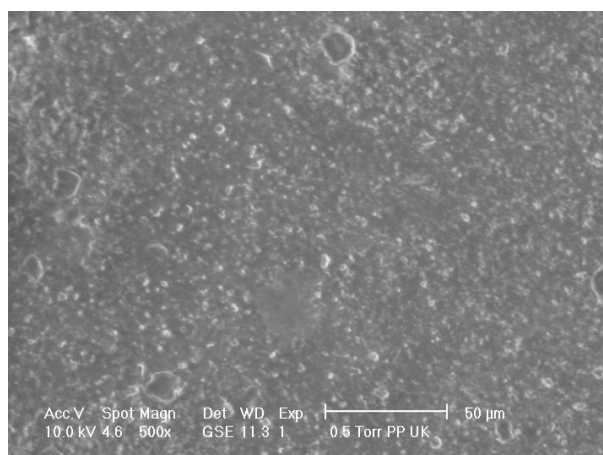
**Figure 2.5. SEM image of reference PP acquired using the BSE detector**



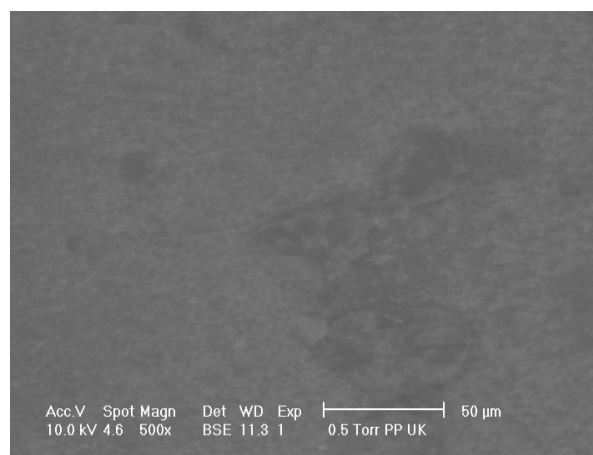
**Figure 2.6. SEM image of PP from Romania acquired using the GSE detector**



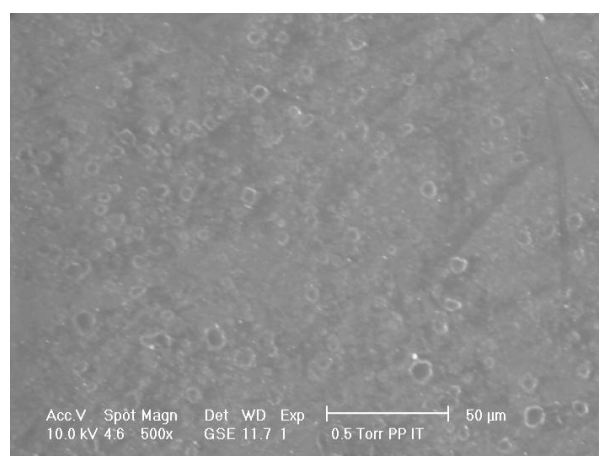
**Figure 2.7. SEM image of PP from Romania acquired using the BSE detector**



**Figure 2.8. SEM image of PP from UK acquired using the GSE detector**

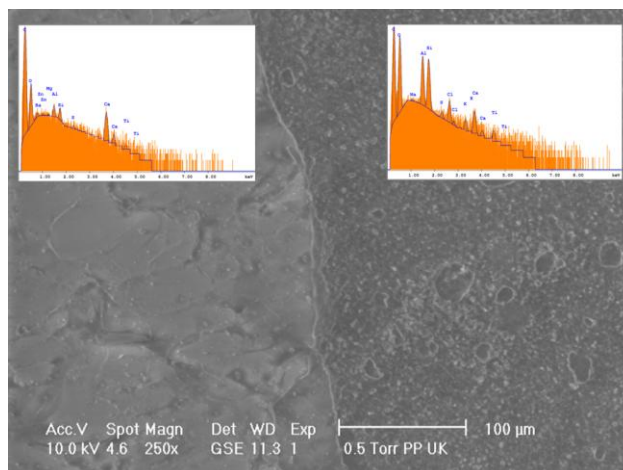


**Figure 2.9. SEM image of PP from UK acquired using the BSE detector**



**Figure 2.10. SEM image of PP from Italy acquired using the GSE detector**

The UK PP material shows different surface microstructures in Figure 2.8. In Figure 2.8 the spectrum is plotted in logarithmic scale. Some elements shown were not considered in the quantification because the number of counts in their peak (P) was not statistically significant with respect to the background counts (B), that is  $P < 3\sqrt{B}$ . The zone characterised by the microstructure in Figure 2.5 and on the right in Figure 2.8, which is the most common in the whole sample, has a higher aluminium (5.5 wt%) and silicon (5.0 wt%) content than the other region, as that on in Figure 2.8, where aluminium and silicon constitute only the 0.3% in weight each.



**Figure 2.11. SEM image of polypropylene from UK acquired using the GSE detector and EDXS spectra of two different zones in the matrix.**

The EDXS analysis highlighted some differences in the composition of the samples (Table 2.5): the matrix of the polymer coming from UK contains more aluminium and silicon than the reference, the Romanian and the Italian samples. A small amount of titanium was detected in the reference sample and not in the other materials.

**Table 2.5. Elemental compositions (wt %) of the matrices of the samples determined by EDXS.**

Sample	C	O	Al	Si	Ca	Ti
PP reference	87.2	10.2	1.1	0.5	\	0.8
PP Romania	96.0	1.8	1.7	\	\	\
PP Italy	79.2	18.5	\	1.9	\	\
PP UK	68.1	21.9	4.0	3.8	\	\
PET reference	71.2	28.7	\	\	\	\
PET Italy	77.5	22.5	\	\	\	\
PET UK	71.8	28.2	\	\	\	\
Paper Italy	56.9	37.3	0.8	1.0	3.9	\
Paper UK	58.6	39.3	\	\	\	\
Cardboard Romania	64.3	34.1	\	\	\	\

The particles deposited are different too (Table 2.6): on the reference sample they contain, in addition to carbon, oxygen, aluminium and silicon, also titanium (1.4 wt%); the dust on the Romanian PP instead has a high silicon content (6.4 wt% compared to 0.8 wt% in the pure sample) and contain calcium (2.0 wt%) and sodium (0.8 wt%); the particle on the PP from the UK contains calcium (2.0 wt%), while on the Italian sample two different kind of particles are deposited: the first is rich in Al (4.7 wt%), Si (7.9 wt%) and K (2 wt%); the second type contains magnesium (3.2 wt%) and lower amounts of silicon (1.5 wt%) and potassium (0.3 wt%).

**Table 2.6. Elemental compositions (wt %) of the particles on the samples determined by EDXS.**

<b>Sample</b>	<b>C</b>	<b>O</b>	<b>Na</b>	<b>Mg</b>	<b>Al</b>	<b>Si</b>	<b>Ca</b>	<b>Cl</b>	<b>K</b>	<b>Ti</b>
PP reference	79.1	16.9	\	\	1.6	0.8	\	\	\	1.4
PP Romania	74.5	13.0	0.8	\	1.6	6.4	2.0	\	\	\
PP Italy	59.1	24.4	4.9	3.2	4.7	\	\	\	2.0	\
PP UK	94.2	4.1	\	\	\	\	1.2	\	\	\
PET Italy	84.4	14.3	\	\	\	\	\	0.6	0.6	\
PET UK	72.1	25.9	\	\	0.3	0.3	\	0.6	0.6	\
Paper Italy	60.9	30.9	\	\	1.6	1.9	4.5	\	\	\
Paper UK	61.9	22.7	2.2	\	\	\	\	6.3	12.1	\
Cardboard Romania	48.1	37.0	2.8	\	2.9	8.3	\	\	\	\

In Table 2.7 they were determinate: average Counts Per Seconds (CPS), Total Integrated Counts (INT) in the S K peak Region Of Interest (ROI) and minimum total intensity ( $INT_{min}$  calculated as  $3\sqrt{B} + B$ ) of the sulphur peak in the EDX spectra acquired on polypropylene samples. The use of the SK ROI (2.250-2.360 keV) aimed at being sure that the number of counts reached in 100 seconds in the energy range of sulphur x-ray emission was sufficient to detect an eventual presence of this element confirmed its absence in the samples. Then, the acquisition time was set in order to stop when the minimum number of counts in the ROI necessary to detect sulphur ( $INT_{min}$ ) was reached (see Table 2.7). When the acquisition time was kept at 100 seconds the number of counts (INT) was always higher of  $INT_{min}$ . The  $INT_{min}$  was calculated from the minimum detectable concentration of the microanalysis system<sup>1</sup> given in Table 2.7 together with the minimum number of counts in the peak (above the background) that would be necessary given the same background counts to state that sulphur is present and consider valid the concentration in wt% calculated by the EDXS software. This value was summed to the background counts in order to estimate the  $INT_{min}$ . The number of CPS in the region was never relevant to suspect the presence of sulphur (see Table 2.7). The absence of sulphur was evident also programming the acquisition time to reach the minimum number of counts in the ROI. In Table 2.8 they were determinate the: Average net intensity (P), background intensity (B) and minimum net intensity ( $P_{min}$  calculated as  $3\sqrt{B}$ ) of the sulphur peak in the EDX spectra acquired on the matrix of the polypropylene samples.

<sup>1</sup> The minimum detectable concentration of the microanalysis system is a measure of the smallest amount of a particular element that can be detected with a defined statistical certainty (Williams and Carter, 1996). The detectability limit, given a certain counting time, depends on the count rate in the characteristic peak range (above background) and on the count rate in the background. To state at the 99% confidence limit that a peak is present, and thereby needs to be identified, the number of counts in the characteristic peaks (above background) must exceed by three times the square root of the number of counts in the background ( $P > 3\sqrt{B}$ ).

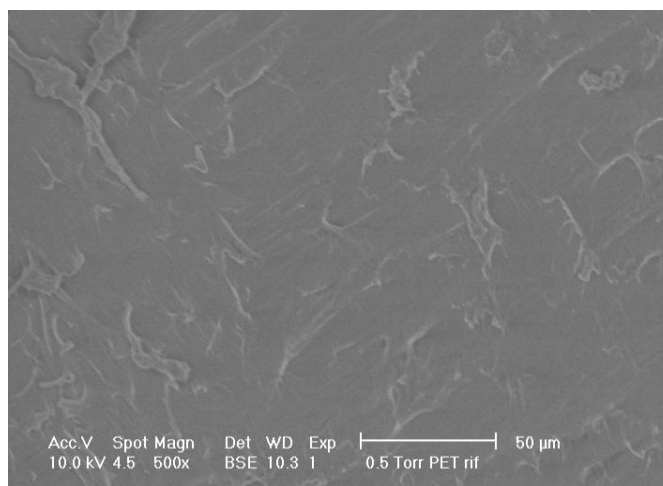
**Table 2.7. Determination of CPS, INT in the S K peak ROI and INT<sub>min</sub>**

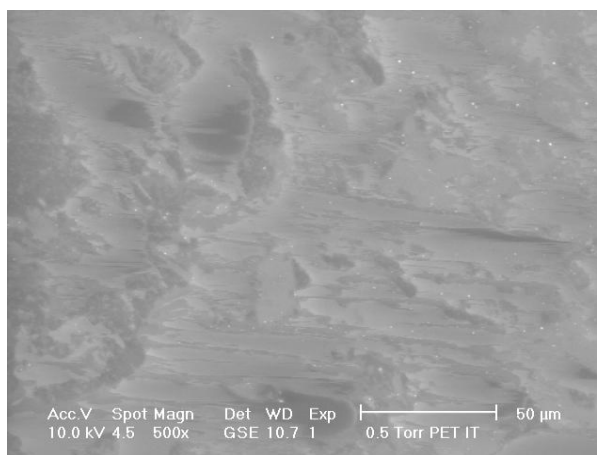
Sample	CPS	INT	INT <sub>min</sub>
PP IT matrix	2	256	6
	2	266	
	2	284	
PP IT particle type 1	2	295	6
PP IT particle type 2	2	278	5
PP UK matrix	3	317	6
	2	281	
	3	315	
PP UK matrix (different area: left side Figure 2.11)	2	209	
PP UK particle	1	199	5

**Table 2.8. Determination of P, B and P<sub>min</sub> of the sulphur peak in the EDX spectra acquired on the matrix of the PP samples.**

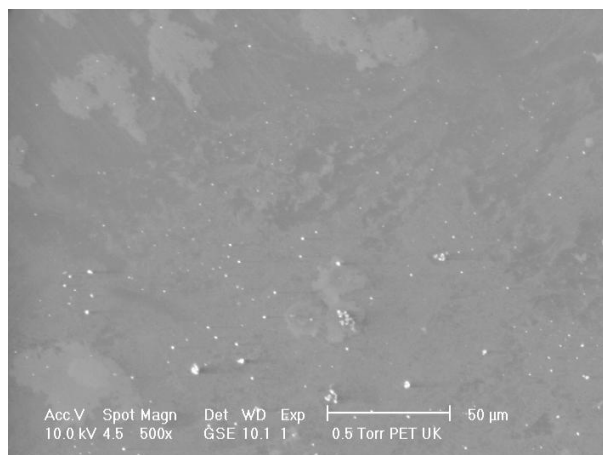
Sample	P	B	P <sub>min</sub>
Reference PP	0.1	1.8	4.0
PP Romania	0.1	0.9	2.9
PP IT	0.5	1.7	3.9
PP UK	0.4	1.9	4.2

The matrices of polyethylene terephthalate (PET) samples, no matter the provenance, seems to contain only carbon (70-80 wt%) and oxygen (20-30 wt%) (see Table 2.5). On the samples from Italy and UK some spherical particles were observed and analyzed (see Table 2.6) and on both materials they contained 0.6 wt% of chlorine and 0.6 wt% of potassium. The particles on the UK PET had also a smaller amount of ravelled (0.3wt%) and silicon (0.3wt%).

**Figure 2.12. SEM image of PET reference sample acquired using the BSE detector**

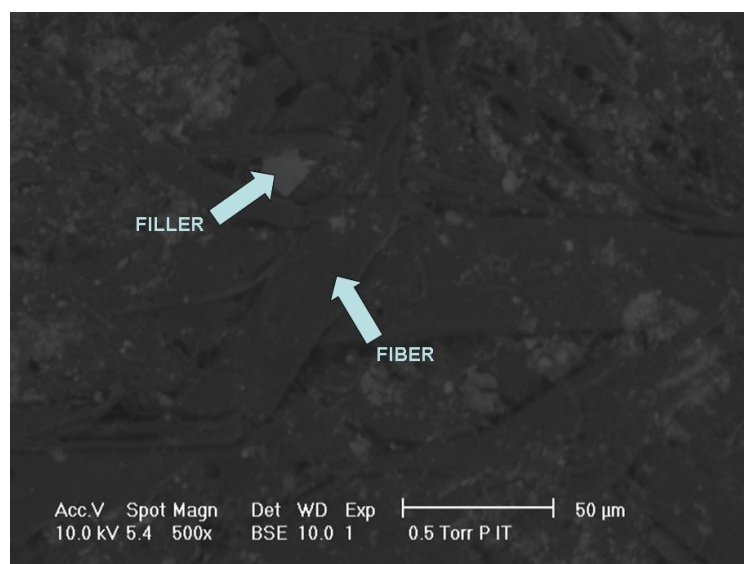


**Figure 2.13.** SEM image of PET from Italy acquired using the GSE detector



**Figure 2.14.** SEM image of PET from the UK acquired using the GSE detector

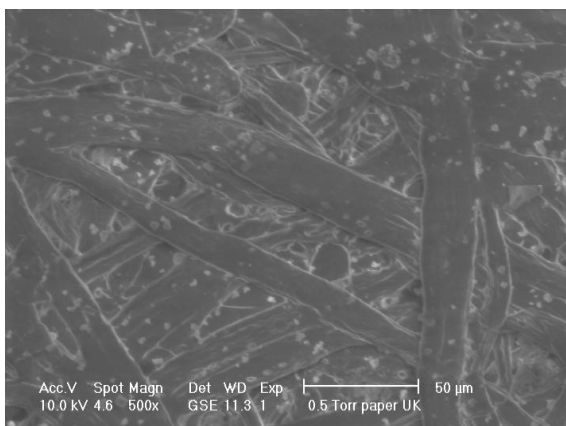
Paper samples show a microstructure characterized by the presence of fibres with heterogeneous dimensions and particles of fillers spread among them. The ability to distinguish between these two components is highlighted through the backscattered electron imaging (BEI) mode which emphasizes the difference in composition of the fibrous matrix and the particles (Figure 2.15). Using BSE imaging mineral fillers stand out as bright particles against the lower atomic number fibrous background. These fillers are fine-grained nonfibrous pulp additives used to add opacity, smoothness, brightness or colour to the paper [74].



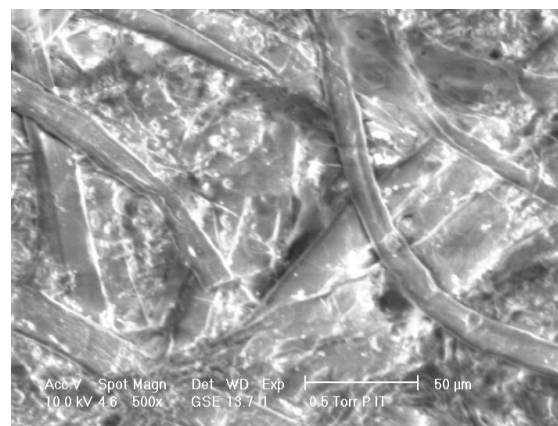
**Figure 2.15.** SEM image of paper from Italy acquired using the BSE detector

The particles in the Italian sample have irregular edges (Figures 2.13 and 2.14) and a high calcium content (Table 2.7.) which may indicate that they are  $\text{CaCO}_3$  fillers [74]. Considering that with SEM a surface layer of a sample is observed and characterized, it has to be considered that the elements detected by EDXS might derive from the paper coating layer. In this context, the presence of calcium carbonate is not surprising as its use to create a pigmented coating, with

the function of providing a glossy, white, smooth surface for printing, has been growing [87]. On the contrary, the Romanian cardboard sample does not contain calcium and has Si-Al based fillers (see Table 2.6). Si-Al particles are to be expected too as a typical coating contains mostly clay (for example kaolin), some calcium carbonate and a binder. Clay, mainly composed of silicon and aluminium is used both for pigmented coatings and as filler because it goes in the void areas on the surface of the paper [87]. The particles spread in the UK sample (Figure 2.14) contain chlorine (6.3 wt%), potassium (4.6 wt%) and sodium (2.2 wt%).

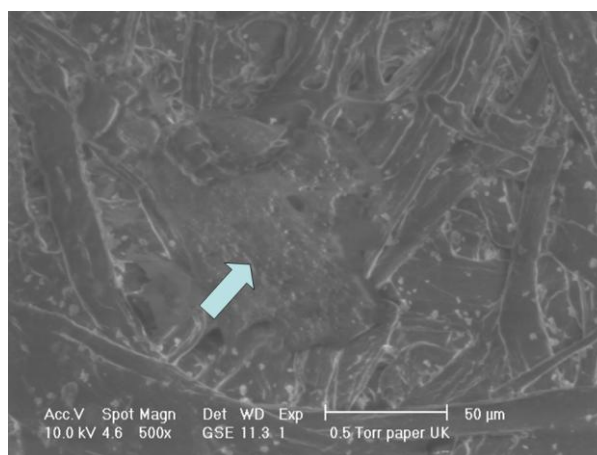


**Figure 2.16.** SEM image of paper from the UK acquired using the GSE detector



**Figure 2.17.** SEM image of paper from Italy acquired using the GSE detector

A EDXS spot analysis was conducted in the area arrowed in Figure 2.18. The counting rate in the sulphur region of interest was higher than in the other areas (5 CPS, 510 INT), however sulphur quantitative analysis is still not statistically significant ( $P$ : 2.34 counts per second <  $P_{min}$ : 4.11 counts per second) and its presence has to be excluded within the detection limit of the system.



**Figure 2.18.** SEM image of paper from UK acquired using the GSE detector.

For the elements for which the quantification is important it is useful to provide the minimum detectability as minimum mass fraction (MMF), that is the smallest concentration (wt.%) that can be measured in the analysis volume. The C (MMF) was calculated.

As  $C(MMF) [wt\ %] = \frac{3conc (wt\ %) \sqrt{2B}}{P - B}$ . The results relative to this calculation for the spectra measured on the matrices of the materials are given in Table 2.9.

**Table 2.9. Measured concentration (wt%) and minimum detectable concentration (wt%)**

Sample	Element	C [wt%]	C(MMF) [wt %]
PP reference	C	87.2	1.1
	O	10.2	2.2
	Al	1.1	0.5
	Si	0.5	0.5
	Ti	0.8	0.3
PP Romania	C	96.0	1.3
	O	1.8	2.4
	Al	1.6	1.0
PP Italy	C	79.2	0.8
	O	18.5	1.4
	Si	1.8	1.1
PP UK	C	68.1	1.0
	O	21.9	1.3
	Al	4.0	1.1
	Si	3.8	1.1
PET reference	C	71.2	1.0
	O	28.7	1.7
PET Italy	C	77.5	0.9
	O	22.5	1.9
PET UK	C	71.8	1.0
	O	28.2	1.8
HDPE Romania	C	94.5	1.4
	O	2.7	2.7
Cardboard Romania	C	64.3	1.6
	O	34.1	1.7
Paper UK	C	58.6	1.1
	O	39.3	1.5
Paper Italy	C	56.9	0.6
	O	37.3	0.7
	Al	0.8	1.4
	Si	1.0	1.2
	Ca	3.9	1.3

It can be concluded that the quantity of sulphur in the samples, if present, is in very low amount, below the detectability limit of the EDXS system. The absence of sulphur is supported by many data found in the literature, although Miskolczi et al. [86] in a study on the opportunity

of obtaining fuel by chemical recycling of waste plastics found 35 mg/kg of sulphur as contaminant in polypropylene from packaging industry.

In recent studies conducted in this research with the CHNS Elemental Analyzer EA 3000 on the same type of samples the presence of sulphur was high above the average from 0.1-1%.

Another set of analysis were conducted on an EA CHNS type EA1110 where sulphur content on paper, cardboard and plastics samples were registered absence. These differences can be explained by the fine and high sensibility operation condition of the instrument. During the proximate analysis, it can be noted, after the compilation of pyrolysis and combustion processes it is visible on the wall of the crucible a yellow residue which is specific to the sulphur content of the sample.

## 2.5 Energetic potential

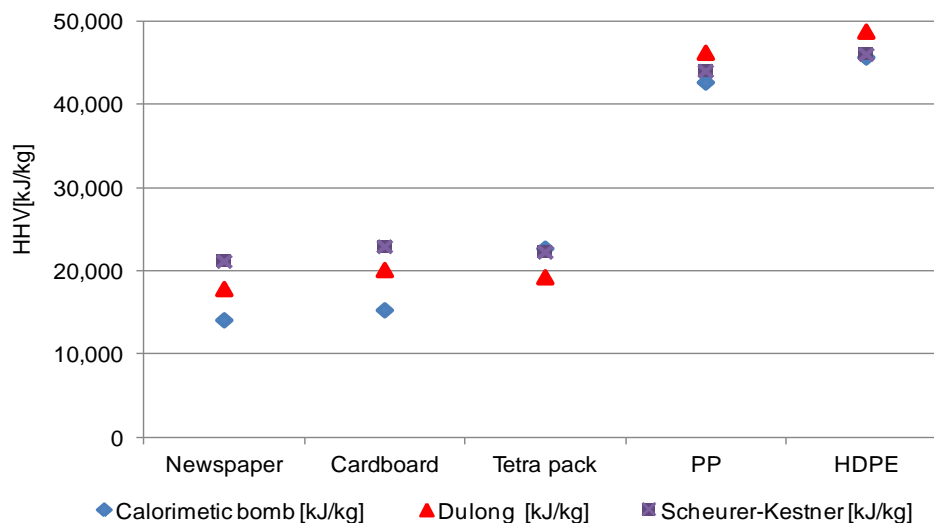
Table 2.10 presents a comparison with the HHV obtained from experiment and one by using empirical formulas. The proximate and ultimate analysis gave a hint regarding the energetic potential by type of fraction. The results obtained with the Calorimetric bomb reveal that HHV ranges of 12.42 –15.38 MJ/kg for cellulosic materials and 42.77 – 45.78 MJ/kg for polymer ones.

**Table 2.10. Energetic potential of samples in dry base**

Sample	Calorimetric bomb		Empirical formulas	
	HHV [kJ/kg]	LHV* [kJ/kg]	Dulong [kJ/kg]	Scheurer-Kestner [kJ/kg]
Newspaper	14,183	11,597	17,940	21,253
Cardboard	15,387	12,801	20,226	23,025
Tetra pack	22,795	20,209	19,357	22,356
PP	42,772	40,186	46,347	44,125
HDPE	45,783	43,197	48,887	46,137

\*LHV was calculated by a correction factor (Equation 2.8)

The comparison between the two methods of determination are presented in Figure 2.19



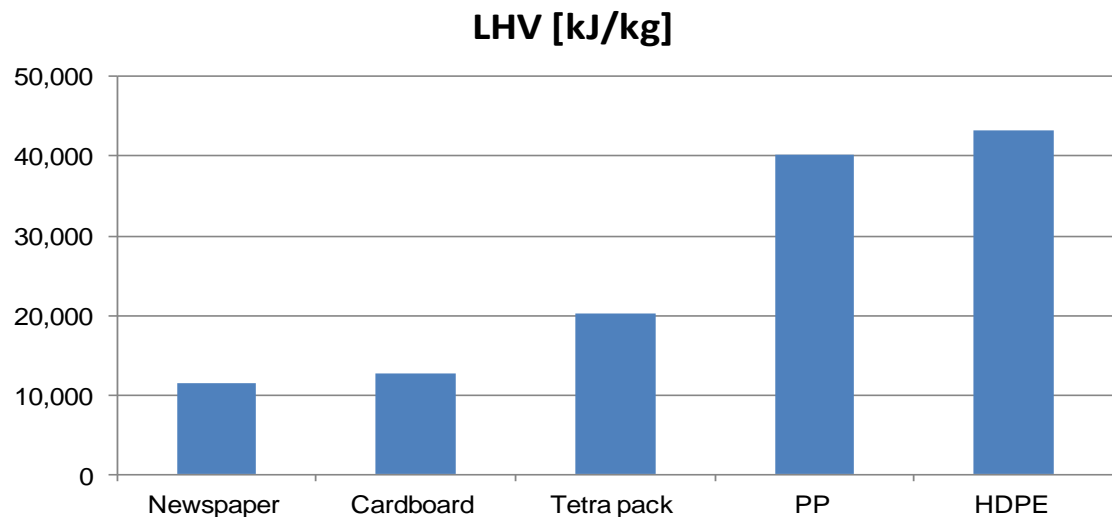
**Figure 2.19. HHV comparison: Calorimeter and Empirical Formula comparison**

The instrument suppliers claim a high accuracy of 99.6% of the Calorimeter instruments. On the other hand these empirical formulas are most common used in the determination of waste fraction high heating value. As figure 2.19 there are some significant differences between the two types of determination.

Even though the error rate doesn't make the aim of the current part of the study, some remarks can be made regarding the differences between the two methods applied:

- The empirical formulas are designated for a general material not on a specific one
- In the construction of the empirical formula several important factors and parameters are considered, as in mention in sub-section 2.3.3.3. This might affect the final results of the HHV.
- The expressed unit might have a notable influence in the calculations
- Overall the empirical formula leads to a relative result respect to the energetic content of the material and can be, at a certain point, a decision maker in the MSW treatment choice.

In figure 2.20 the LHV by type of fraction is presented. The LHV of the material will not succeed 43 MJ/kg for polymers material and 12 MJ/kg for lignocellulosic one for 10% moisture content considered.



**Figure 2.20. Low Heating Value by waste fraction**

The contribution of each fraction (paper, cardboard, PE and ravelled) of Tetra Pack is reflected in proximate, ultimate and energetic potential analysis. The results are more appropriate to cardboard since the content of PE is levelled if by the effect of non-volatile ravelled materials [37]. The 22 MJ/kg is higher than paper due to the PE contribution of carbon and hydrogen.

The study revealed the gap between experimental and predicted values that mainly is given by the leak of empirical formulas on type of waste fraction. Still the methods offer a first insight of utilizing such fuel at industrial scale by choosing the most appropriate technology suitable for the local need. These renewable resources can provide inexpensive primary or auxiliary fuel by reducing the landfilling problem and complying with the EU legislation.

### 3.2. . Conclusion

The data obtained in this sub-chapter provide a more accurate evaluation of packaging waste life cycle assessment, engineering development in conventional WtE plants and its environmental impact.

The volatile matter quantity release during the combustion process will dictate the primary process parameters such as: feedstock, temperature and retention time. The ash produced during the process reveals the storage space volume needed. The ultimate analysis points out the carbon content with 40% higher at polyolefines products, in comparison with lignocellulosic materials (Table 2.4). It's expected that these results will be revealed both in the composition of the samples by waste fraction but also in the composition of the secondary products resulted from the pyrolysis and gasification process of the mixtures studied.

The EDXS analysis highlighted some slightly differences in the composition of the packaging waste coming from different countries. The matrix of the polymer coming from UK contains more aluminium and silicon than the reference, the Romanian and the Italian samples. A small amount of titanium was detected in the reference sample and not in the other materials.

The particles deposited are different too (Table 2.6): on the reference sample they contain, in addition to carbon, oxygen, aluminium and silicon, also titanium (1.4 wt%); the dust on the Romanian PP instead has a high silicon content (6.4 wt% compared to 0.8 wt% in the pure sample) and contain calcium (2.0 wt%) and sodium (0.8 wt%); the particle on the PP from the UK contains calcium (2.0 wt%), while on the Italian sample two different kind of particles are deposited: the first is rich in Al (6.2 wt%), Si (7.9 wt%) and K 2 wt%); the second type contains magnesium (3.2 wt%) and lower amounts of silicon (1.5 wt%) and potassium (0.3 wt%).

The particles in the Italian sample have irregular edges and a high calcium content which may indicate that they are  $\text{CaCO}_3$  fillers. Considering that with SEM a surface layer of a sample is observed and characterized, it has to be considered that the elements detected by EDXS might derive from the paper coating layer. In this context, the presence of calcium carbonate is not surprising as its use to create a pigmented coating, with the function of providing a glossy, white, smooth surface for printing. On the contrary, the Romanian cardboard sample does not contain calcium and has Si-Al based fillers. The particles spread in the UK sample contain chlorine (6.3 wt%), potassium (4.6 wt%) and sodium (2.2 wt%).

The quantity of sulphur in the samples, if present, is in very low amount, below the detectability limit of the EDXS system. The accuracy of the results is concluded also in the elemental analysis of the materials. The elemental analysis of packaging waste fractions reveals a significant content of sulphur (0.1-1%) which can contribute to the dioxin formation. In this context, another technological problem could be the corrosion of the installation and settling in time of the various combustion by-products. Further studies will be dedicated to this discussion in order to determine if new different substances that might come from the life cycle use change the chemical composition of both paper and plastics materials.

Beside the laboratory instrumentation and operation mode accuracy, the primary elemental composition difference between the samples studies might come from:

- materials processing mode prior to market entry
- the assimilation chemicals through their commercialization
- heterogeneity

This all might affect the energetic potential by chemical and physical properties losses, associated with the degradation rate and usage in time, especially if the waste stream is coming from landfill sites.

Overall the C/H and C/N ratio is approximately higher at polyolefins material in comparison with lignocellulosic ones. This means that the amount of liquid or gaseous hydrocarbons will facilitate the use of secondary fuel product in other processes or their recirculation in the system.

The high energetic potential of the materials studied could be compared with primarily combustible as peat, lignite, sub-bituminous and bituminous coal, anthracite or graphite. This type of materials can be considered a raw material in the thermal plants in order to produce energy. The HHV was established directly using calorimetric determination and indirectly using elemental determination and semi-empirical formula for a better accuracy. The semi-empirical formulas are usually adapted for common combustibles such as coals, petrol, wood etc. The validity used on different waste materials is more or less proved.

On the basis of these considerations, there are three main hypothesis of energetic valorization that must be compared, and they consist in [88]:

- direct destination of waste to traditional combustion systems (Waste-to-Energy);
- production from original waste of an optimal combustible fraction (SRF), that must be sent to exterior production systems (cement kilns, thermoelectric plants);
- destination of a refined waste fraction to innovative gasification (or pyrogassification) plants, with a subsequent energetic destination for the produced gas.

## CHAPTER 3

### 3. EXPERIMENTAL STUDY OF PYROLYSIS AND GASIFICATION PROCESS ON LAB-SCALE PILOT PLANTS

#### 3.1. Pyrolysis of light packaging waste

For the pyrolysis and gasification experimental treatment, four mixtures of plastic solid waste (PSW), paper and cardboard waste (PCW) were chosen (Table 3.1 ). The amount of PSW and PCW fractions from the scenarios is representative for the MSW flow of Eastern European countries.

Table 3.1.Light packaging waste mixtures used in pyrolysis process

Waste fraction	Mixtures			
	Mix 1 PCW %	Mix2 PSW %	Mix 3 90%PCW:10%PSW	Mix 4 67%PCW:33%PSW
Paper	50	-	44	33
Cardboard	50	-	44	33
TP	-	-	1	1
PE	-	33.33	3.66	11
PP	-	33.33	3.66	11
PET	-	33.33	3.66	11

#### 3.1.1. Experimental set-up and procedure

##### 3.1.1.1. Electric furnace

The mass variation was determined using Nabertherm electric furnaces, type L9/11/SW described in section 2.3.1.1. It consist in one electrically heated oven (up to 1300°C) and a precision balance that continuously measures the sample mass. The sample retention time didn't exceed 60 min. This analysis provides useful information on the devolatilization times and therefore the retention time for the future analysis in the pyrolysis reactor [89,90]. On the other hand, it will bring data on the kinetics reaction and matter reduction which corresponds to formation of char as well fixed carbon remained.

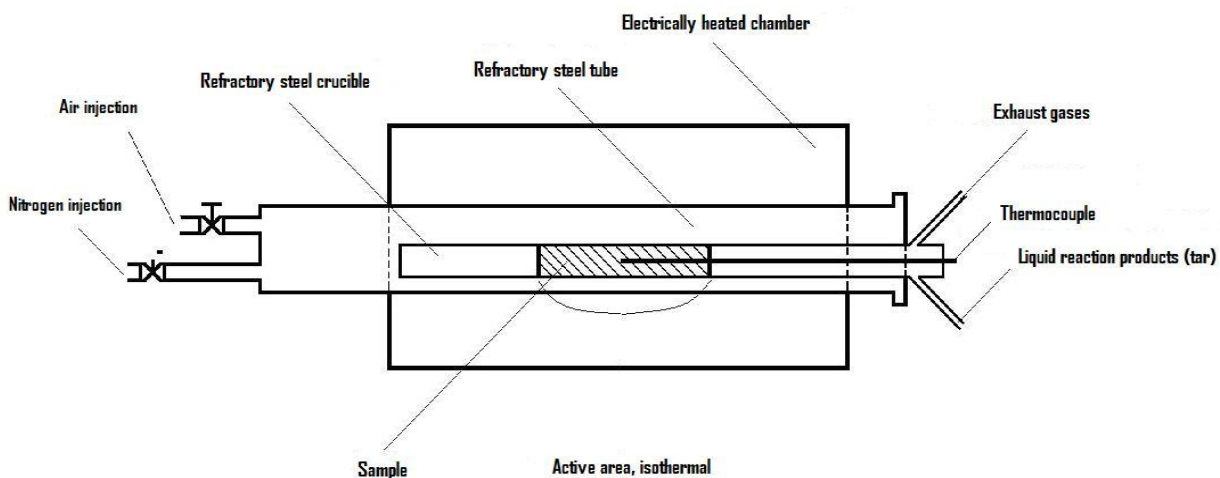
##### 3.1.1.2. Installation description and analytical procedure of pyrolysis process

The laboratory installation used throughout this study was developed in the laboratory of Renewable Source Laboratory, Power Faculty, Politehnica University of Bucharest.

The pyrolysis process of the four mixtures was investigated in a cylinder fixed bed reactor, NABERTHERM RO 60/750/13 model (Figure 3.1). This adjustable device is designed to

function on a laboratory scale study that can reproduce the thermal degradation processes of solids in conditions of incineration, pyrolysis and gasification. Therefore the treatment atmosphere can be oxidant or reductive depending on the thermo-chemical process chosen [91]. The reactor consists of a rectilinear tube, with external electric heating and an interior diameter of 60 mm. The active zone has a long heating area of 750 mm and a capacity up to 100 g depending on product specific weight. At its extremities, the reactor is provided with two gas inlets which offer the possibility to develop different experimental conditions: air / oxygen / nitrogen / water vapour. For the gas flow constant input and control of the process, a rotameter is used.

The device is equipped with a control pad that allows temperature programming process, working time (residence time at process temperature) and heating rate. The horizontal tube furnace has two outlets for the gas and liquid discharges resulting from treatments applied to solid products. The thermocouples (PtRh-Pt type) are located in the central heating area. In these conditions the temperature control is monitored from both outside and inside the reactor. The working temperature range is between 20 °C to 1300°C. The test samples that will be subjected to thermal treatment processes are introduced into the furnace in a crucible with tubular parallelepiped form of refractory steel W4541-size: 100 cm long, 4 cm wide and 3 cm in height.



**Figure 3.1 Tubular electric furnace diagram**

The pyrolysis of the four PSW and PCW mixes (Mix 1, Mix 2, Mix 3, Mix 4) were conducted under the same pyrolysis reaction conditions: about 60 min, temperature range 400-600°C under purified N<sub>2</sub> (99.9995%) at a gas pressure 50–100Pa [92]. The medium size of the sample didn't exceed 10 mm, therefore the temperature profiles inside the sample are eliminated and the contact surface is reduced during thermal degradation. The total amount of the mixture that entered in the crucible was in a range 25- 30 g depending on the form and structure of the waste fractions. The samples were distributed on the middle of the crucible in order to have the isothermal temperature distribution. Before starting the actual pyro-analysis, the tubular reactor is continuously feed with an inert gas (nitrogen) in order to eliminate air. After each test, the reactor was cooled at room temperature in order to avoid the oxidation of char resulted from the process. Subsequently the reaction, the gaseous, liquid and solid products were separated and analyzed by fraction in order to determine the mass balance and energy potential of char and tar products.

### 3.1.2 Mass balance results and discussion

In all experiments, the weight sample analyzed, varied between 15-20 g, with particle sizes ranging approximately from 5 mm to 10 mm. The samples were subject to a pyrolysis process, in iso-thermal conditions, at different temperatures from 400°C – 600°C. The inferior temperature range was chosen above the plastics devolatilization point (approximately 380°C). The 600°C represents the limit where air/oxygen gasification can be used and pyrolysis is no longer required and also the temperature where the devolatilization process of plastic compound ends. The residence time of each experiment was determined according to the weight loss of the sample. The process has ended in the moment when the mass stopped varying.

**For Mix 1 case, paper & cardboard waste 1:1**, the 70% matter loss corresponds to 60 minutes residence time at maxim temperature chosen for this test 600 °C (Figure 3.2). Note that the degradation time and mass reduction are consistent with the increasing of temperature. The decomposition of the samples takes in the first 150 seconds of the test. This corresponds to first cellulosic weight loss that occurs at temperatures between 200-250°C. The stabilization time starts more rapidly at lower temperature due to hemicelluloses presence that favour cellulose to rich its maximum at temperature decomposition lower then 370°C. The rest of the time is intended for the formation of secondary reactions that lead to water and volatile matter release in form of gaseous species, formation of char and tar.

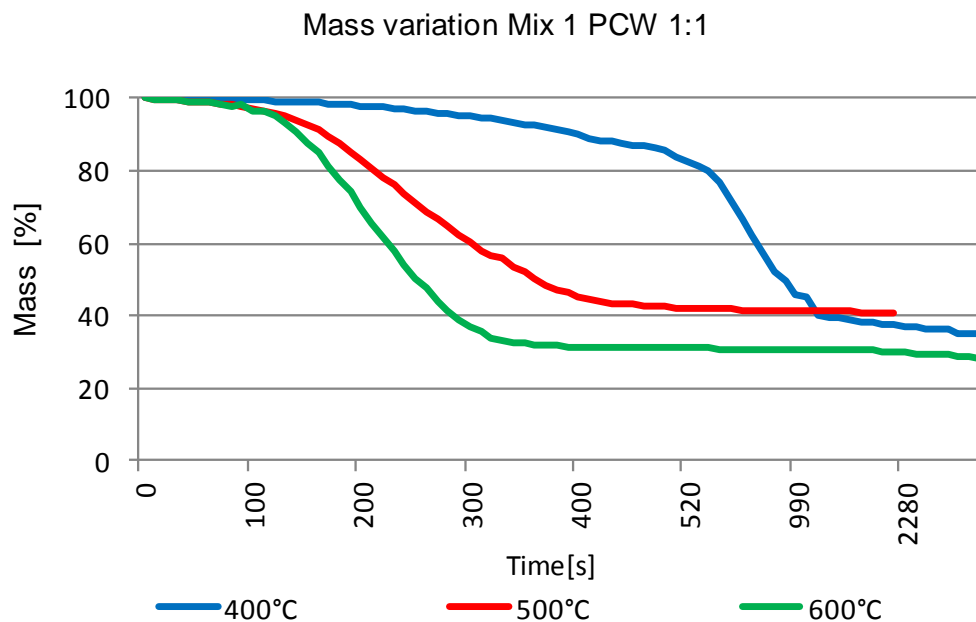


Figure 3.2. Mass variation Mix 1

**For Mix 2 case**, the curves show that **plastic solid waste** (PE:PP:PET) thermal degradation starts at the end of the residence time (50 min) at 400 °C (Fig.29). According to the data found in literature, the thermo-gravimetric analysis (TG) of polymers thermal degradation starts at 660 K and is almost complete at approximately 840 K. At higher heating rate the maximum degradation

rate shifted from 724 K at 2 K/min to 776 K at 50 K/min [93]. It was noticed by Siddiqui and Rehwi (2009) [57] that conversion for single component reactions such as LDPE and HDPE yielded lower conversion. However, PP and PET remained in the moderate to high conversion efficiency. Therefore the thermal and catalytic reactions of these polymers in mixture are affecting the secondary products stabilization and distribution.

The data presented in the literature are consistent with the current test where the mass loss at 400°C is 15%. Furthermore, as it is shown in Figure 3.3, after a significant increasing of time (a peak) the curve becomes rapidly constant. For temperature below 450°C the solid conversion and stabilization is low even at longer times. As the experiments shows, above these temperature the reaction is very rapid the maximum solid conversion being approximately 1.0.

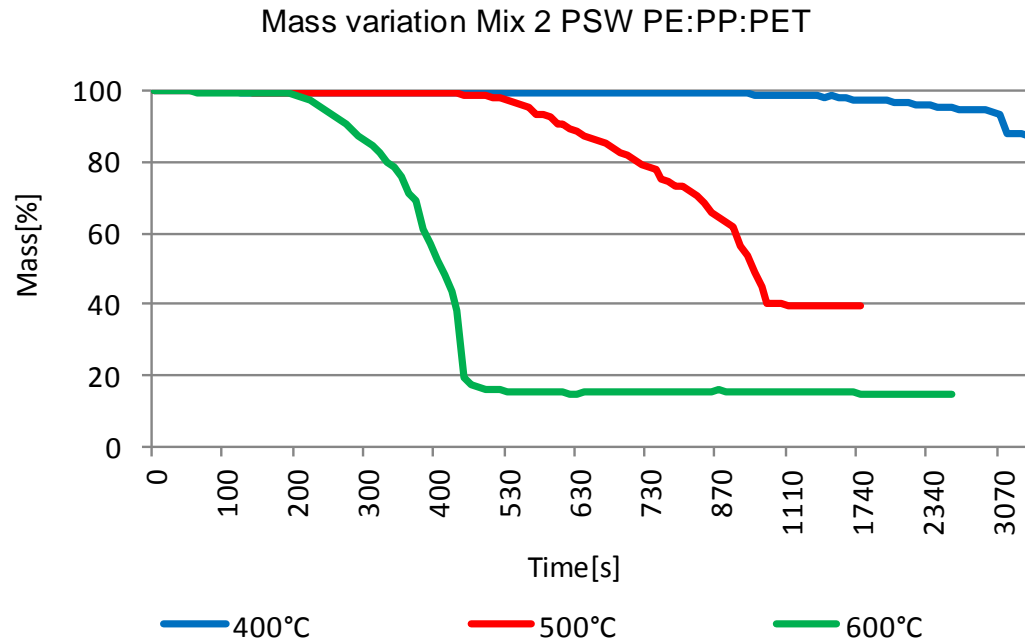


Figure 3.3. Mass variation Mix 2

**For Mix 3, 90%PCW:10%PSW**, from the kinetic process it is observed that the predominant material is paper and cardboard therefore the mass loss is achieved without the fast fluctuations like in plastic case (Fig. 3.4). The mass loss variation will be in a range between 45-75% depending on the temperature. The devolatilization time is specific for PCW material and will not exceed 300 seconds for 400°C temperature. Nevertheless the polymers present in Mix 3 delays the decomposition starting moment with approximately with 100 s. For industrial applications the minimum residence time for the waste to achieve the complete carbonization will be imposed by the component with the slowest conversion rate. Nevertheless if the fraction of such component is low, the influence becomes negligible. Moreover the installation type will strongly influence the minimum residence time, mainly through the heat transfer efficiency.

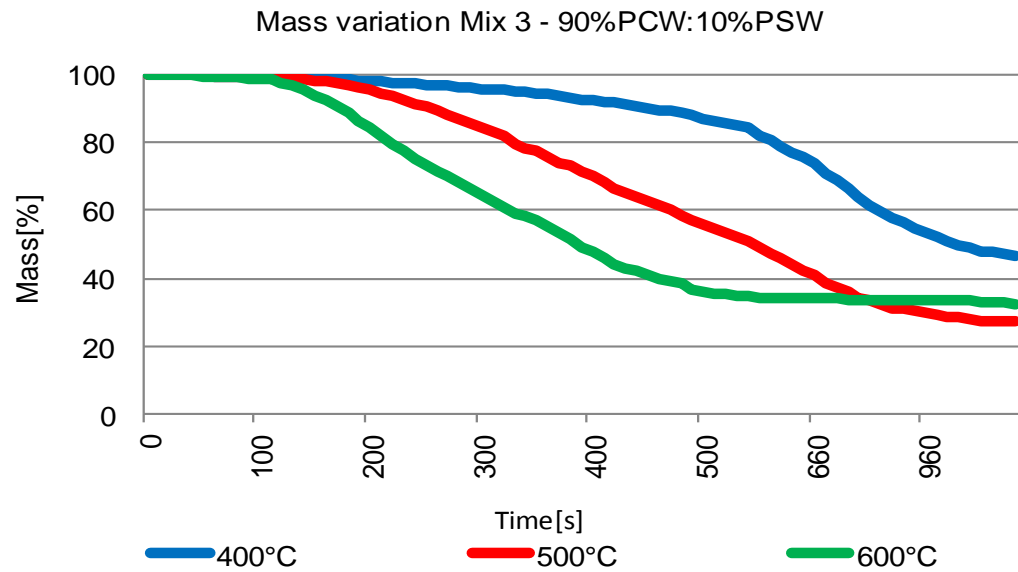


Figure 3.4. Mass variation Mix 3

**For the Mix 4, 67%PCW: 33%PSW** it is observed a significant influence of the plastics fraction compared with Mix 3 (Fig. 3.5). The degradation time will remain constant for 400°C temperature and it will be double for 500 °C. The mass balance will be uniform for the lowest temperature of the process and will increase by 3-10% for higher temperatures due to the high volatile matter of polymeric materials.

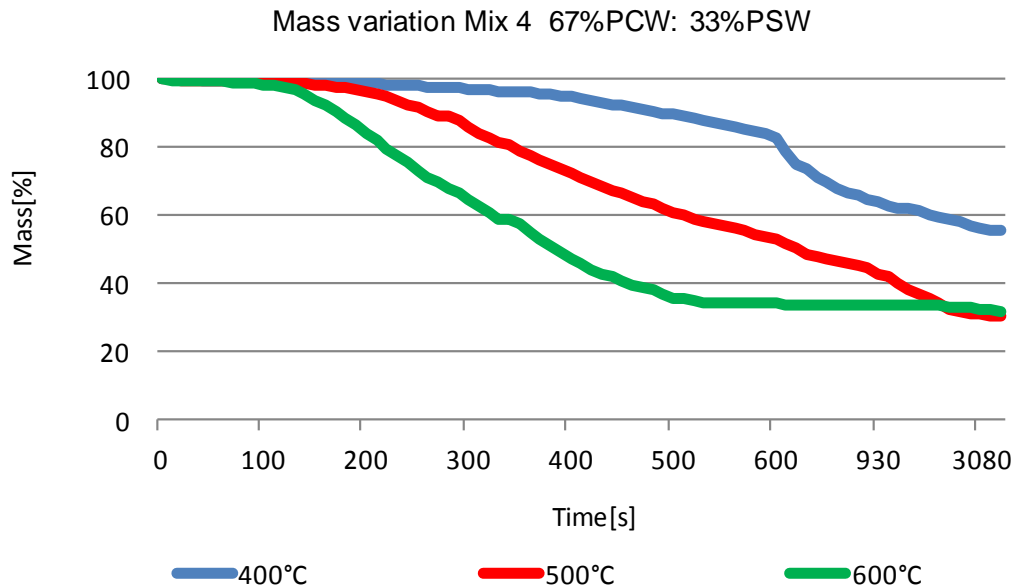


Figure 3.5. Mass variation Mix 4

It can be concluded that the pyrolysis of light packaging waste (so called chemical recycling) is one perspective way of former utilization at their life use cycle. The end product properties are a key point of the industrial leading process taking into account the kinetic behaviour.

The pyro-analysis of the fraction wastes mixtures reveals that materials with the slowest kinetic reaction impose the residence time during the process. The main devolatilization stage of lingo-cellulosic materials occurred at lower temperatures in comparison with polymers. The latter will be revealed in Mix 3 and 4 where the char formed from PCW will influence the degradation process of PSW. As is shown in Fig. 28 and 29, plastic pyrolysis residence time at 400°C and 500°C is double compared with paper and cardboard. During the process the largest mass loss will be recorded for the process parameters at 600 °C with 85% for polymers fractions (Mix 2 PSW). This result will be revealed also in Mix 4 where the matter loss in these conditions is 70% due to PSW dominance in the composite.

### 3.1.3. Determination of Activation Energy

The composition of by-products formed in generally by cracking reactions is mainly influence by temperature that depends on the activation energies ( $E_a$  [kJ/mol]). A simplified model used in other studies [94,95] for determining the global kinetic parameters of PCW and PSW pyrolysis was used. The rate coefficient ( $k_i$  [K/min]) is taken to be in Arrhenius form. In this case,  $k_i$  was estimated by correlating it with the material mass loss that is given by a differential equation as function of non-liberated volatile fraction and sample mass variation gradient.

$$\frac{dm}{dt} = -k_i \times [m(t_s) - m_c] \quad \text{Equation 3.1}$$

$$k_i = A_0 \times e^{\frac{-E_a}{RT_i}} \quad \text{Equation 3.2}$$

Usually the frequency factor ( $A_0$ ) is considered as a constant all over the temperature range that has been investigated in past studies [96]. The rate coefficient  $k_1$  is specific for temperature  $T_1$  and  $k_2$  specific for temperature  $T_2$ . In the present study  $k_{1,2}$  were estimated from the mass balance distribution curve function of temperature. The activation energy is determinate by a first order equation given by  $k_1/k_2$  ratio [97]. The gas universal constant is noted with  $R$ .

$$E_a = R \times \frac{T_1 T_2}{T_1 - T_2} \times \ln \frac{k_1}{k_2} \quad \text{Equation 3.3}$$

Table 3.2 presents the activation energies by type of mixture used in non-oxidant thermal treatment.

**Table 3.2. Activation energies of mixtures**

Type of product	Activation Energy $E_a$ [kJ/kmol]
Mix 1 50%:50% PCW	111- 228
Mix2 50%:50% PSW	206 - 310
Mix 3 90%PCW:10% PSW	148 -234
Mix 4 67% PCW:33% PSW	189-280

The results obtained are in the same range as several authors reported for celluloses, hemicelluloses and polymers decomposition [64,65,66,98]. Although the materials can be

characterized by similar structures the activation energies are different. For example, the degradation of polystyrene has lower activation energy than high-density polyethylene, therefore at lower temperature the ratio of cracking of polystyrene is greater than other polymer in the mixture [99]. Over more, Calahorra et. al 1989 [100] reported that the thermal stability enhances within the increasing of the molecular mass, therefore the cellulose pyrolysis process cannot have a single value of activation energy during the entire pyrolysis.

### 3.1.4. By-product characterization

#### 3.1.4.1. Pyrolysis by product mass balance

The mass balance variation of secondary products from pyrolysis process will be commented in the following. The residence time in the pyrolysis reactor was 1 hour. The next figures show the yield and composition of char, tar and gas when the weight of the sample is normalized to 100%.

**For Mix 1 case, paper & cardboard waste 1:1**, a significant amount of 40% of liquid product in form of tar ,oil and wax has resulted at 600°C. Conform to Figure 3.6, it's found at 500°C with: 20% Tar, 40% char and 40% gas secondary pyrolysis products matter.

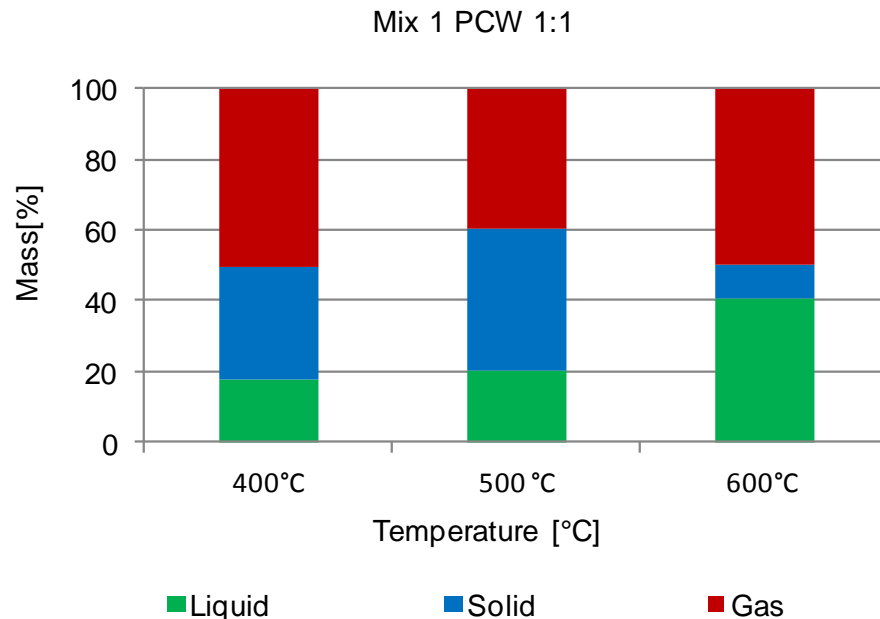


Figure 3.6 . Pyro products yield, Mix 1

**For Mix 2, plastic waste (PE: PP: PET)**, the available data for the 400°C pyrolysis process weren't cogent (Figure 3.7). That might be explained from the second step of the pyro-analysis where the secondary reactions of tar cracking occur at higher temperatures (>400°C) [101]. However, mixed polymers materials are expected to degrade partly under high pressure (8Mpa) even though the temperature is lower than 400 °C [101].

Previous studies of plastics waste have indicated that the optimum temperature for thermal-treatment in non-oxidant atmosphere is 500°C Adrados et. al. (2012) [35]. It was demonstrated earlier that at lower temperature the polymeric waste decomposition is not fully complete and at higher ones the formation of gaseous products is favourable. It can be marked that during the present experiments, at 500 °C the agglutination rate was still increased.

In the present study, for temperatures of 500°C and 600°C, the resulting coke amount varies between 10-12%. Disregarding its high agglutination level at low temperatures, the solid product resulted from the process can be more easily energetic valorised. Note that during the experiments the recovery of char was hampered by the fact that plastic melts easily and deposits on the sides of the crucible making it very difficult to remove. Therefore in mixture with other waste fractions it may cause technical problems. For example, the stock of the melted products on the reactor wall will overload it and will limit the char removal from the batch.

The yields obtained from polymers pyrolysis at 500°C and 600°C give 40-50% gaseous olefins from the PSW that can be immediately treated in a polymerization plant. The content of naphtha residue can be reformed and used for energetic proposed (e.g. gasoline generation). The lower hydrocarbons gaseous species can be thermally recycled and used as support in the process. The generation of PSW ensures a constant feedstock of the plant with minimum cost of the raw material. Unfortunately the further pre-treatments of gaseous and liquid products (e.g. tar/oil/wax) have highly operation costs limiting the grand scale application of the pyrolysis process in industrial plants without combined cycle.

The liquids pyro products are decreasing with the increasing of temperature, influencing the pyrolytic gas yield and composition. Li et. al. 1999 and Hernández, et. al. 2007 presented similar results, that can be associated with the C-C bonds cracking that is produced at higher temperatures, which conduct to the formation of lighter hydrocarbons with shorter carbon chains. [102,103]

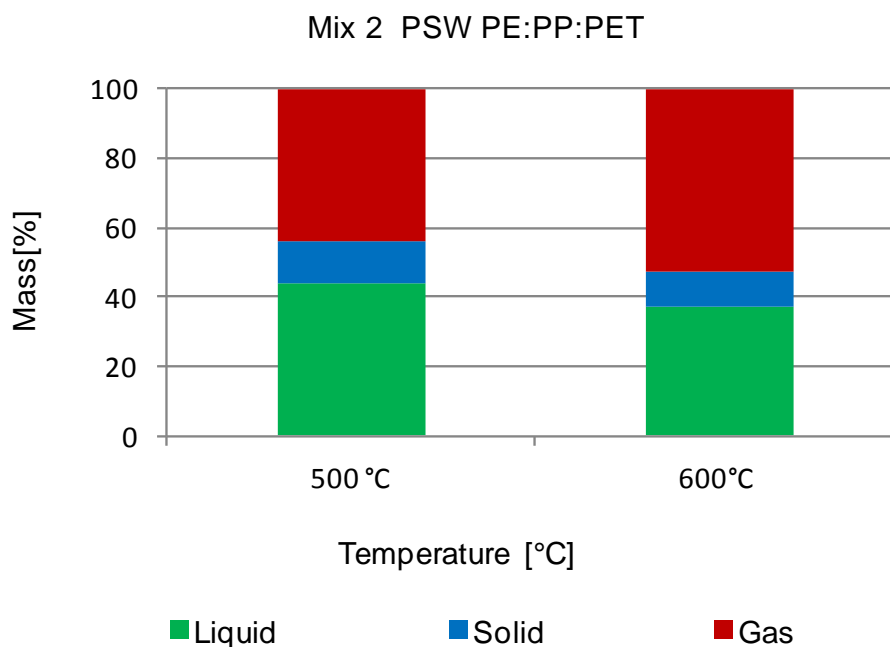


Figure 3.7. Pyro products yield, Mix 2

**For the Mix 3, 90%PCW:10%PSW,** we can observe that the amount of almost 20% tar is about the same at 500°C and 600°C (Figure 3.8). It seems that at 400°C process parameters the resulted products are distributed uniformly. According to the mass variation previously made, it was expected that the content of char will decrease with the increasing of temperature. In the present pyrolysis process conditions, the char increases by approximately 10% at 600 °C.

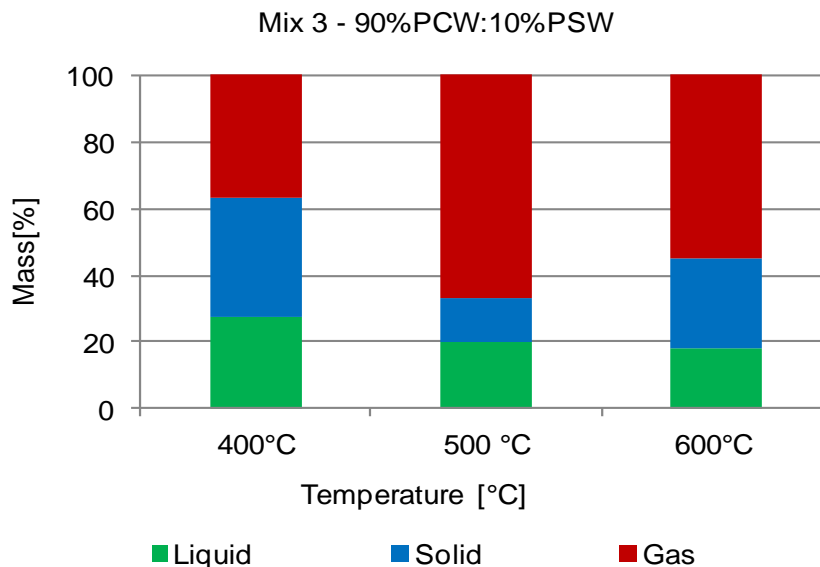


Figure 3.8. Pyro products yield, Mix 3

**For the Mix 4, 67%PCW: 33% PSW** presented in Figure 3.9 is observed a significant amount of liquid products (tar/oil/wax) in comparison with Mix 3. That can be explained by the presence of polymers where the devolatilization time is slower in comparison with lignocellulosic. The gases produced with will have a higher calorific value due to the significant quantity of synthetic materials in the mixture. The pyrolysis gas will typically have a calorific value of 22–30 MJ/Nm<sup>3</sup>.

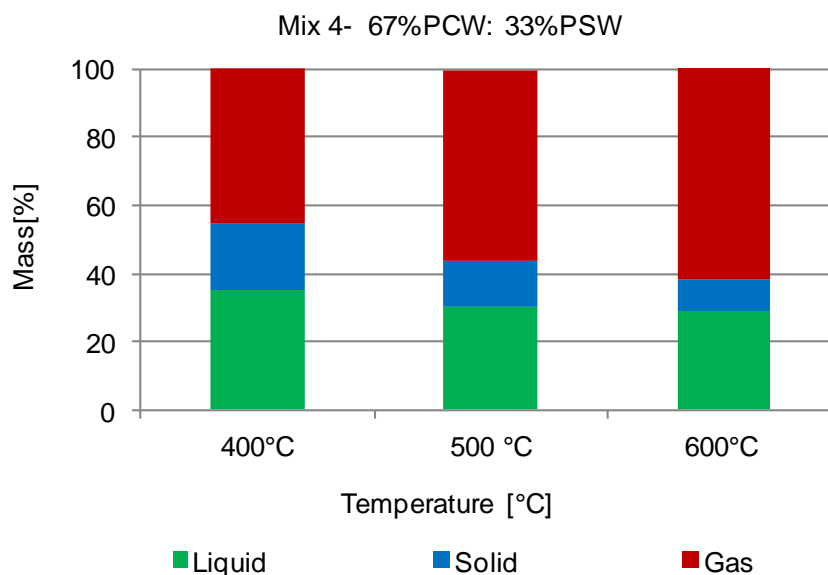


Figure 3.9. Pyro products yield, Mix 4

### 3.1.4.2. Energy potential of solid and liquid by-products

To highlight the energy potential of char and tar resulted from the pyrolysis process the heating value was determined by using the calorimetric bomb (Table 3.3).

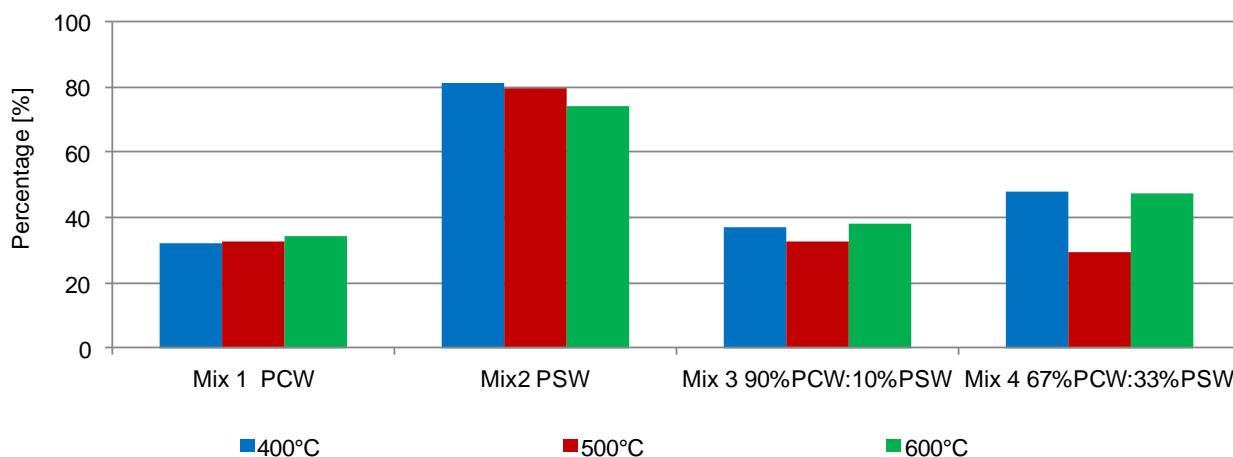
**Table 3.3. Energy potential of char and tar**

Product	High Heating Value [kJ/kg ]					
	400 °C		500 °C		600 °C	
	Char	Tar	Char	Tar	Char	Tar
Mix 1 PCW	12,082	18,653	10,155	18,529	28,335	23,230
Mix 2 PSW	N.a	N.a	36,378	42,450	22,626	43,012
Mix 3 90%PCW:10%PSW	24,147	20,337	10,098	20,181	11,744	30,459
Mix 4 67%PCW:33%PSW	25,640	18,994	31,732	20,360	16,425	20,410

Due to double content of carbon from plastics material in comparison with lignocellulosics one, the fixed carbon remaining after pyrolysis process will lead to a higher calorific power with 20 MJ/kg on both char and tar resulted from devolatilization of PSW. The energy carrier products can be integrated in cycle turbines, reciprocating engines or utilized offsite in other thermal processes as fuel support. Over more the reduced amount of secondary wastes decreases the landfill disposal. The continuous feedstock regeneration of the waste stream input makes packaging waste pyrolysis attractive for smaller scale plants.

### 3.1.4.3. Chemical composition of solid and liquid pyrolysis products

It is remained that the isothermal pyrolytic process was stopped after one hour so the solid product formed from inorganic and char was collected. From the mixtures studied, the liquids with high viscosity and solid materials corresponding for temperatures ranging between 400-600°C were elemental analyzed. The elemental analysis of the sample was made using the EA 3000 elemental analyzer. During the analysis the liquid form could not be analyzed. The composition was determinate only for wax/oil products. The results of elemental analysis are presented in the next Fig. 3.10-3.13.



**Figure 3.10. Carbon wt% content from solid pyrolysis product**

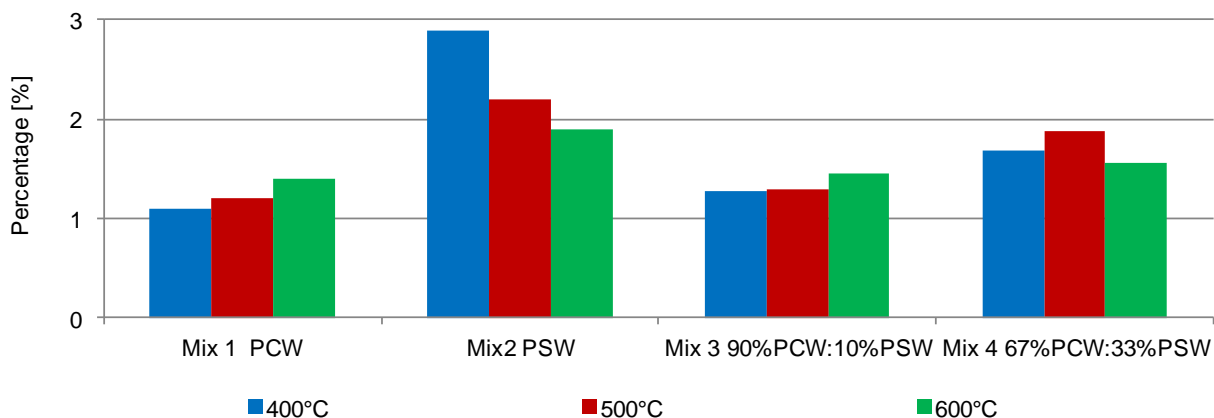


Figure 3.11. Hydrogen wt% from solid pyrolysis product

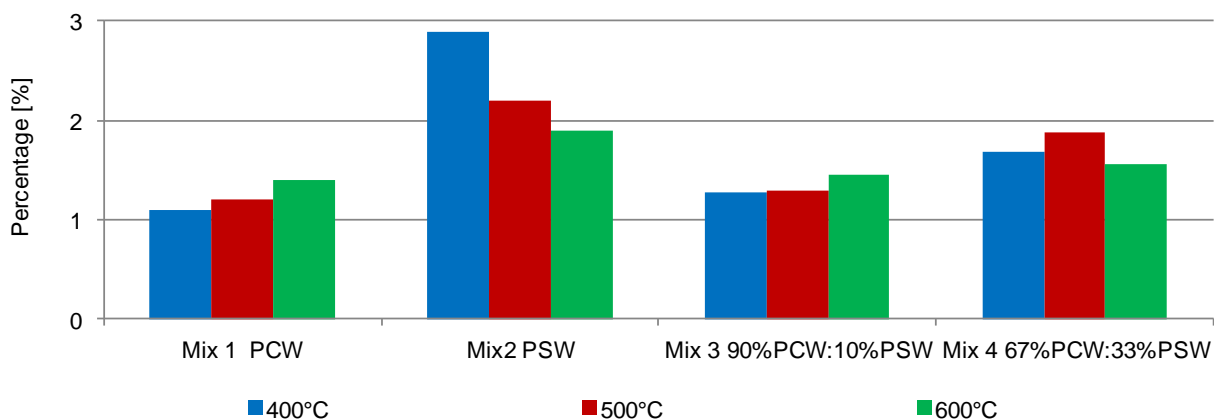


Figure 3.12. Carbon [%] content from liquid pyrolysis product

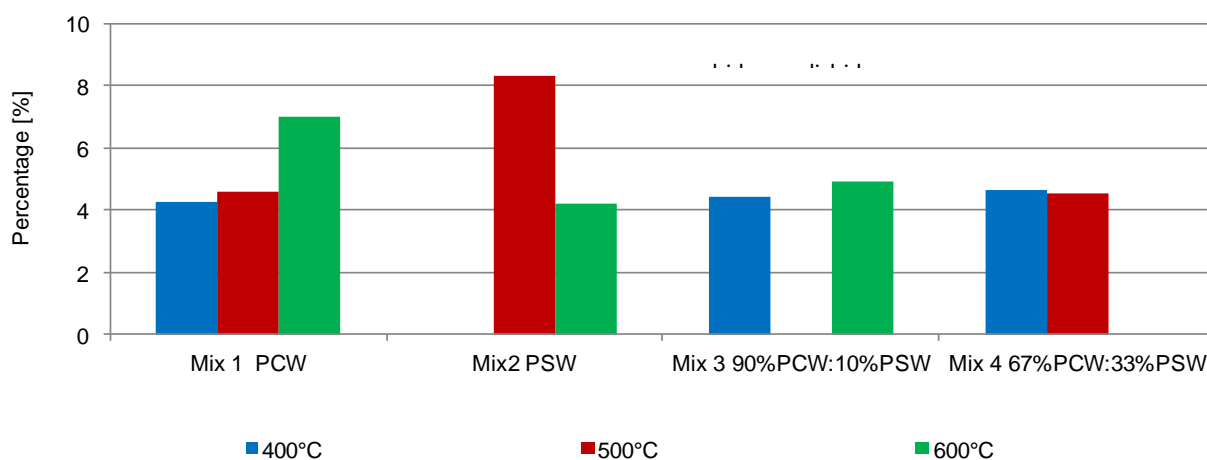


Figure 3.13. Hydrogen [%] from liquid pyrolysis product

These results indicate that C and H are major constituents both in solid and liquid phase. The paper and cardboard waste C/H ratio is decreasing with the increasing of temperature. The

polymeric waste C/H ratio presents opposite results increasing in value with the increasing of temperature. Table 3.4 presents the C/H ratio by type of mixture, product and temperature range.

**Table 3.4. C/H ratio by type of mixture, product and temperature range**

<b>Type of mixture</b>	<b>Temperature range</b>	<b>C/H ratio solid</b>	<b>Temperature range</b>	<b>C/H ratio liquid</b>
Mix1 PCW	400°C- 600°C	29 – 24	400°C- 600°C	9.6-8
Mix2 PSW	400°C- 600°C	28- 39	500°C- 600°C	8.08-8.89
Mix 3 90%PCW:10%PSW	400°C- 600°C	28- 26	400°C- 600°C	10.12-8.89
Mix 4 67%PCW:33%PSW	400°C- 600°C	28-30	400°C- 600°C	11.93-8.55

The results are sustained by primary and ultimate analysis of the waste fractions where the C and H are the dominants element with 40% C for paper and cardboard and 88% C from plastics and 7% H, respectively 8%. These are all supported also by the product distribution. In Figure 3.12 at 400°C-500°C the carbon content of lignocellulosic fraction (Mix 1), in liquid phase decrease from 40% at 37%. This can be explained by the pyrolysis and gasification reactions of C-CO and CO<sub>2</sub> at the second stage mass change. Even thou the char energetic qualities are high, small quantities are obtained during the isothermal pyrolysis treatments. In the polymers case this can be attributed to the secondary repolymerization reactions among the derived products.

### 3.1.5. Conclusion

The information obtained from these experiments can be useful for the design of the pyrolysis reactor where the thermal decomposition of the solid takes place.

The fixed carbon depositing time that is produced after the volatile emission period influences the structure and quality of char and therefore the kinetic process.

The experiment was confirmed by the observation that more than 85% of carbon from the sample was recovered as char, condensate liquid and gas. Also in this case the amounts of polymeric materials will double the calorific value of both char and tar resulted from the pyrolysis of PCW and PSW mixtures.

During the analysis it was observed that the agglutination grade increases in presents of polyolefines products. It is clear that a PSW pyrolysis at 400-450 °C is not suitable for this type of process due to the fact that above this temperature the material starts the formation of liquid and solid by-products. For industrial scale plants, the risk of the melted material stick to the mobile parts of the installation grows.

In all cases the char can either be further processed on site to release the energy content of the carbon, or utilized offsite in other thermal processes.

The hydrocarbon content of the waste can be converted into a gas, which is suitable for utilization in either gas engines, with associated electricity generation, or in boiler applications without the need for flue gas treatment.

During the analysis it was observant that the agglutination grade increases in presents of polyolefines products. For industrial scale plants, the risk of the material stick to the mobile parts of the installation grows.

By comparison with current studies, the main challenge of the future researches comes with the study of the blend waste materials taken directly from landfill sites due to their high heterogeneity, moisture and significant inert content (metals and glass).

## **3.2. Gasification of light packaging waste**

This experimental study leads to the optimisation of gasification process parameters at industrial scale in a rotary reactor lab-pilot installation using light packaging waste mixtures.

The pilot installation used in this study was developed in the Renewable Source Laboratory, Power Faculty, Politehnica University of Bucharest with the patent number RO127125-A0 and name Process and plant for characterizing/processing fuel and non-fuel products (solids, slimes and liquids) in a thermo-chemical way by combustion, pyrolysis and gasification [104].

The experimental study of light packaging waste gasification was carried out in a modified lab-scale rotary kiln with external heat input that can reproduce laboratory-scale industrial processes such as incineration and gasification. The operating temperatures of the experiment range between 800°C -900°C using air as gasifying agent.

In this part of the research it will be discussed: operating process parameters chosen function of: rotary furnace, feedstock input (Combustible Ratio), temperature, amount of gasifying agent and gas velocity. The chemical reaction resulted in the partial oxidation process will be also discussed. The syngas investigation is made using a Gas Chromatography-Mass Spectrometry (GS-MS) analysis. The mass and energy balance of the gasification process will complete the last part of this chapter.

### **3.2.1. Experimental set-up and procedure**

#### ***3.2.1.1. Sampling stage***

The sampling preparation stage represents a critical point in the feedstock designated for the gasification process. The light packaging wastes were provided directly from the selective collection of MSW. The preparation of the material was made using a mill designated for waste shredding (Figure 3.14). The mill has a maximum flow rate of 30 kg/h (depending on the type of fuel). The instrument is equipped with a rotary knives system and separation of the cut material in different diameters. In the present sampling stage 66 kg of HDPE, PET, PP, cardboard and paper were shredded at different diameters up to 5 mm. In the gasification experiments a mixture 1:1 of the packaging waste mention above was used.



Figure 3.14. Cutting mill Fritsch

### ***3.2.1.2. Installation description and instruments used in the gasification process***

#### **➤ LAB-SCALE ROTARY KILN PLANT**

The experiments have been performed in continuous flow, in a modified lab-scale rotary kiln, with external electric heating system presented in Figure 3.15. The pilot installation used in this study was developed in the Renewable Source Laboratory, Power Faculty, Politehnica University of Bucharest with the patent number RO127125-A0 and name Process and plant for characterizing/processing fuel and non-fuel products (solids, slimes and liquids) in a thermo-chemical way by combustion, pyrolysis and gasification [103].

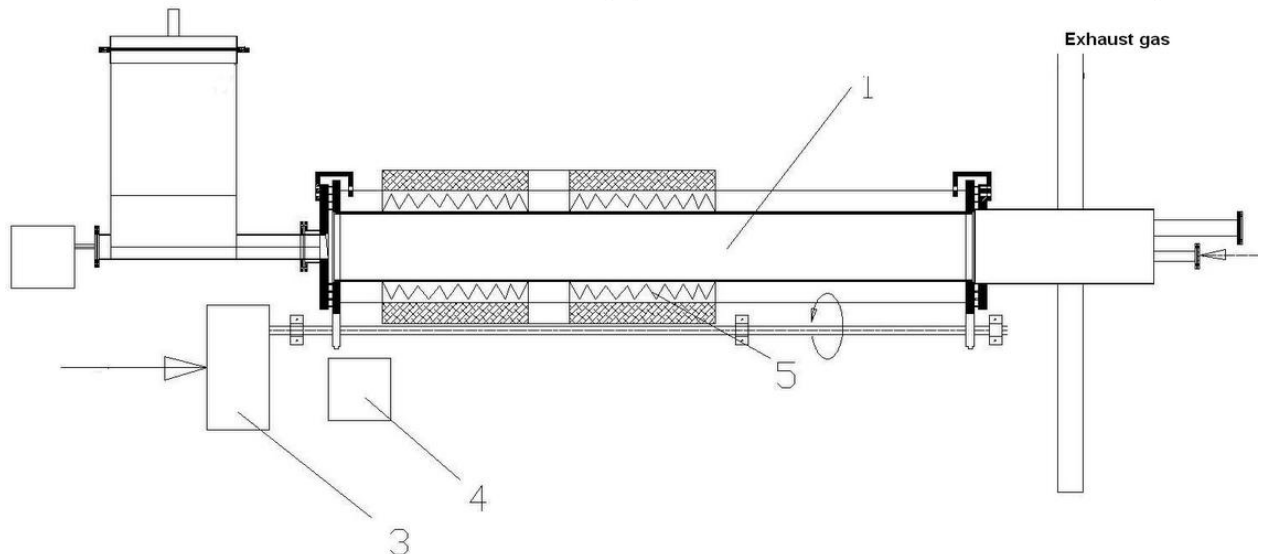


Figure 3.15. Schematic rotary kiln gasifier lab-scale plant

1. Pyrolysis/gasification reactor; 2. Feeding system; 3. Rotation system;  
4. Inclination system; 5. Heat system;

The reactor is an external heated rotary kiln and then has an overall volume of about 8 dm<sup>3</sup>. The speed rotation can be varied. The columnar main kiln body, electrically driven by frequency variator-motor assemblies, has an obliquity system from 0 up to 20 degree angle to the level standard that is placed on the carrier roller.

The operating temperature of the reactor reaches up to 1100°C. The two-zone heating system ensures the creation of a temperature gap between the inlet and outlet sections. The device is equipped with a control pad that allows temperature programming process, working time (residence time at process temperature) and heating rate. The horizontal tube furnace has two outlets for the gas and solid discharges resulting from treatments applied to waste products. The thermocouples are located in the central heating area. In these conditions the temperature control is monitored from both outside and inside the reactor. The temperature difference between the upper and bottom reactor ranges between 80-100°C.

At its extremities, the reactor is provided with two gas inlets which offer the possibility to develop different experimental conditions: air/oxygen/water vapour or nitrogen controlled atmosphere, at the atmospheric pressure, by combustion, pyrolysis and gasification. For the gas flow constant input and control of the process, a rotameter is used.

The feeding system consists of an Archimedes screw, whose rotation is controlled by a frequency electronic controller. The flow rate reaches up to 30 kg/h depending on the type of waste. From the feeding system, the ground waste is pushed forward by screw rotation and dropped into the reactor.

The resulting solid sub-products are collected on the bottom of the reactor due to the gravity in ash/coke collector.

#### ➤ **TESTO 350 XL EXHAUST GAS ANALYZER**

TESTO 350 M / XL exhaust gas analyzer is an advanced equipment for determination of gaseous emissions from the combustion/gasification/pyrolysis gases, their determination being made in special cells, following electro-chemical reactions Peltier type. Analyzed gases are SO<sub>2</sub>, CO, C<sub>m</sub>H<sub>n</sub>, O<sub>2</sub>, NO and NO<sub>2</sub>.

Also cause excess air ratio and CO<sub>2</sub> concentration, gas flow velocity and mass flow rate (only if one takes into account the flow section) for all gas species analyzed. Principle of analysis is based on intensity change galvanic current generated by a galvanic cell whose electrolyte modify their properties from the reaction of its gas component to be detected and the concentration must be measured. As cells are even some galvanic elements. This generates a current proportional to the number of ions in the electrolyte solution dissociates as a result of interaction with the gas in question. It is important that only gaseous component that the entire gas mixture analyzed to produce this effect. The machine can be equipped with several gas sampling probes. They differ depending on the characteristics of gas taken. Thus there are differences between wells for sampling exhaust gases or exhaust gases to the chimney, the range of operating temperatures, the gas flow channel dimensions and can be heated or unheated probes.

#### ➤ **GAS CHROMATOGRAPHY – MASS SPECTROMETER (GS-MS)**

The GCMS instrument is made up of two parts. The gas chromatography (GC) portion separates the chemical mixture into pulses of pure chemicals and the mass spectrometer (MS) identifies and quantifies the chemicals.

The GC separates chemicals based on their volatility, or ease with which they evaporate into a gas. It is similar to a running race where a group of people begin at the starting line, but as the race proceeds, the runners separate based on their speed. The chemicals in the mixture separate based on their volatility. In general, small molecules travel more quickly than larger molecules.

The MS is used to identify chemicals based on their structure. Let's say after completing a puzzle, you accidentally drop it on the floor. Some parts of the puzzle remain attached together and some individual pieces break off completely. By looking at these various pieces, you are still able to get an idea of what the original puzzle looked like. This is very similar to the way that the mass spectrometer works.

#### 1. *Gas chromatography (GC)*

- Injection port – One microliter (1  $\mu$ l, or 0.000001 L) of solvent containing the mixture of molecules is injected into the GC and the sample is carried by inert (non-reactive) gas through the instrument, usually helium. The inject port is heated to 300° C to cause the chemicals to become gases.
- Oven – The outer part of the GC is a very specialized oven. The column is heated to move the molecules through the column. Typical oven temperatures range from 40°C to 320°C.
- Column – Inside the oven is the column which is a 30 meter thin tube with a special polymer coating on the inside. Chemical mixtures are separated based on their volatility and are carried through the column by helium. Chemicals with high volatility travel through the column more quickly than chemicals with low volatility.

#### 2. *Mass Spectrometer (MS)*

- Ion Source – After passing through the GC, the chemical pulses continue to the MS. The molecules are blasted with electrons, which cause them to break into pieces and turn into positively charged particles called ions. This is important because the particles must be charged to pass through the filter.
- Filter – As the ions continue through the MS, they travel through an electromagnetic field that filters the ions based on mass. The scientist using the instrument chooses what range of masses should be allowed through the filter. The filter continuously scans through the range of masses as the stream of ions come from the ion source.
- Detector – A detector counts the number of ions with a specific mass. This information is sent to a computer and a mass spectrum is created. The mass spectrum is a graph of the number of ions with different masses that travelled through the filter.

#### 3. *Computer*

- The data from the mass spectrometer is sent to a computer and plotted on a graph called a mass spectrum. [105]

### **3.2.1.3. Determination of operating air-fuel ratio**

The goal of the following calculation is to determine the operation air-fuel ratio used in the packaging waste gasification experimental process. In order to define this parameter, the starting point of the argument was the selection of Equivalent Ratio (ER). It's recalled that the ER is the ratio of operating air-fuel ratio to stoichiometric air-fuel ratio for complete combustion of the fuel:

$$ER = \frac{\text{Operating } \left(\frac{A}{F}\right)_O}{\text{Stoichiometric } \left(\frac{A}{F}\right)_S} \quad \text{Equation 3.4}$$

Syngas composition at the chemical equilibrium as a function of equivalence ratio for the gasification of lignocellulosic material at 1 atm shows in Figure 1.13, that 0.25–0.35 ER appear to maximize char conversion. These values are typically used in large-scale commercial plants. In the present study, due to the literature review on lignocellulose, biomass and polymer gasification review an 0.2-0.3 ER was chosen.

For the determination of the minimum amount of theoretical air necessary for complete stoichiometric combustion of packaging solid waste the following assumption have been made:

- complete combustion occurs that means that CO is not formed
- sulphur is oxidized until the formation of SO<sub>2</sub>
- NO<sub>x</sub> is not formed
- 1.3% excess of air is considered
- Dry basis of the material
- 10 g<sub>water</sub>/kg<sub>wet air</sub> of relative humidity of wet air is considered

The calculations are based on the elemental analysis of the light packaging waste determined earlier.

Briefly, in the following the empirical equations used for the determination of the minimum amount of theoretical air necessary for complete stoichiometric combustion and exhausting gas are presented.

First the volumetric composition of dry air as 21% O<sub>2</sub> and 79% N<sub>2</sub> or gravimetric 23.19% O<sub>2</sub> and 76.81% N<sub>2</sub> is considered.

- The *theoretical dry air volume*  $V_a^\circ$  is determinate in equation 24

$$V_a^\circ = 0.0889 \times (C + 0.375 \times S) + 0.265 \times H - 0.0333 \times O \quad [\text{Nm}^3/\text{kg}_{\text{waste}}] \quad \text{Equation 3.5}$$

- The *theoretical wet air volume*  $V_{a \text{ wet}}^\circ$  is:

$$V_{a \text{ wet}}^\circ = (1 + 0.00161 \times x) \times \alpha \times V_a^\circ \quad [\text{Nm}^3/\text{kg}_{\text{waste}}] \quad \text{Equation 3.6}$$

where: x is the relative humidity of air and its considered 10 g<sub>water</sub>/kg<sub>dry air</sub>

$\alpha$  is the excess of air and its considered 1.3

- The *theoretical volume of triatomic gases*  $V_{RO_2}^\circ$

$$V_{RO_2}^\circ = V_{CO_2}^\circ + V_{SO_2}^\circ = \frac{1,867}{100} \times (C + 0.375 \times S) \quad [\text{Nm}^3/\text{kg}_{\text{waste}}] \quad \text{Equation 3.7}$$

- The *theoretical volume of diatomic gases*  $V_{NO_2}^\circ$

$$V_{NO_2}^\circ = 0.79 V_O^\circ + \frac{0,8}{100} \times N \quad [\text{Nm}^3/\text{kg}_{\text{waste}}] \quad \text{Equation 3.8}$$

- The *theoretical volume of water vapors from the flue gas*

$$V_{H_2O}^\circ = 0.111 \times H + 0.01244 W_t + 0.00161 \times x \times V_a^\circ \quad [\text{Nm}^3/\text{kg}_{\text{waste}}] \quad \text{Equation 3.9}$$

where  $W_t$  is the total waste moisture

- The *theoretical volume of flue gas*

$$V_{fg}^o = V_{RO_2}^o + V_{N_2}^o + V_{H_2O}^o \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.10}$$

- The *theoretical volume of dry gas*

$$V_{dg}^o = V_{RO_2}^o + V_{N_2}^o \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.11}$$

- The *dry flue gases real volume*

$$V_{dg} = V_{dg}^o + (\alpha - 1) \times V_a^o \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.12}$$

- The *water vapour real volume*

$$V_{H_2O} = V_{H_2O}^o + (\alpha - 1) \times 0.00161 \times x \times V_a^o \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.13}$$

- The *flue gas real volume*

$$V_{fg} = V_{dg} + V_{H_2O} \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.14}$$

- The *minimum theoretic oxygen amount for complete combustion*  $V_{O_2}$

$$V_{O_2}^o = \frac{1.868}{100} \times (C + \frac{5.604}{100}) \times (H - \frac{O}{8}) + \frac{0.7}{100} \times S \quad [Nm^3/kg_{waste}] \quad \text{Equation 3.15}$$

In the results obtain for the air require and gaseous species form for complete combustion are present in Table 3.5 for PE, PET, PP, cardboard and paper mixtures 1:1 .

**Table 3.5. The air require and gaseous species form for complete combustion**

<b>Flue</b>	$V_a^o$	$V_{a_{wet}}^o$	$V_{RO_2}^o$	$V_{NO_2}^o$
	$[Nm^3_{air}/kg_{waste}]$	$[Nm^3_{wet air}/kg_{waste}]$	$[Nm^3/kg_{waste}]$	$[Nm^3_{NO_2}/kg_{waste}]$
	6.97	7.082	1.239	5.514
<b>Mix 1:1 Packaging waste</b>	$V_{H_2O}^o$	$V_{fg}^o$	$V_{dg}^o$	$V_{dg}$
	$[Nm^3_{H_2O}/kg_{waste}]$	$[Nm^3_{fg}/kg_{waste}]$	$[Nm^3_{dg}/kg_{waste}]$	$[Nm^3_{dg}/kg_{waste}]$
	0.867	7.621	6.754	8.845
	$V_{H_2O}$	$V_{fg}^o$	$V_{O_2}^o$	$V_{air}^o (A/F)_s$
	$[Nm^3_{H_2O}/kg_{waste}]$	$[Nm^3_{fg}/kg_{waste}]$	$[Nm^3_{O_2}/kg_{waste}]$	$[Nm^3_{air}/kg_{waste}]$
	0.901	9.745	1.47	6.98

The results obtained lead to the next operating air-fuel ratio used in the experiments present in Table 3.6.

**Table 3.6. Operating air-fuel ratio used in the packaging waste gasification experiments**

<b>ER</b>	<b>Stoichiometric air-fuel ratio for complete combustion (A/F)<sub>s</sub> [Nm<sup>3</sup><sub>air</sub>/kg<sub>waste</sub>]</b>	<b>Operating air-fuel ratio in the experimental gasification process</b>	
		<b>(A/F)<sub>o</sub> [Nm<sup>3</sup>/min]</b>	<b>(A/F)<sub>o</sub> [l/min]</b>
0.2	6.98	0.07	69.8
0.25	6.98	0.09	87.3
0.3	6.98	0.10	104.8

### 3.2.1.4 Methods of data processing

The lower heating value (LHV) of product gas is calculated with [48]

$$\text{LHV}_{\text{syngas}} = (\text{CO} \times 30 + \text{H}_2 \times 25.7 + \text{CH}_4 \times 385.4 + \text{C}_n\text{H}_m \times 151.3) + 4.2 \text{ [kJ/Nm}^3\text{]}$$

Equation 3.16

where CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>n</sub>H<sub>m</sub> are expressed in percentage.

The conversion energy efficiency (Y), which represents the fraction of the chemical energy of the fuel that is transferred to the syngas, has been calculated using the following formula:

$$Y = \frac{Q_{\text{syngas}} \times \text{LHV}_{\text{syngas}}}{Q_{\text{fuel}} \times \text{LHV}_{\text{fuel}}} \quad \text{Equation 3.17}$$

Where Q<sub>syngas</sub> and LHV<sub>syngas</sub> are the flow rate and the lower heating value of syngas  
Q<sub>fuel</sub> and LHV<sub>fuel</sub> are the feed rate and the lower heating value of the fuel

### 3.2.1.5 Analytical procedure of gasification process

The feeding rate of the packaging waste mixture 1:1 in the rotary kiln gasifier was established by decoupling the screw system from the reactor body and setting the flow diagram. During the experiments the frequency controller was set to a minimum rot/min flow due to the operation process parameters and maintenance of the gasification process stable conditions.

The operation parameters used in the gasification process were:

- Sample: Mixture 1:1 packaging waste of HDPE, PET, PP, cardboard and paper
- Input flow: 1 kg/h of packaging waste mixture
- Temperature: 800-900°C
- 10 degree inclination
- ER 0.2-0.3
- The operation time for each experiment was about 30 min

The flow rate up to 1 kg/h was determined by the feeding rate and its advancement in the reactor due its inclination. The flow feedstock parameter is influenced by the temperature operation conditions. The latter will influence the ER parameter. The latter enables the material entry and moving from the upper to the bottom reactor. This facilitates also the bottom ash/char removal by

the end of the process. The packaging waste mixture as well as the solid residue have been fed and discharged from the reactor in a continuous way.

The gases produced are analyzed both with Testo instrument and GS-MS. The Testo instrument use choice was made due to knowledge necessity of the process stabilization moment. When the process was in gasification regime the GS-MS extracted a small amount of gas that was analysed. During the experiments was observed that the process enters in gasification regime after 10-12 min since the reactor feeding time. The differences temperature between the reactor inlet and outlet is about 100 °C. During the gasification process, heat energy deliver in the reactor due to packaging waste mixture gasification increase the outlet with almost 20-30°C.

However there is an estimated one minute delay from the moment of gas extraction until starting gas chromatographic analysis. Overmore one gas sample analysis by GS-MS instruments takes about 20 minutes. For a better accuracy of the results the stable conditions process must be maintain.

### 3.2.2. Gas and solid product analysis from gasification of light packaging waste

The producer gas was analyzed via a gas chromatography using a thermal conductivity detector (TCD) and a flame ionization detector (FID) with helium used as carrier gas. Three runs were made for the same experimental conditions in order to facilitate and increase the accuracy of the results.

Figure 3.16 and 3.17 presents the gas produced composition function of ER.

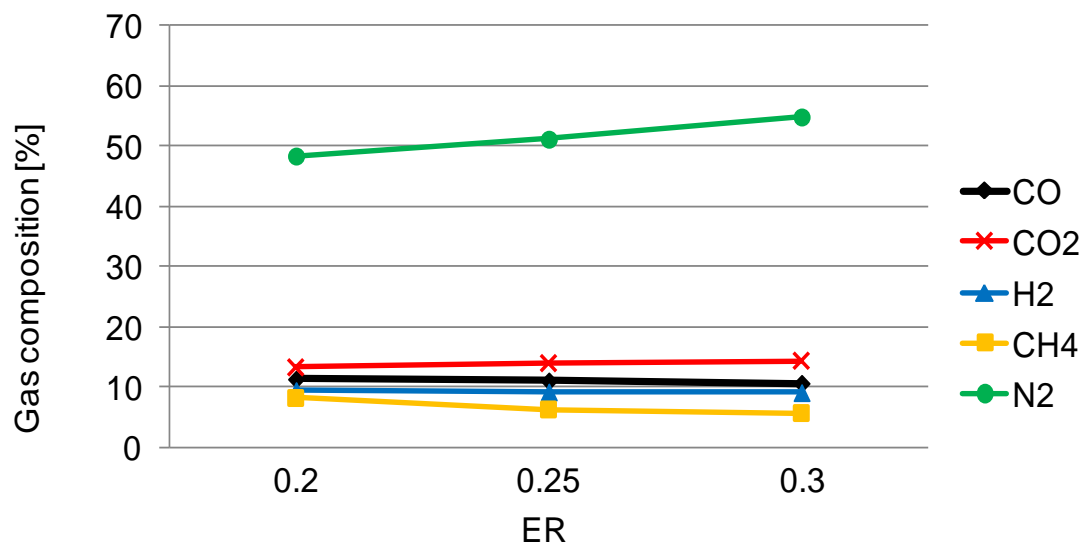


Figure 3.16. Gas analysis from gasification of light packaging waste at 800°C

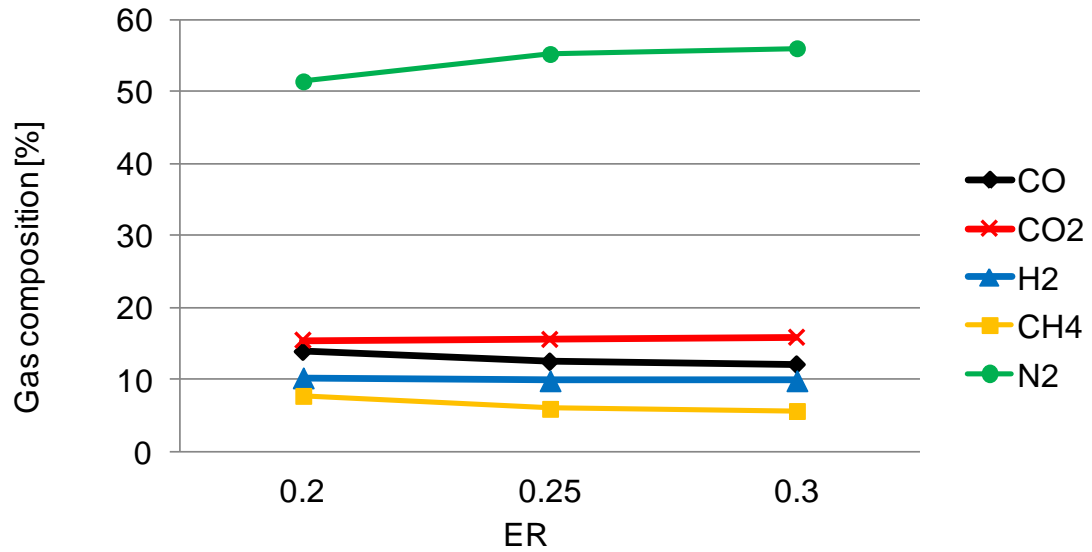


Figure 3.17. Gas analysis from gasification of light packaging waste at 900°C

From the results obtained in Figure 3.17 and 3.18 it can be concluded:

- The packaging waste mixture 1:1 contains up to 2% nitrogen (as it was demonstrated in Chapter 2) and no other sources of nitrogen except air is considered in the gas produced composition. Even though in other researches the nitrogen content resulted in the gas produced is not presented, and therefore neglected this important element influence the heating value of the gas produced.
- At 800°C the char conversion is lower as the CO and CO<sub>2</sub> results show
- It is observed that methane tends to decompose more at higher temperatures. The latter can affect the tar production. As it was remarked above then tar content registers a decrease at temperatures above 1000°C
- High degree of combustion occurs at high ER which supplies more air into the gasifier and improves char burning to produce CO<sub>2</sub> instead of combustible gases such as CO, H<sub>2</sub>, CH<sub>4</sub> and C<sub>n</sub>H<sub>m</sub>.
- By increasing the temperature it is observed that the CO<sub>2</sub> breaks down to form CO; This can be explained by the O<sub>2</sub> reaction with carbon to form CO and CO<sub>2</sub> which is more powerful in comparison with hydrogen for water formation.
- Nevertheless the hydrogen content increases with the increasing of temperature and it decreases with the ER increasing.

In the experiments the solid residue amount is strongly influenced by temperature and ER as demonstrated in Figure 3.18.

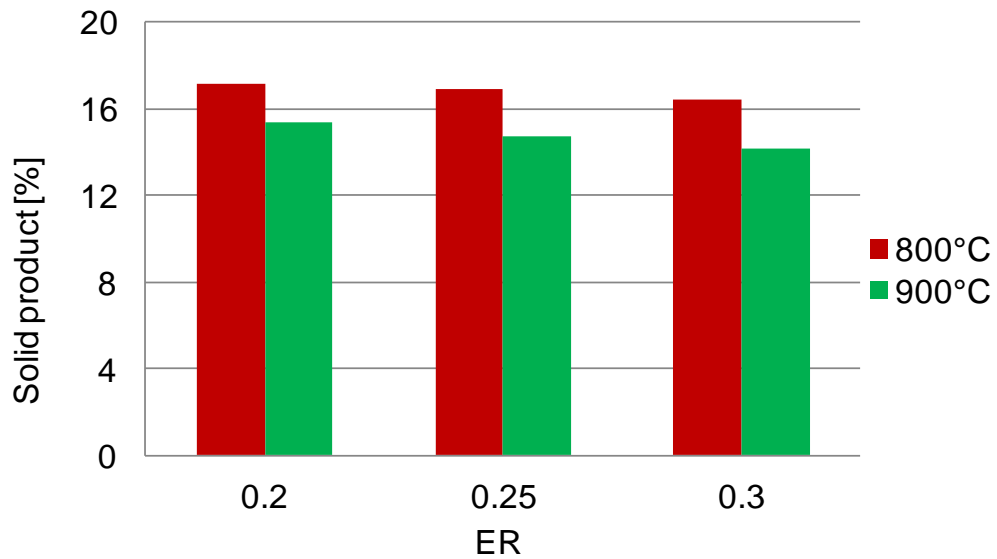


Figure 3.18. Solid residue product [%] at 800°C and 900°C

The solid residue is composed by char and ash. As figure 3.18 shows the char content is presented even at higher temperatures and part is discharged as unconverted carbon in the unusable ash. The latter limit the efficiency conversion given the fact that only 5% of solid residue product represents ash.

### 3.2.3. Energy assessment of gasification products and overall process

By increasing the ER the nitrogen provided by air, dilutes the producer gas which in turn results in its low energy content. The latter will be revealed in the LHV syngas production as presented in figure 3.19.

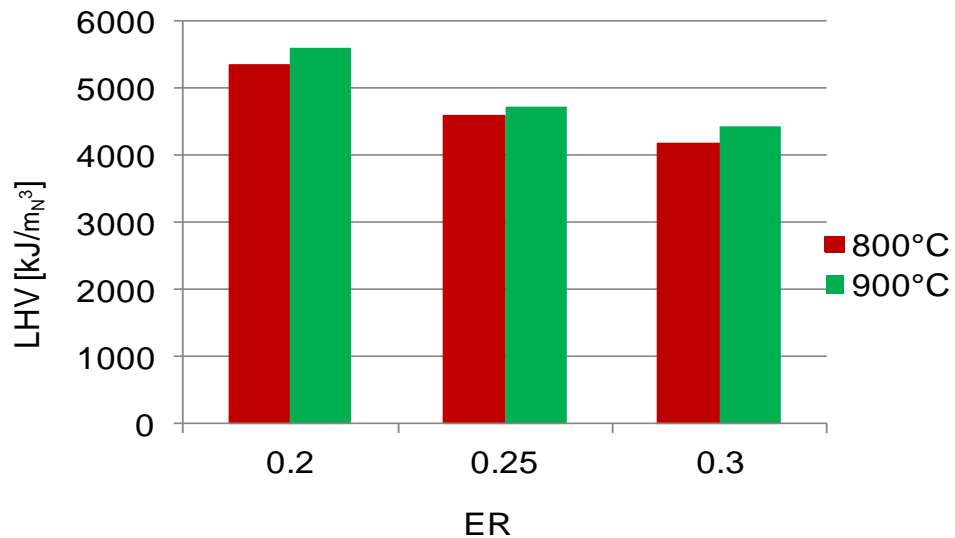


Figure 3.19. Low heating value of the syngas produced

The LHV of the gas produced was calculated with equation 36 taking into account only the CO, H<sub>2</sub>, CH<sub>4</sub>. The missing data regarding the hydrocarbons content such as acetylene (C<sub>2</sub>H<sub>2</sub>),

ethylene ( $C_2H_4$ ), ethane ( $C_2H_6$ ) decrease the application of the formula and accuracy of the results. As reported in other studies at temperatures of  $850^\circ\text{C}$  - $890^\circ\text{C}$  and an equivalent ratio of 0.21 the biomass LHV will reach up  $8.84 \text{ Nm}^3/\text{kg}_{\text{biomass}}$ , while plastics reaches up to  $7500 \text{ Nm}^3/\text{kg}_{\text{plastic}}$  [106]. In the present experiments the gas LHV will reach to its maximum at  $5600 \text{ Nm}^3/\text{kg}_{\text{packaging waste}}$  at  $900^\circ\text{C}$  with an ER of 0.2.

As reported by Arena, 2012 [43] lower values of ER leave unconverted char and higher tar content while higher values of ER determine the oxidation of part of syngas and the consequent reduction of syngas heating value: this could cause incomplete combustion in the combustion chamber that is usually downstream of the gasifier. The temperature parameter is not only influencing the syngas production and its combustible qualities but also the content of tar in syngas. The LHV of the syngas still is increased by the polyolefin's presence as direct consequences of the extension of the recalled decomposition reaction.

The obtained syngas is suitable for final application, especially with energy generation in internal combustion reciprocating engines or turbines, but also production of hydrogen or feedstock for the chemical industry (which requires costly and complex treatment in order to fulfil all the specific requirements).

The conversion energy efficiency was calculated by estimating the syngas flow rate from the gasification process. The gas flow rate ( $Q_{\text{syngas}}$ ) was estimated from the data registered by Testo instrument. As figure 3.20 shows, the gas flow rate at  $800^\circ\text{C}$  and ER ranging between 0.2 -0.3 is  $1.5\text{-}1.99 \text{ m}^3_{\text{N}}/\text{kg}_{\text{PW}}$ . As it was expected, the gas yield increase with the increasing of temperature and gasifying agent. At  $900^\circ\text{C}$  and 0.2-0.3 ER the gas flow rate registered varies between  $1.58\text{-}2.1 \text{ m}^3_{\text{N}}/\text{kg}_{\text{PW}}$ .

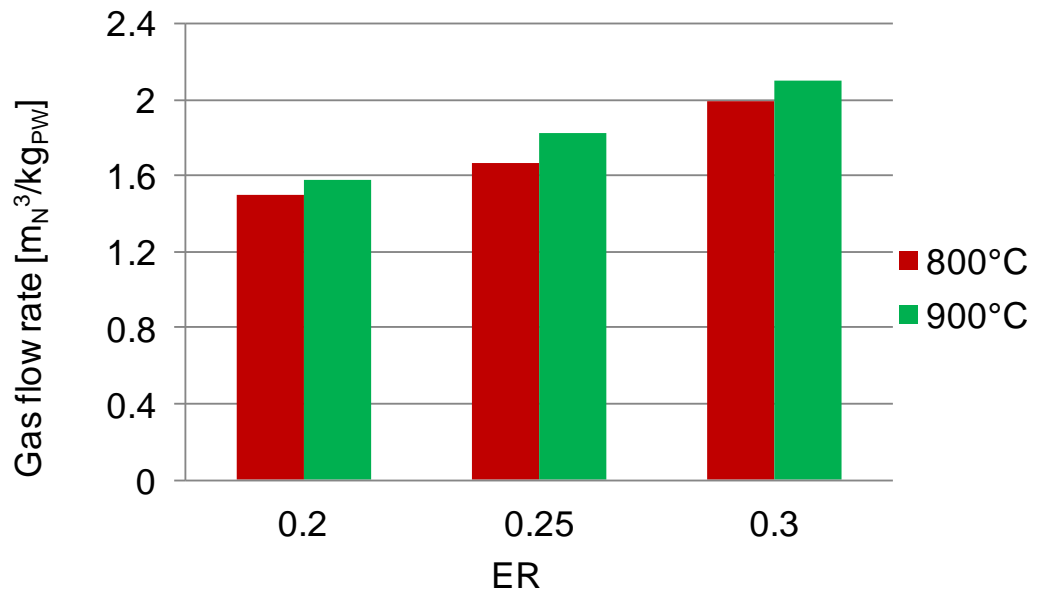


Figure 3.20. Gas flow rate

Figure 3.21 presents the conversion energy efficiency. It is assumed that neither the elutriated carbon nor the tar contributes to Y. Even if the combustible gases decrease due to the air that has dilution proprieties the conversion energy increase due to the increasing of gas flow rate. The

maximum conversion energy efficiency up to 71% rate it's registered at higher temperature of the experiments and maximum ER rate.

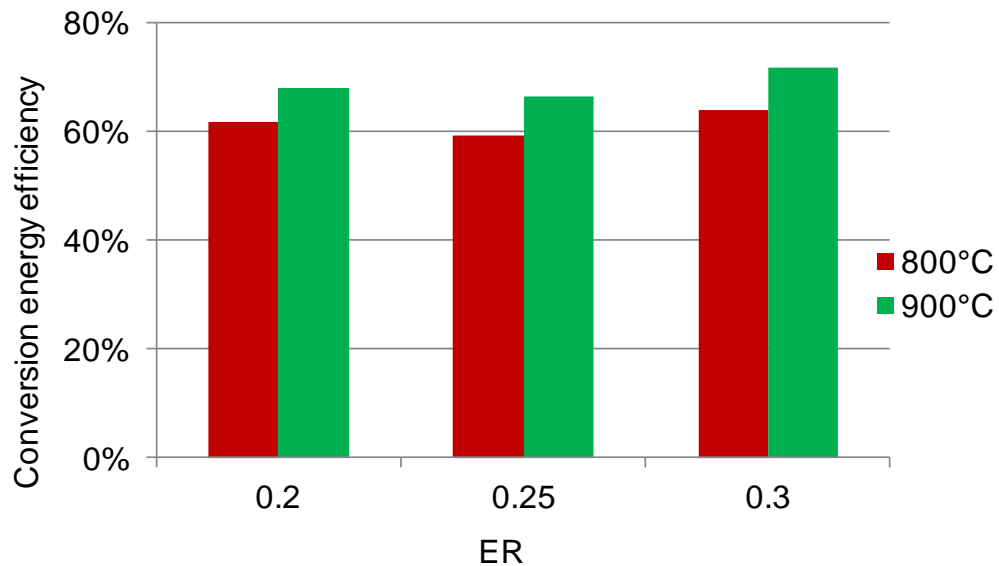


Figure 3.21. Conversion energy efficiency

### 3.2.4. Conclusion

From the gasification of packaging waste mixture the following conclusion can be drawn:

- The first stage of the gasification process which is pyrolysis of the material is associated with the results obtained in the pyrolysis experiments. The solid and gas products analyzed are influenced by the plastics and paper behaviour regarding the thermal cracking of each waste fraction. In comparison with polymers, the cellulose and lignocelluloses are very stable and refractory to cracking by thermal treatment.
- The hydrogen content is increasing with increasing of temperature and decreasing with increasing of ER. In the present results indicated that hydrogen content varied little in the range of ER while gas yield increased as figure 3.18 and figure 3.19 are showing.
- Higher ER lowers the gas quality because of more oxidization reactions at the being of the process.
- Without taking into account the  $C_nH_m$  hydrocarbons except  $CH_4$ , in the present experiments the gas LHV will reach to its maximum at  $5600 \text{ Nm}^3/\text{kg}_{PW}$  at  $900^\circ\text{C}$  with an ER of 0.2
- The solid residue is composed by char and ash and reach to maxim of 17 % from the initial feed input at low temperature used in the experiments of  $800^\circ\text{C}$  and 0.2ER.
- The gas flow rate at  $800^\circ\text{C}$  and ER ranging between 0.2 -0.3 is  $1.5\text{-}1.99 \text{ Nm}^3/\text{kg}_{PW}$ . As it was expected, the gas yield increases with the increasing of temperature and gasifying agent. At  $900^\circ\text{C}$  and 0.2-0.3 ER the gas flow rate registered varies between  $1.58\text{-}2.1 \text{ Nm}^3/\text{kg}_{PW}$ .

## CHAPTER 4

### 4. INTEGRATED MUNICIPAL SOLID WASTE SCENARIO MODELS

The experimental results have led to the present study by creating a complete Integrated Municipal Solid Waste (IMSW) scenario model (SM) with practical application in waste management sector. The model integrates WtE transformation sequences: quantification and characterization of solid waste streams from different sources, selective collection (SC), advanced mechanical sorting (AMS), material recovery, advanced thermal treatment (ATT) and input mass flow hypothesis. While other studies have mainly focused on combination of multiple treatments, including aerobic/anaerobic mechanical-biological treatments [107,108,109], the IMSWS developed aims the ideal target of “zero emissions waste to energy” using AMS and ATT.

The study provides a unique chain of advanced waste pre-treatment stages of fully commingled waste stream, leading to an original set of suggestions and future contributions to a sustainable Integrated Municipal Solid Waste System (IMSWS), taking into account real data and the EU principles.

The selection of the input data was made on MSW management real case studies from South-Eastern and Central Europe-like regions.

The system allows not only the recycling of sellable materials but also the minimization of landfilling thanks to pre-treatments that extract low LHV materials.

In practice the analyzed scheme balances the pathways of material and energy valorisation. Concerning the presence of a gasificator, it was supposed to be able to move in the analysed area, the experience of gasification that characterizes countries like Japan.

A comprehensive critical analysis of the presented integrated MSW scenario models is considered at the end of the study, in order to understand the viability of the scenarios.

#### 4.1. Material and methods

##### 4.1.1. Selection criteria and assumptions used in the IMSW scenario models

Because on the rapid deadlines implementation of the EU waste management measures, the two chosen case studies are represented by a densely inhabited urban area *from South-Eastern and Central Europe-like, with nearly 600,000 inhabitants that generate 300,000 t<sub>MSW</sub>/y* [8]. The current IMSWS is developed taking into account the present and future trend in waste management based on: waste streams, material balance and flow, physico-chemical characterization and energetic potential. The selection of the two areas was made based on MSW management development stage.

For the IMSW scenario models a set of **criteria** were chosen in order to define and select the system boundaries by taking into account:

- Same material flow input that is treated into the scenario models (300,000 t<sub>MSW</sub>/y)
- Same IMSW scenario model conversion line for all case studies

- Same energy consumptions specific for each treatment which are used in all scenario models
- Same environmental impact indicators by type of treatment, only for recycling, combustion and gasification treatments.

The **assumptions** used in the IMSW scenario models are:

- The present scenario models are based on recovery maximization of plastics, glass and metal from the Residual Municipal Solid Waste (RMSW) stream. It was assumed that the emissions from the advanced mechanical sorting line are less than 5%. By applying the presented IMSWS at real scale, the advanced mechanical sorting line can become optional depending on the requests. In the present scenario models the emissions from the AMS line are considered negligible.
- The transportation of the waste is not included in the system boundaries.
- Two types of distinct WtE plants were considered for the energetic recovery which are: combustion treatment in co-generation and steam gasification.

#### 4.1.2. Waste stream and IMSWS process stages characterization

Generally, the MSW stream is generated by households, commercial work, and other sources whose activities are similar to those of households and commercial enterprises, (wastes from hotels, supermarkets, schools, institutions, offices, shops) and from municipal services (street cleaning and maintenance of recreational areas).

The MSW composition varies due to: geographical location, population, amount of wastes generated and techno-economic potential existing. Beside this, the SC optimization plays an important role in the curbside collection efficiency that is influenced by the lack of professional standards for waste management and must therefore be educated to achieve improved sorting quality.

In figure 4.1, the real case study regions from Central Europe-like (where the SC is developed) and South-Eastern Europe (where the SC is in an incepted stage) shows the visible differences on the MSW composition due to different waste management procedures.

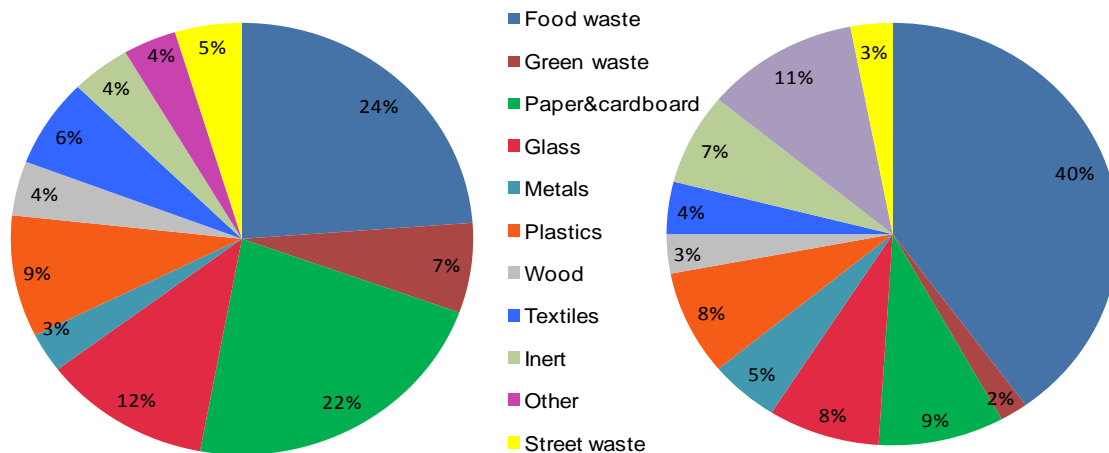


Figure 4.1. MSW composition in Central Europe-like and South-Eastern Europe

In the first scenario model (SM<sub>1</sub>) the SC of packaging waste, it's in an early stage of implementation (up to 10%), a reality usually found in South-Eastern European countries. The second scenario model (SM<sub>2</sub>) is developed for Central European regions where the SC reaches up to 68 %, due the optimization of curbside collection efficiency. It was estimated that in 20 years of waste management improvement, the increase of SC was about 3.3 % per year [8].

The South-Eastern European region MSW composition shows high percentage of food fraction and low percentage of packaging fraction compared to other EU countries that are affecting the energetic qualities of the waste. This might be explain by the being differences on waste management, especially SC.

In both scenarios models the unselected waste stream, so-called Residual Municipal Solid Waste (RMSW) is subject to a treatment line: extrusion, bio-drying, AMS. After each treatment stage, the resulted materials where classified as SRF. From the treatment chain, the last SRF stream produced is sent to energy recovery for both combustion and gasification processes. Using the same RMSW treatment line, these WtE options were chosen in order to compare the combustion and gasification processes from both energetic and environmental point of view taking into the current MSW management situation in South-Eastern (SM<sub>1</sub>) and Central European (SM<sub>2</sub>) countries.

In the present scenario models the valorisation of the last SRF flow in a combustion plant was noted with SM<sub>1A</sub> for the first scenario model respectively SM<sub>2A</sub> for the second scenario model. The same approach was used also for gasification with SM<sub>1B</sub> for the first scenario model, respectively SM<sub>2B</sub> for the second scenario model.

Since the MSW is an inherently non – homogenous material the AMS is essential for the stabilization and performance of thermo-chemical process. The design of the present IMSWS relies on the following waste management stages:

- SC for recyclable fractions of packaging waste such as: plastics, paper and cardboard, glass and metals for first scenario model SM<sub>1</sub> and by adding organic, wood, inert and other particular waste for the second scenario model SM<sub>2</sub>. The street waste collection was considered in all scenarios. The efficiency of MSW selective collection has an important role in the characteristics of RMSW, therefore also on the choice of thermal treatment technology [15].
- the RMSW is first sent to a *ballistic separator*. This technology is based on density and elasticity separation that removes the inert and oversized materials.
- *shredder* pre-treatment represents a critical point in the preparation of RMSW for extrusion process and ATT. The particle size of MSW ranges from 1 to 900 mm. By shredding the waste, the particle size is reduced between 3 to 4 times [110]. Overmore, the waste density increases at 33% in wet basis and 22% at dry basis, effectively reducing the transport and storage volume.
- *extrusion* technology is a relatively new concept in the MSW treatment. The pressure extrusion process consists in high-pressure treatment that separates the waste in two flows: wet fraction (mainly consisting of organic waste) and dry fraction (paper&carboard, plastic, traces of wood and inert material).
- *electrostatic separation system* (ESS) is used to remove the plastics and metal waste fractions in order to facilitate the magnetic separation process and minimize the unwanted plastic scrap in the ferrous second raw material.
- *magnetic separation (MS)* process separate the ferrous metals from the waste stream. This process registers high efficiencies on iron and steel removal, but doesn't separate aluminium, copper and other non-ferrous metals.
- *eddy-current separation system ECSS* (electric field separation) is performed near the end of the separation process. Using exerting repulsive forces on electrically conductive materials

this system is designed to separate of non-ferrous material (aluminium, copper, brass, magnesium and zinc) from lightweight commingled waste (plastic, paper, glass).

- *optic sorting process (OS)* was used for glass recovery propose.
- *bio-drying* is a treatment that exploits the exothermic reactions for evaporating the highest part of the moisture of the waste with the lowest consumption of volatile solids [111, 112].

The efficiency and energy consumption assumed for each treatment are presented in Table 4.1. Generally the low efficiencies of the pyro-gasification plants are given by the reduced feed in flow imposed by the small capacities of the units [113,114,115].

**Table 4.1. Recycling and energetic consumption**

Material /Treatment	Recycling/ Pre-treatment efficiency [% in weight]	Electric energy consumption [kWh/t <sub>waste</sub> ]	References
Aluminium	88.35	79	[116]
Glass	94	18.4	
Paper	85.5	7	
Wood	85.5	36	
Plastic	58.75	414	
Food and green waste	30 (composting)	50	
Ballistic separator	40% wood	0.75	[117]
	30% close		
	40% other		
Extrusion	65% dry fraction	11	
Shredding HSLT	85%	6-22	
Bio-drying	63%	33	
Magnetic separator	90%	1.3	[118,119]
Electrostatic separation	47% plastic; 46% metals	1	
Eddy current separation	75-90%	290	[120]
Optic separation	90%	1	[8]
WtE plant	Efficiency	Energy required for start-up (kWh/t <sub>waste</sub> )	
Combustion	20% net electric efficiency	77.8	[116,121, 121]
	64% net thermal efficiency		
Steam Gasification	30% net electric efficiency	333.3	
	80% net thermal efficiency		

The **Nitrogen (N)** and **Phosphorus (P)** values for the produced **compost** were considered 28.2 kg<sub>N</sub>/t<sub>waste</sub> and respectively 3.9 kg<sub>P</sub>/t<sub>waste</sub>. Carbon dioxide (CO<sub>2</sub>) and ammonia (NH<sub>3</sub>) emissions were considered 1.85 t<sub>CO2</sub>/t<sub>waste</sub> and respectively 0.37 t<sub>NH3</sub>/t<sub>waste</sub> [122].

The overall recycling rate has been calculated with the following equation:

$$\text{Recycling} = \frac{\text{Recycled material}}{\text{Material available for recycling}} [\%] \quad \text{Equation 4.1}$$

#### 4.1.3. Environmental impact assessment

In this study, the scenarios models SM<sub>1A</sub>, SM<sub>1B</sub>, SM<sub>2A</sub>, SM<sub>2B</sub>, are compared by their environmental properties taking into account recent studies on environmental assessment of MSW management. The **main environmental indicators** that are analysed for each scenario model are:

- Global Warming Potential- GWP (kg CO<sub>2</sub> eq), which accounts for the emission of greenhouse gases;
- Acidification Potential -AP (kg SO<sub>2</sub> eq), which accounts for the emissions of SO<sub>x</sub>;
- Human Toxicity Potential-HTP (kg 1,4 DCB eq) addresses a wide range of toxic substances, including, in this study, the secondary particulate matter;
- Photochemical Ozone Creation Potential - POCP (kg C<sub>2</sub>H<sub>2</sub> eq) which accounts for the substances that cause the photochemical ozone production in the troposphere.

In the present study the environmental indicators values (Table 4.2) for pyrolysis-gasification, combustion plant and landfill option are used from a early work developed by Zaman [123]. In Zaman's study the life cycle impact assessment of the WtE technologies has been done for one tonne of waste mass by applying the CML 2 baseline (2000) method. The impact of transportation system is not considered for any of the processes.

**Table 4.2. Environmental impact indicators by type of treatment**

<b>Type of treatment</b>	<b>Global Warming Potential (kg CO<sub>2</sub> eq)</b>	<b>Acidification Potential (kg SO<sub>2</sub> eq)</b>	<b>Human Toxicity Potential (kg 1,4 DCB eq)</b>	<b>Photochemical Ozone Creation Potential (kg C<sub>2</sub>H<sub>4</sub> eq)</b>
Combustion	424.4	0.584	1178.6	-0.0077
Gasification	412.1	0.247	805.5	-0.0244
Landfill	746.4	0.243	8.149	0.116

According to Rigamonti et. al. and Bovea et. al. [115,124], the environmental impact indicators for material recovery by fraction, have positive environmental impact which are presented in Table 4.3. The recycling inventory presented in these researches have been modelled from Ecoinvent (2007) and BUWAL 250 data, assuming 1:1 substitution ratio among the avoided primary material production and the production of secondary material.

Table 4.3. Environmental impact indicators for material recovery

Material	Global Warming Potential (kg CO <sub>2</sub> eq t <sub>SSW</sub> <sup>-1</sup> )	Acidification Potential (kg SO <sub>2</sub> eq t <sub>SSW</sub> <sup>-1</sup> )	Human toxicity Potential (kg 1,4 DCB eq t <sub>SSW</sub> <sup>-1</sup> )	Photochemical Ozone Creation Potential (kg C <sub>2</sub> H <sub>4</sub> eq t <sub>SSW</sub> <sup>-1</sup> )
Metals	-9855	-52	-47001	-2.9
Glass	-722	-2.9	-141	-0.185
Paper	-557	-3.3	-126	-0.237
Wood	-166	-1.2	-93	-0.317
Plastic	-1120	-7.1	-248	-1.2

\*SSW- Source Separate Waste

The **depletion of non-renewable resources** and its environmental impact was calculated through the Abiotic Depletion Potential (ADP) indicator. The indicator offers a clear vision regarding the substitution of fossil fuel with high quality waste in power co-generation plants. In present case study the high quality waste is obtain after the treatment of the RMSW in form of Solid Recovered Fuel (SRF).

Brown coal is one of the major sources of world energy supplies and used in the majority of power generation plants. The ADP indicator of this soft coal can be calculated with [125]:

$$\begin{aligned} \text{ADP}_{\text{softcoal}} &= \text{ADP}_{\text{fossil energy}} \times \text{Heating Value}_{\text{soft coal}} \\ &= 4.81 \times 10^{-4} \times 13.96 = 0.00671 \text{ [kg antimony equivalents/kg soft coal]} \end{aligned} \quad \text{Equation 4.2}$$

where the  $\text{ADP}_{\text{fossil energy}}$  is expressed in [kg antimony equivalents/MJ fossil energy]

Heating Value is expressed in [MJ/ kg soft coal]

Taking into account as assumption the predominant used of brown coal as non-renewable fuel in power generation plants the APD indicator was calculated in Equation 39 respect to its substitution by high quality waste.

$$\sum \text{ADP} = \text{ADP}_{\text{softcoal}} \times M \text{ [kg antimony equivalents]} \quad \text{Equation 4.3}$$

where is  $\text{ADP}_{\text{soft coal}}$  is expressed in [kg antimony equivalents/kg soft coal]

M – Mass of quantity of source extracted [kg soft coal].

To more explicit, in the present study the mass quantity is represented by the quantity of SRF obtain in the IMSW scenario models that can replace the usage of softcoal.

Moreover, for an accurate estimation of the **landfill land area** and its environmental impact, the used data in the calculation were considered as a whole and not by type of MSW. The ecological scarcity method (BUWAL 133) was applied [126].The CORINE codes 132 (“dump site”) from the Ecoinvent database were used for the determination of landfill occupations and eco-factors for occupied landfill volume [127]. An average landfill depth of 15 m and a waste density of 1000 kg m<sup>-3</sup> were chosen. In order to differentiate the environmental quality of the

dump site, an eco-factor was applied, in accordance with ISO Standard 14044. In the present research, a constant mid-point eco-factor of 500 eco-points was attributed for each kilogram of landfilled waste.

## 4.2. Results and discussion

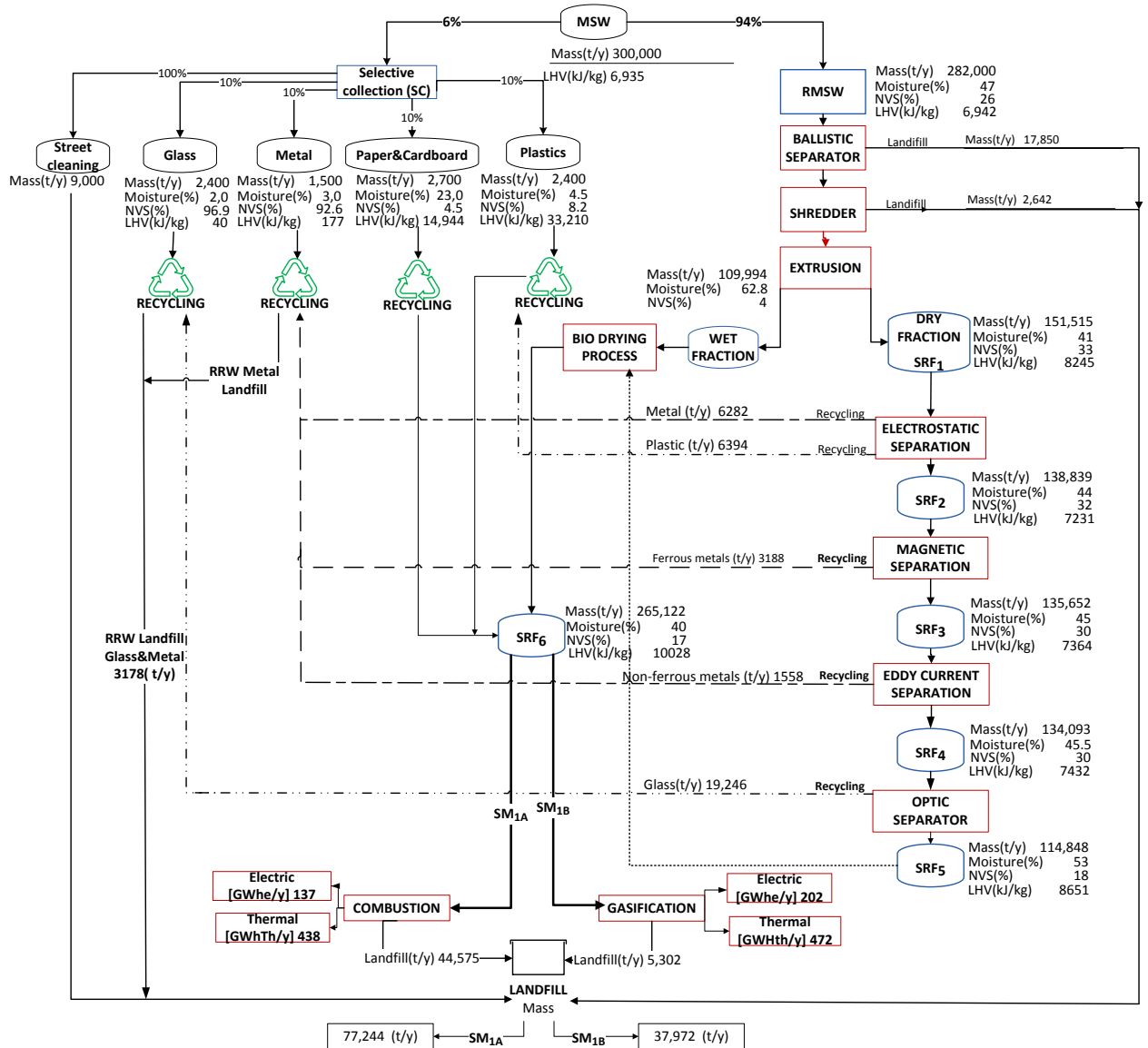
### 4.2.1. Mass and energy balance

The results of this study can be used as technical support during the decision-making processes by the local authorities, in order to justify the selection of the best alternative waste management system in connection with environmental aspects. In Figure 4.2 and 4.3, mass and energy balances for the proposed IMSWS are presented. For each process the mass, moisture, non volatile solids (NVS = Inert), and LHV [kJ/kg] are also calculated considering the MSW composition by fraction.

In the present scenario models, the SRF obtained were numbered from 1 to 6 (SRF<sub>1</sub>-SRF<sub>6</sub>) depending on their production on the treatment chain. As explained in previews section, the last combustible stream (SRF<sub>6</sub>) is sent to a combustion plant in scenarios SM<sub>1A</sub> and SM<sub>2A</sub> or gasification plant in scenario SM<sub>1B</sub> and SM<sub>2B</sub>. At real industrial scale, the choice of the process is mainly linked with the technological simplicity and economical aspect, even though in the last decades the environmental considerations are restricting the operations.

Only paper, cardboard, plastics and wood, from the Refused Recycled Waste (RRW) stream, are sent into SRF<sub>6</sub> for energy recovery purpose through the **“Take back program”**.

In Figure 4.2, looking over the South-Eastern European situation, in the first scenario model SM<sub>1</sub> the SC is still in a early stage of implementation with an overall efficiency of 6% for recyclable materials and street waste collection.

Figure 4.2. Scenario model (SM<sub>1</sub>) for South-Eastern Europe

Even if the remaining RMSW (94%) contains oxidable materials (especially carbon and hydrogen) which can free considerable energy, the moisture (47%) and inert (26%) content decrease its energetic qualities. In order to overcome these detriments, the RMSW is primarily treated for inert material removal and size reduction minimizing the possible technical damage of the AMS line. By applying ESS, MS, ECSS and OS sorting treatments the recyclable materials recovery reaches up to 15% from the MSW initial stream with: 50% for glass, 33% metals and 17% plastics. In all the scenarios the Residual Recycled Waste (RRW) is sent to energy recovery for rich carbon content materials (plastics, paper and cardboard) or to landfill for inert ones (glass, metal). The proficiency of the system increases with the reduction of NSV content at 4% for SRF<sub>6</sub> that is subject to two different WtE processes: combustion (SM<sub>1A</sub>) or gasification (SM<sub>1B</sub>).

The decrease of inert material content in SRF<sub>6</sub> facilitates the material total oxidation in combustion processes or partial oxidation in IGCC plants and enables recycling for the recovered materials.

The extrusion process offers a new perspective in the MSW treatment, by extracting dry combustible materials ( $\text{SRF}_1$ ) that can be further subject to WtE treatments. The LHV of the wet fraction will be strongly influenced by the 62.8 % moisture due to the cellulosic and ligno-cellulosic content. For the wet fraction the bio-drying process reduces moisture content with 22%. This is possible thanks to the air flow inlaid and left to rest in special biocells leaving the natural process of organic fermentation for a period ranging between 7 and 14 days matter. In mixture with  $\text{SRF}_5$ , the new  $\text{SRF}_6$  represents 88% from the MSW feedstock and can be used in mixtures with primary fuels or as feedstock in pyrolysis, gasification or combustion plants. In  $\text{SM}_1$ , the  $\text{SRF}_6$  can be sent to a combustion process ( $\text{SM}_{1A}$ ) where is produced a thermal energy output of 438  $\text{GWh}_{\text{th}}/\text{year}$  and electrical energy output of 137  $\text{GWh}_e/\text{year}$ . In  $\text{SM}_{1A}$ , the combustion process produces 44,575  $\text{t}_{\text{ash}}/\text{y}$ . The overall waste disposal of  $\text{SM}_{1A}$  is 26% respect to the MSW initial stream.

Taking into account the same input flow in  $\text{SM}_{1B}$  the vapour-gasification process was considered due to the considerable 40% moisture content of  $\text{SRF}_6$ . On the data mentioned, the overall syngas production was considered 80% and ash with 2% from the feedstock input. The syngas energetic value above 4  $\text{MJ}/\text{Nm}^3$  meets the gas quality requirements suitable for gas engine (Otto cycle) or gas turbine (Brayton/Joule cycle) or in manufacturing of chemicals like ammonia, methanol,  $\text{H}_2$  and others. Part of the untreated syngas may be heat recovered with a steam turbine (Rankine cycle) thus cogeneration. Since it is not possible to do experimental flow measurement on syngas yield the data are limited. The gas yield varies between 3-4  $\text{Nm}^3/\text{kg}_{\text{SRF}}$ . However about 20% of the syngas LHV is lost in the cleaning system. Part of the syngas produced can be used for bio-drying energy input. The tar content represents 1%-8% from the initial waste mass and decreasing along with increasing of temperature. By tar cracking catalyst the removal efficiency ranges between 90-95% minimizing future corrosive problems. The tar tolerance limit for gas turbine/engine might vary with 0.008  $\text{mg}/\text{Nm}^3$ - 50  $\text{mg}/\text{Nm}^3$ .

Ash produced during gasification is either removed as fly ash from the product gas using cyclones or filters, or is removed from the bottom of the gasifier vessel using another auger. The gasification scenario model  $\text{SM}_{1B}$  reveals a thermal energy output of 472  $\text{GWh}_{\text{th}}/\text{year}$  and electrical 202  $\text{GWh}_e/\text{year}$ . The landfilled waste is reduced by half in comparison with  $\text{SM}_{1A}$ .

In the second scenario model ( $\text{SM}_2$ ) the RMSW is using the same pathway conversion chain as one described in the first scenario model ( $\text{SM}_1$ ). In  $\text{SM}_2$  (Figure 4.3), the waste flow input data are characteristic for Central European region where SC of MSW reaches up 68%.

# Critical analysis of pyrolysis and gasification applied to waste fractions with growing energetic content

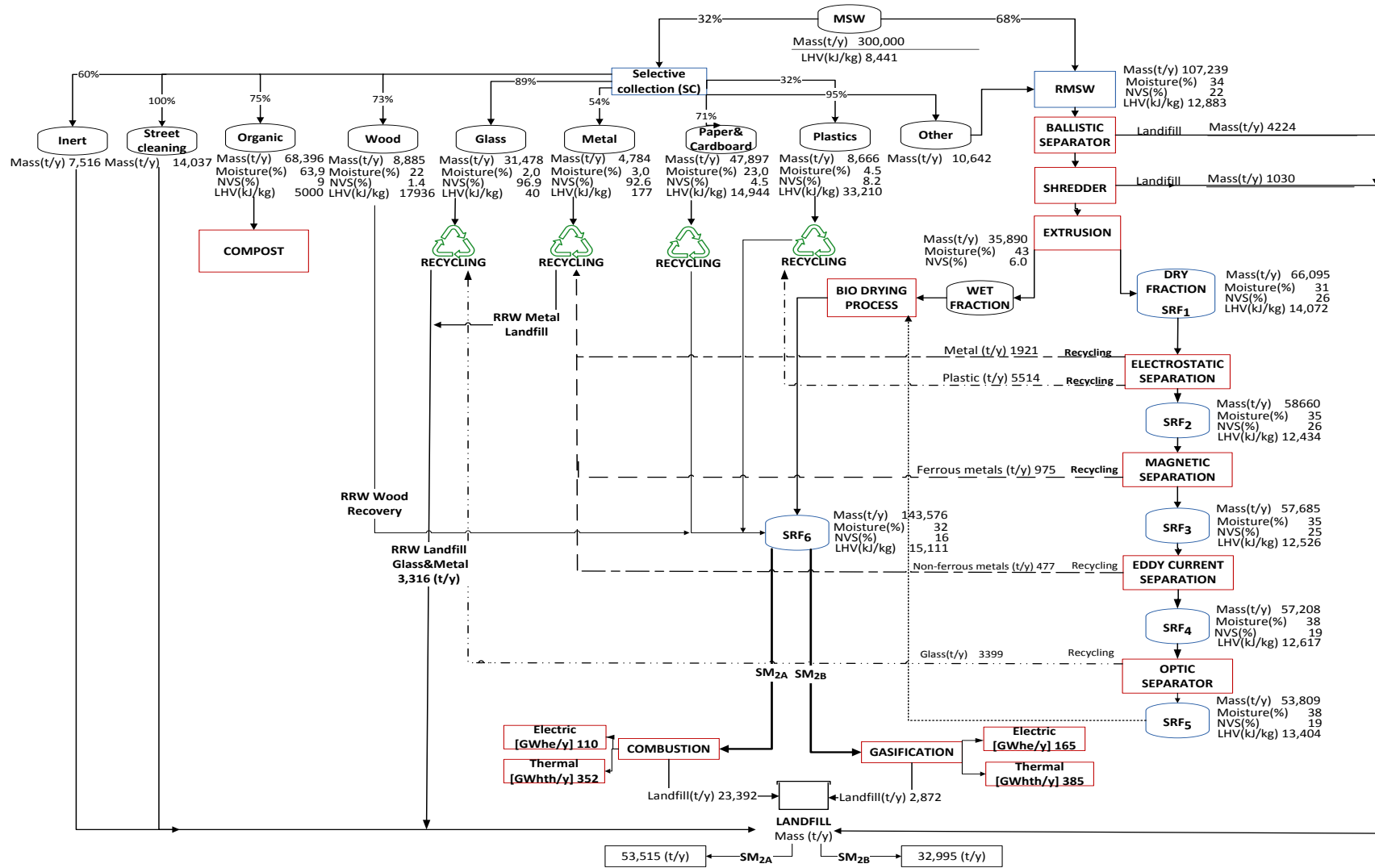


Figure 4.3. Scenario model SM<sub>2</sub> for Central Europe

In comparison with SM<sub>1</sub>, in SM<sub>2</sub> the benefits of SC are quickly observed by recycling growth rate up to 33. In Central European regions, the curbside collection of organic waste reaches up to 75% increasing the overall proficiency of the system from several perspectives:

- the collected organic fraction can be sent to anaerobic digestion with biogas production or compost production that can be used as substitute for peat and mineral fertilizers.
- The overall recycling rate reaches up to 39%.
- the mass wet flow from the extrusion process is decreasing with 67% in comparison with SM<sub>1</sub> which leads to a 43% moisture content.
- the SRF<sub>6</sub> moisture content will not exceed 32% and 15,111 kJ/kg facilitating the WtE conversion with 352 GWh<sub>th</sub>/year and 110 GWh<sub>e</sub>/year for the combustion process (SM<sub>2A</sub>) and 385 GWh<sub>th</sub>/year and 165 GWh<sub>e</sub>/year for steam gasification one (SM<sub>2B</sub>). The overall second scenario model disposal will drop up to 18% for SM<sub>2A</sub> and 11% for SM<sub>2B</sub>.

Due its significant quantity, the biodegradable waste, mainly food waste, can be subjected to several treatments such as: composting or anaerobic digestion. For the valorization of this stream, in the last scenario, the **compost** process was chosen (30% efficiency) due to its technological simplification and the EU market interest. The equivalents of nutrients produced are 1929 t<sub>N</sub>/t<sub>waste</sub>\*year and 267 t<sub>P</sub>/t<sub>waste</sub>\*year. The CO<sub>2</sub> emissions are 126,533 t<sub>CO2</sub>/t<sub>waste</sub>\*year and NH<sub>3</sub> 25,307 t<sub>NH3</sub>/t<sub>waste</sub>\*year. The compost resulted from the process can be used as substitute for peat and mineral fertilizers [128]. This process, at low/pilot scale is already present in European Union countries, facilitated by the EU structural funds. The process results show an amount of 23% material composted from the MSW initial stream.

In the calculation outputs the Combustible Ratio (CR) parameter is introduced in order to evaluate the effect of input feedstock over the energetic balance of the model. The CR parameter is defined as the ratio between plastic and organic waste introduced in the system. Figure 4.4 presents the CR comparison between SM<sub>1</sub> and SM<sub>2</sub> by type of waste stage.

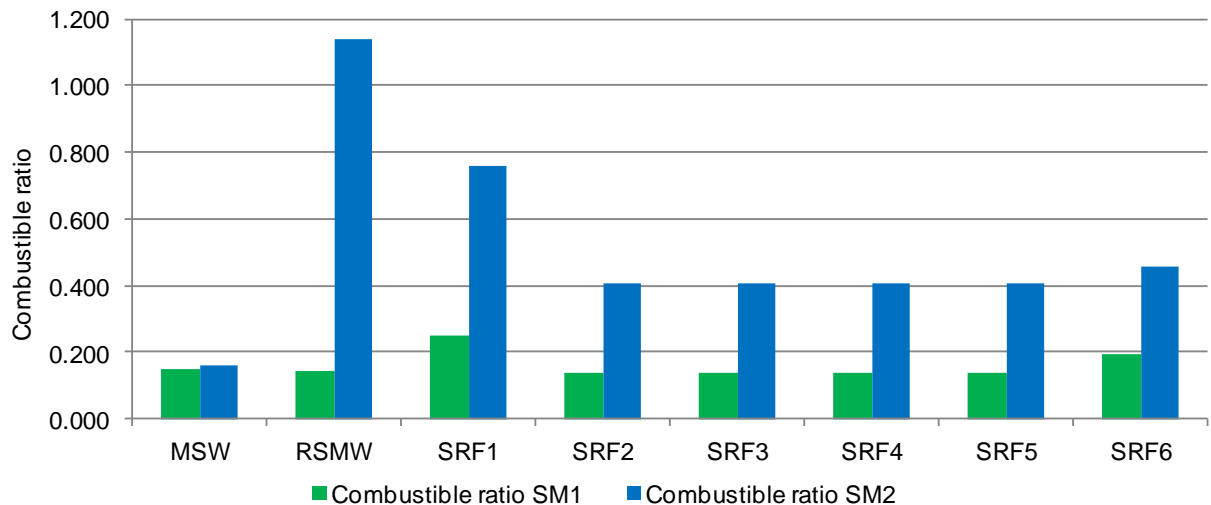
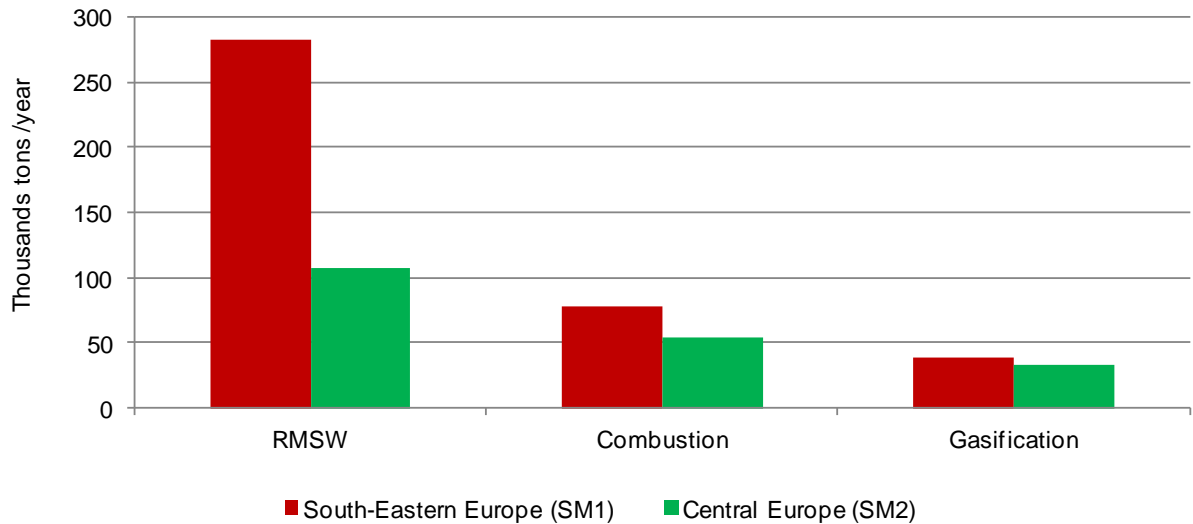


Figure 4.4. Combustible Ratio SM<sub>1</sub> and SM<sub>2</sub>

This parameter is a fast and efficient indicator that can give indications about the ability of the waste energy recovery in any IMSWS. As figure 4.4 shows, by reducing the amount of organic

flow in the RMSW stream through selective collection, the CR of the SRF<sub>6</sub> designated for WtE recovery doubles up to 0.4 in SM<sub>2</sub>. The latter is mainly influenced by the moisture reduction from the RMSW stream.

In all the scenarios models the minimization of landfilling achieves the standards imposed by law concerning the biodegradable materials, maximizing the inert material by taking the advantage role of the AMS line. As Figure 4.5 shows, the practical combination of SC and advanced pre-treatment is far a better option instead of MSW or RMSW direct disposal.



**Figure 4.5. Quantity of residue landfilled by type of disposal**

The bottom ash produced has some practical usage as for soil and embankment levelling, road sub-bases, landfilling restoration of degraded zones due to extractive activities etc.

#### 4.2.2. Environmental balance

Taking into account the sets of criteria, the assumption made and the environmental indicators values, the environmental balance is normalized to the IMSW scenario models. The GWP, AP, HTP and POCP environmental indicators are presented from Figure 4.6 - Figure 4.9.

The greenhouse gases are responsible for global warming because they absorb the infrared radiation emitted by earth resulting in higher global temperatures. It is estimated a 0.4°C increase every ten years as a result of the increase in greenhouse gases gas concentration in the atmosphere. The global warming effect applied in this LCA study involved the conversion of all gases into CO<sub>2</sub> equivalents using the GWP (Table 4.2). Not all the CO<sub>2</sub> compounds released from the atmosphere have the global warming effect. The CO<sub>2</sub> from fossil fuel use is of great concern because there is no way it is returned and absorbed on earth while the CO<sub>2</sub> produced by biological activity such as biogas is considered unharmed because of its short life cycle.

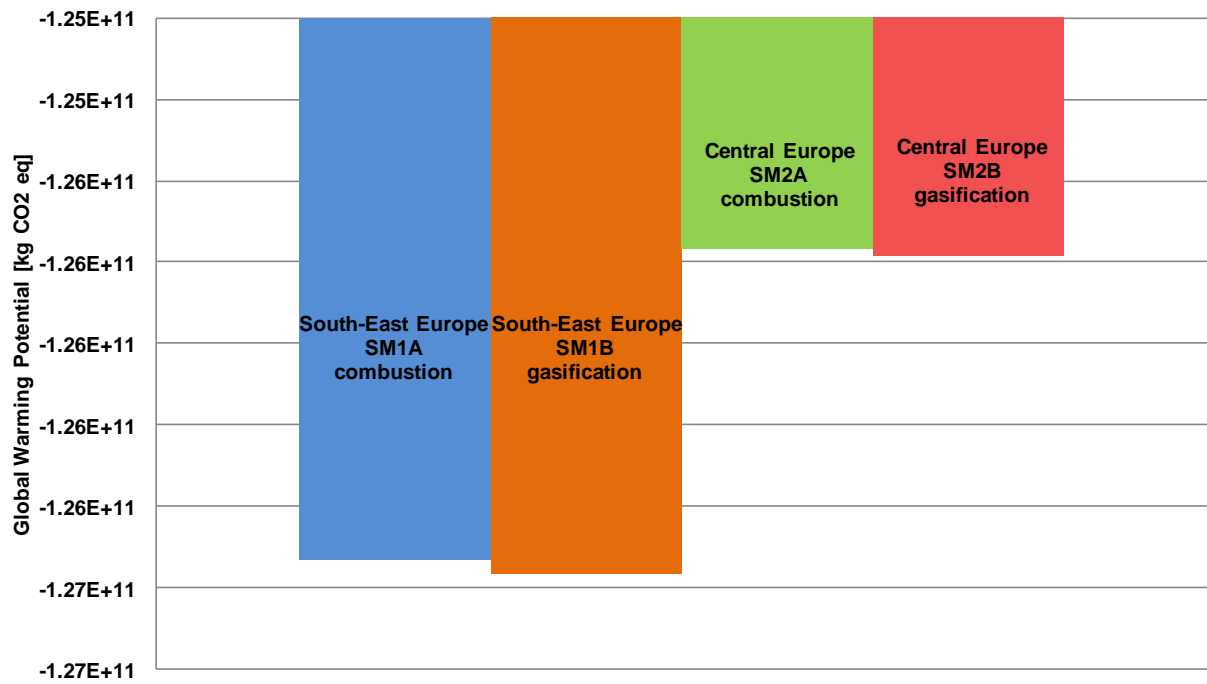


Figure 4.6. Global Warming Potential [kg CO<sub>2</sub> eq]

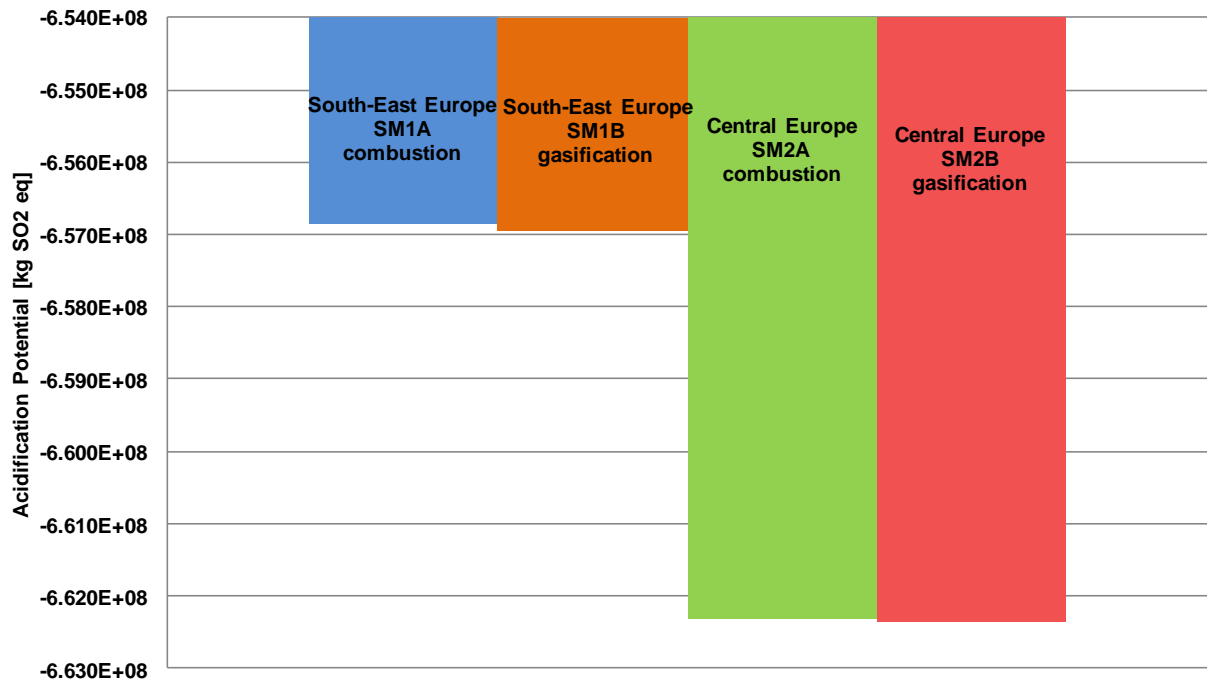


Figure 4.7. Acidification Potential [kg SO<sub>2</sub> eq]

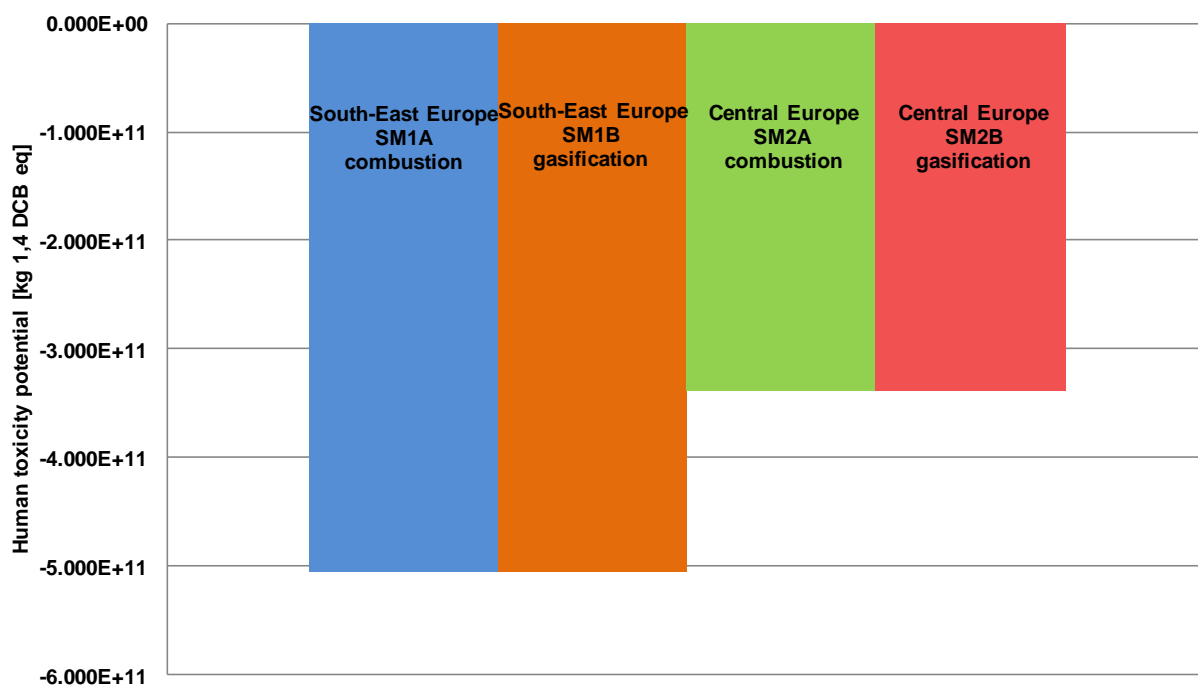


Figure 4.8. Human Toxicity Potential [kg 1,4 DCB eq]

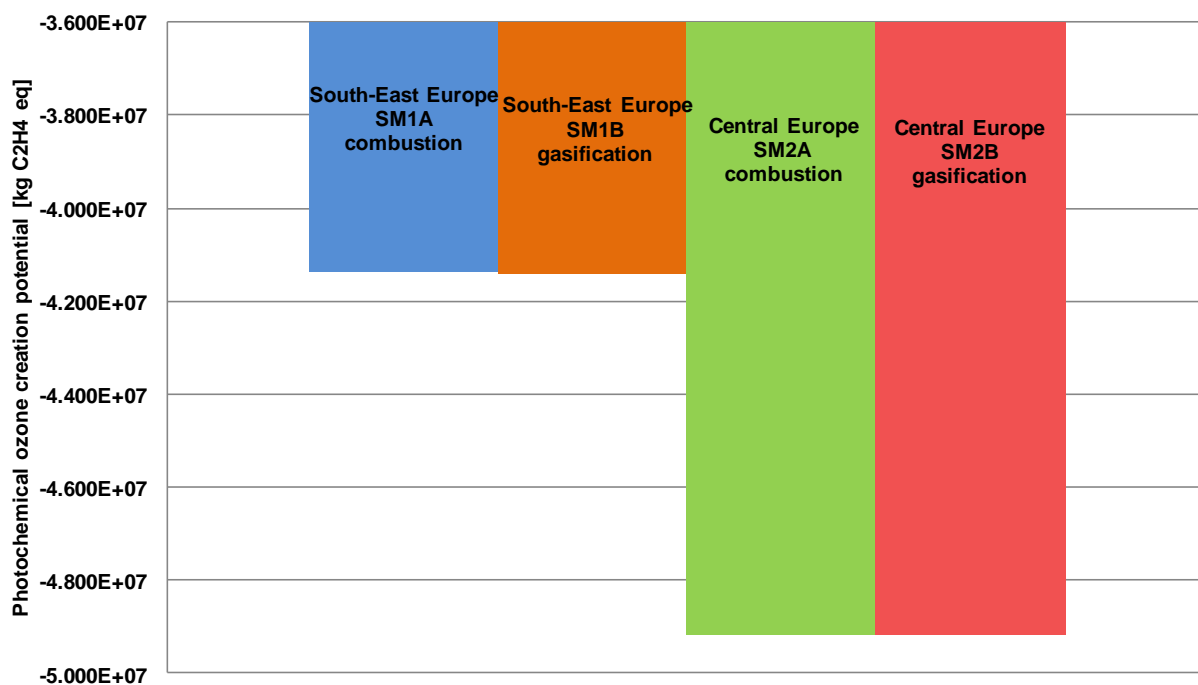


Figure 4.9. Photochemical ozone creation potential [kg C<sub>2</sub>H<sub>4</sub> eq]

Some conclusion can be drawn regarding the environmental impact indicators assessment:

- all scenarios model are an eco-friendly IMSWS with a positive environmental impact registered by all the impact categories studied;
- there is no considerable environmental change by using the combustion or gasification treatments ;
- though recycling processes the pollution is decreased for all impact categories, since it avoids the consumption of virgin material according to the substitution rate of 1:1.
- in SM<sub>2</sub> (Central Europe region) reveals a substantial negative environmental impact registered for HTP with 33% higher in comparison SM<sub>1</sub>(South European regions) due to the increasing of recycling rate;
- even if the SC rate is by 10 times higher in Central Europe (SM<sub>2</sub>) regions, the GWP and AP remain stable in all scenarios with no significant fluctuations (no more than 1%); this could be explained by the increasing of recyclable rates of waste fractions as input flow such as wood.

In all case studies the scenarios models achieve better environmental performances in comparison with direct disposal of MSW. From the technological and environmental point of view, SM<sub>2</sub> is a good example of future applicable waste management models that offers a sustainable IMSWS of life cycle recovery (material and energetic) with positive environmental impact by using the best available technologies suitable for commercial scale practice. For a better choice of each a scenario model alternative, an economical analysis combine with a social costs study will offer the overview of the waste management trend and its full scale implementation. This work will continue along future studies.

The **Abiotic Depletion Potential** is presented in Figure 4.10. A positive environmental impact is observed in both scenario models specially for South-East European region (SM<sub>1</sub>). This can be explained by the SRF designated to thermal treatment which is double in the first scenario model in comparison with the second one. This means that in the SM<sub>1</sub> the depletion of fossil fuel is higher in comparison with the SM<sub>2</sub>. However this results is obtained do to the increased SC (68%) in SM<sub>2</sub> that focuses more on the direct recycling of the materials.

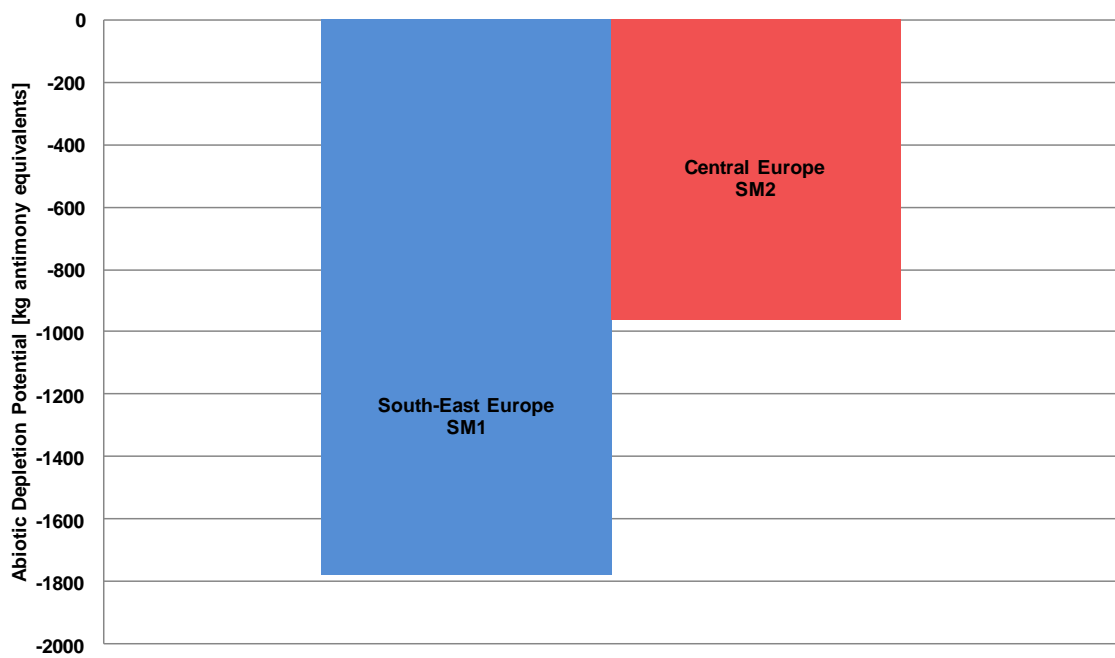


Figure 4.10. Abiotic Depletion Potential [kg antimony equivalents]

According to Rada et. al., 2005 one tonne of SRF<sub>6</sub> can substitute conventional fuels [129]:

- Brown coal : 0.49-0.77 t;
- Anthracite: 0.36 – 0.39 t;
- Coke: 0.44 t.

The **waste landfilled area** by type of case studied are represented in Figure 4.11. The next conclusion can be drawn:

- In absence of an IMSWS, for 300,000 t<sub>MSW</sub>/year produced, 4500 t/m<sup>2</sup>\*year will be deposited.
- In absence of advance mechanical sorting and energy recovery in all scenario models, the RMSW in SM<sub>1</sub> will have an increased landfilled occupied area with 62% in comparison with SM<sub>2</sub>. This can be explained by the SC which is higher with almost 62% in SM<sub>2</sub> Central Europe regions.
- By keeping all the treatment lines and combustion plant, the landfilled area inventories in SM<sub>1</sub> will necessitate a 31% of landfill area in comparison with SM<sub>2</sub>.
- By keeping all the treatment lines and gasification plant, the landfilled area inventories in SM<sub>1</sub> will necessitate a 13% of landfill area in comparison with SM<sub>2</sub>.

The improvement of waste management through the IMSW scenario models developed decrease the residual waste landfilling and increase the material and energetic recovery of the waste (e.g. recycling, compost, RRW sent through Take back program etc.). Still the SM<sub>2</sub> is far a better option regarding the minimization of landfilled used in all assumptions made. In comparison with SM<sub>1</sub>, SM<sub>2</sub> maximizes the inert disposal, 4% coming from the SC of the initial MSW.

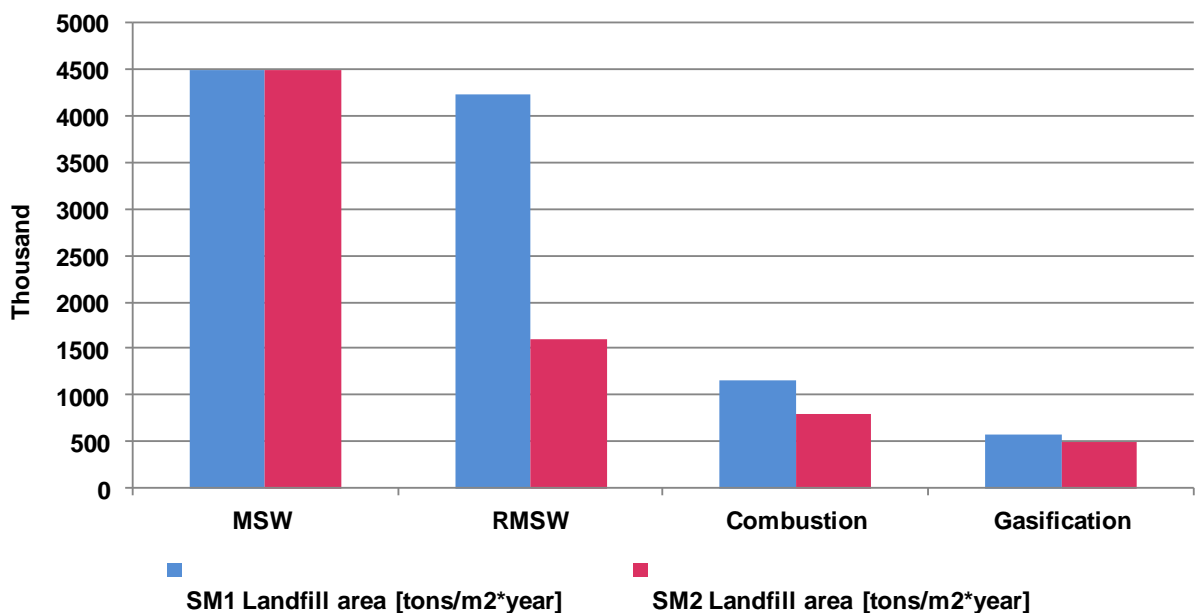


Figure 4.11. Landfill area

The **eco factors** by type of case studied are represented in Figure 4.11. This ecological scarcity is related with the landfill area inventories. Taking into account the landfill area inventory determined in absence IMSWS, for 300,000 t<sub>MSW</sub>/year produced, the dump site eco-factor reaches up to 2.25 thousands eco-points/m<sup>2</sup>\*year will be produced. In all cases by applying the SC and optional AMS and ATT the eco-factor decreases. This value assesses the deposited wastes in above ground landfills mainly on their carbon content. In all case studies, the IMSWS is an environmentally preferable alternative reducing the landfill eco-factor up to 90% in comparison with direct disposal of MSW.

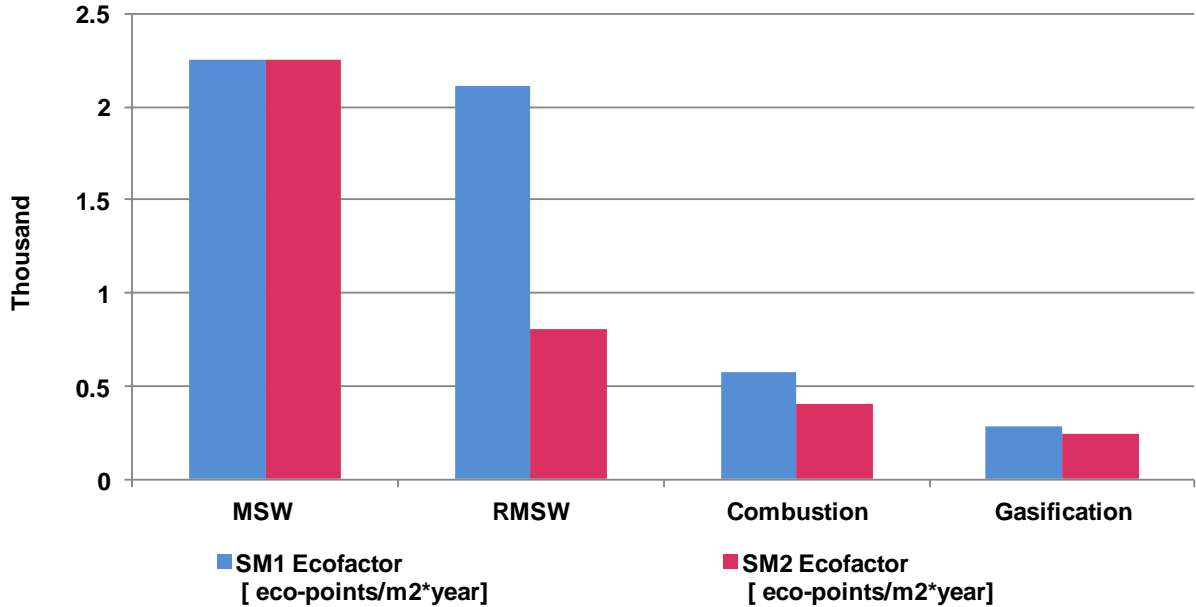
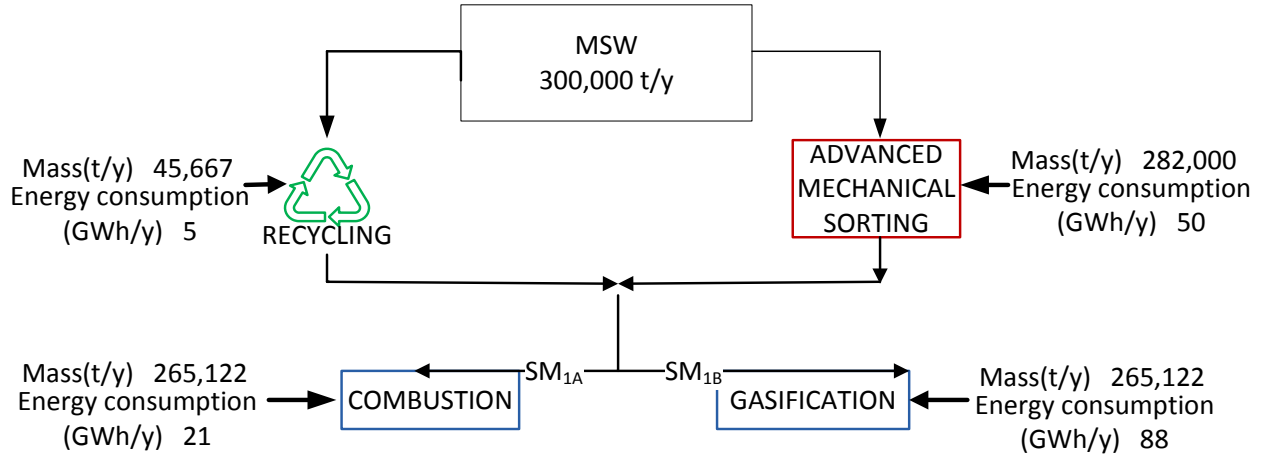


Figure 4.12. Eco factor

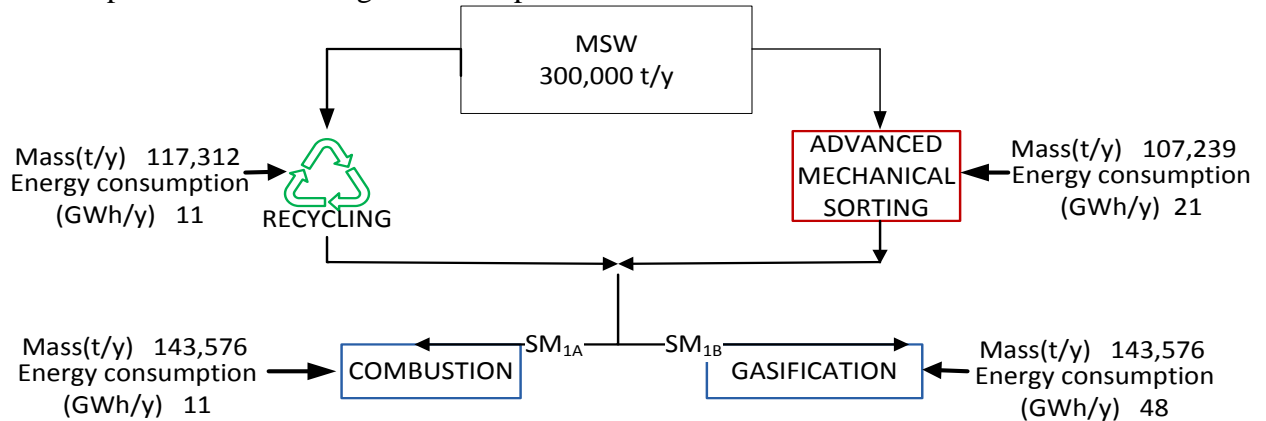
### 4.2.3. Energy balance

Figure 4.13 presents the energy consumption used in SM<sub>1</sub>. The overall energy consumption used is 76 GWh/year for SM<sub>1A</sub> (with combustion option), respectively 144 GWh/year for SM<sub>1B</sub> (with gasification option).

In SM<sub>1A</sub> the normalized electric consumption is most used in AMS with 66%, followed by combustion with 27% and recycling with 7%. In SM<sub>1B</sub> the steam gasification process start-up consumes 61% from the overall IMSW scenario model energy consumption.

Figure 4.13. Energy consumption  $SM_1$ 

In comparison with  $SM_1$ , in  $SM_2$  (Figure 4.14) the overall energy consumption is less with 43 GWh/year for  $SM_{2A}$  (with combustion option), respectively 80 GWh/year for  $SM_{2B}$  (with gasification option). This can be explained by the increasing rate of SC and material recovery. In  $SM_{2A}$  the electric consumption is most used in AMS with 48%, followed by combustion with 26% and recycling with 26%. The  $SM_{2B}$ , 60% from the IMSW scenario model energy consumption is used in the gasification process.

Figure 4.14. Energy consumption  $SM_2$ 

#### 4.2.4 Sensitive analysis

This section offers a rough comprehensive analysis of the technological impediments that might occur during the RMSW conversion treatment line of the scenarios model developed:

- the shredder treatment has an important role in AMS chain. There are two main types of shredders used at industrial scale, high speed, low torque hammer mills (HSLT) and low speed, high torque shear (LSHT). The most common technological problems using HSLT are the explosions during shredding caused by the accumulation of volatile explosive vapour around the rotor. Therefore, at high rpm (700-1200 rpm), the accident risk increases due to the tendency to create sparks during the impact with metal objects. Even though the LSHT are safer, the input flow of the materials milled are half in comparison with HSLT. Thanks to LSHT lower rpm (10-50

rpm), textiles waste can hang around the rotor shaft, causing overloading and disruption of the operation. On the other hand the input feedstock can reach up to  $150 \text{ t h}^{-1}$  allowing high feedstock moisture content of 40%. Due to the high heterogeneity of the product, the design of the shredder system has to be robust and flexible.

- the ballistic separator limits at  $30\text{-}90 \text{ m}^3/\text{h}$  feedstock input. The energy and process efficiency is strongly influenced by the size of the waste treated no more than 4000 mm.
- the magnetic separation allows only the ferrous metal recovery. Further treatments have to be applied in order to extract other type of valuable recyclable metals.
- the eddy current separation allows an input flow of 1500 t/h. As disadvantage, it has been shown that particle size, shapes and concentration can affect the travel distance in eddy-current separators.

Taking into account the results presented in section 3 it can be concluded that the SC and AMS are dictating some of WtE parameters such as: material size, feedstock input, specific surface area which is dependent of process temperature, reaction rate and residence time. In order to use MSW as a feedstock, it either needs to be reduced in size so that it can be fed into a batch using an auger, or the plant feeding system needs to be designed processing larger objects. The main benefit of the pre-shedding system is the RMSW homogenizing and decreasing its dimensions. By decreasing its particle size the contact surface increases through rapid heating and mass transfer by speeding the formation of gas/syngas or combustible by-product.

At gasification process, the waste chemical composition can cause problems in the downstream process due the gas contaminants (sulphur and nitrogen oxides, volatile mercury and other pollutants). For air gasification, the moisture content is an economical drawback due to the drying pre-treatment and dilution of fuel components that decrease the heating value of the feedstock. As far as energy efficiency is concerned, if the plant isn't IGCC, the complete combustion of the fuel is more efficient than any other thermal process. This underlines that gasification/pyrolysis thermal conversion efficiencies are in the range of 55-75%, maybe more if the syngas is directly used in a steam boiler without any pre-cooling. For small scale IGCC industrial plants the net generation efficiency could be around 41%.

Overall, there are some impediments that still obstruct the optimal parameters for a WtE large scale plant such as: waste feed flow that should be representative for local or regional area, the results accuracy on the reproduction of the environment process which has a direct connection with the output of secondary products in terms of characteristics, purity and pollution emission.

In terms of environmental aspects, during WtE, tars, heavy metals, halogens and alkaline compounds are released. All these compounds led to: human health risk and operational difficulties such as slagging or deposit formation in the gasification vessel. In comparison with traditional combustion, the sub-stoichiometric atmosphere limits the formation of dioxin and large quantities of  $\text{SO}_x$  and  $\text{NO}_x$  with smaller and less expensive gas cleaning equipment. The risk of  $\text{NO}_x$  lower emission comes with the syngas combustion or its utilization in a gas engine [116]. Regarding carbon dioxide ( $\text{CO}_2$ ), the high concentrations and high pressure make it easier to capture and store in comparison with incineration.

A critical analysis regarding the environmental impact by type of indicator is presented in Table 4.4. A comprehensive environmental analysis is made by comparison between  $\text{SM}_1$  and  $\text{SM}_2$ .

**Table 4.4. Sensitive analysis by type of environmental impact indicator**

<b>Environmental impact indicator</b>	<b>SM<sub>1</sub></b>	<b>SM<sub>2</sub></b>	<b>Observation</b>
GWP [kg CO <sub>2</sub> eq]	++	+	By increasing the SC and recycling rates in SM <sub>2</sub> , increases only with 1% the GWP indicator impact. The latter is also explained by the waste fraction material recovery which is higher in the second case study model.
AP [kg SO <sub>2</sub> eq]	+	++	SM <sub>2</sub> registers a slightly improvement where the AP indicator decreases with only 1% in comparison with SM <sub>1</sub> . This can be explained by the quantity of SRF <sub>6</sub> designated for energy recovery which is with half in comparison with SM <sub>1</sub> .
HTP [kg 1,4 DCB eq]	++	+	The significant difference obtained is explained by the increasing of the recycling rates but also the different MSW composition.
POCP [kg C <sub>2</sub> H <sub>2</sub> eq]	+	++	SM <sub>2</sub> is more advantageous from the eco-friendly point of view due reduction of flue gas emission resulted from the ATT processes.

\*where + quite good; ++ good

Primarily the challenges of a MSW gasification plant commercialization, comes from the non-uniformity, heterogeneity, size and moisture of the feedstock. This increased its important because generally dictates the minimum scale for the process. In addition, the pre-treatment processing costs, conversion of MSW into SRF and advanced flue gas cleaning might affect the overall economic balance. The capital and operating costs for 100,000 t<sub>waste</sub>/year using the combustion process is 55 million Euro, respective 3,765,000 Euro/year, while for pyrolysis and gasification is almost double with 73.20 million Euro initial investments and 6,700,000 Euro/year for operation and maintenance [21].

#### 4.2.5. Conclusion

The analyzed system complies with the EU principle of biodegradable materials minimization and is in agreement with the principle of adopting energy recovery after the implementation of material recycling options.

The main benefits of the pre-shedding system are MSW homogenizing and increasing density up to 30% of the feed to the grate. It can be concluded that the reduction of inert materials facilitates the partial oxidation of combustible products and enables recycling for the recovered materials.

In all cases studied, the analyzed IWMS minimizes the landfilling of materials and modify the LHV of the materials sent to energy recovery. Due to the decrease of the volume of landfilled waste, in the IMSW system the dump site eco-factor decrease up to four times in comparison

with direct MSW disposal. This value assesses the deposited wastes in above ground landfills mainly on their carbon content.

The energetic recovery could cover a neighbourhood given the fact that a typical standard consumption of a household is  $0.1745 \text{ MW}_{\text{el}}/\text{year}$ . In all case studies the scenarios models achieve better environmental performances in comparison with direct disposal of MSW.

The overall energy consumption used is  $76 \text{ GWh}/\text{year}$  for  $\text{SM}_{1\text{A}}$ , respectively  $43 \text{ GWh}/\text{year}$  for  $\text{SM}_{2\text{A}}$  (with combustion option), and  $144 \text{ GWh}/\text{year}$  for  $\text{SM}_{1\text{B}}$ , respectively  $80 \text{ GWh}/\text{year}$  for  $\text{SM}_{2\text{B}}$  (with gasification option). In this case the IMSW  $\text{SM}_2$  represents the most suitable option from the energetic point of view.

In  $\text{SM}_1$ , the  $\text{SRF}_6$  can be sent to a combustion process ( $\text{SM}_{1\text{A}}$ ) where is produced a thermal energy output of  $438 \text{ GWh}_{\text{th}}/\text{year}$  and electrical energy output of  $137 \text{ GWh}_{\text{e}}/\text{year}$ . In  $\text{SM}_{1\text{A}}$ , the combustion process produces  $44,575 \text{ t}_{\text{ash}}/\text{y}$ . The overall waste disposal of  $\text{SM}_{1\text{A}}$  is 26% respect to the MSW initial stream.

In second scenario model, the WtE conversion with  $352 \text{ GWh}_{\text{th}}/\text{year}$  and  $110 \text{ GWh}_{\text{e}}/\text{year}$  for the combustion process ( $\text{SM}_{2\text{A}}$ ) and  $385 \text{ GWh}_{\text{th}}/\text{year}$  and  $165 \text{ GWh}_{\text{e}}/\text{year}$  for steam gasification one ( $\text{SM}_{2\text{B}}$ ). The overall second scenario model disposal will drop up to 18% for  $\text{SM}_{2\text{A}}$  and 11% for  $\text{SM}_{2\text{B}}$  respect to the initial MSW stream.

From the technological and environmental point of view,  $\text{SM}_2$  is a good example of future applicable waste management models that offers a sustainable IMSWS of life cycle recovery (material and energetic) with positive environmental impact by using the best available technologies suitable for commercial scale practice. Even if the SC rate is by 10 times higher in Central Europe regions, the GWP and AP remain stable in all scenarios with no significant fluctuations; this could be explain by the increasing of recyclable rates of waste fractions as input flow such as wood.

The sensitive analysis reveals the technological impediments that still obstruct the optimal parameters for a WtE large scale plant such as: waste feed flow that should be representative for local or regional area, the results accuracy on the reproduction of the environment process which has a direct connection with the output of secondary products in terms of characteristic, purity and pollution emission.

## CHAPTER 5

### 5. CONCLUSIONS AND FUTURE DEVELOPMENT

The research **aim** was achieved by combining theoretical and experimental data obtained from pyrolysis and gasification processes of light packaging waste with application for a decentralized integrated model of material and energy recovery from MSW.

The research, in particular, **was focused** on the experimental and theoretical characterization of the light combustible packaging waste patterns conversion process, which can be considered as contribution for future development of an integrated plant for syngas production.

The research was **concluded** with a unique model based on advanced waste pre-treatment leading to an original set of conversion chain configurations to a sustainable Integrated Municipal Solid Waste System (IMSWS) that can be applied both for EU and non-EU countries.

The research **main research contributions** are:

*1. Literature review and state of the art on*

- MSW treatment current statues, trend and issues
- MSW legislation
- State of the art on advanced mechanical sorting waste treatments
- Pyrolysis of MSW , particular light packaging waste
- Gasification of MSW, particular light packaging waste

*2. Experimental physical-chemical characterization of light packaging waste*

- contribute to the knowledge on cellulose and polymers waste physical-chemical characterization coming from different regions and results comparison with literature
- analysis of formulas for estimate energy expenditure based on empirical data and experimental results obtain with the calorimeter instrument.
- contribution to the knowledge of physical-chemical characterisation of solid and liquid by-products resulted from the pyrolysis process

*3. Experimental study of pyrolysis and gasification of light packaging waste*

- contribute to the knowledge of transformations during pyrolysis and gasification processes;
- optimal temperature setting of light packaging waste mixture pyrolysis process
- contribution on light packaging waste air gasification by using a rotary kiln
- optimize the light packaging waste mixture gasification process in order to provide high quality syngas and energy efficiencies;

#### **4. *Integrated Municipal Solid Waste Scenario Model***

- contribution to the present and future development of waste management through and original and flexible IMSWS scenario model with practical applicability or EU and non-EU countries that focuses on: feasibility assessment study, sensitive analysis, technological and environmental analysis.
- development of an IMSWS focused on: feasibility assessment study, sensitive analysis, environmental and economical benefits.

Some **original research contribution** could be highlighted:

- the study and its results of pyrolysis of light packaging waste in a stationary lab scale modified plant
- the study and its results of air gasification in a lab-scale modified rotary kiln plant
- the development of a flexible IMSW scenario model with practical applicability.

Still there are some questions raised of the current research activity. Therefore, **further research** activities are currently in progress in different areas:

- energy balance results from the pyrolysis experiments
- energy balance results from the gasification experiments
- economical balance of the IMSW scenario models proposed.
- based on experimental result the application of a gasification model

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